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INTENSITY-SELECTIVE-SCANNING:
A NEW PARADIGM FOR
STUDYING PHOTOIONIZATION IN
STRONG LASER FIELDS

Peter Hansch

The Ohio State University

1997
INTENSITY-SELECTIVE-SCANNING:
A NEW PARADIGM FOR STUDYING PHOTOIONIZATION
IN STRONG LASER FIELDS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the
Graduate School of The Ohio State University

By

Peter Hansch, M.S., M.B.A.

*****

The Ohio State University
1997

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Chemical Physics Graduate Program
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1997
ABSTRACT

The interaction between light and matter is one of the fundamental means of studying the nature of atoms and molecules. The development of ultrashort pulsed lasers has been crucial for attaining laser intensities greater than one atomic unit. In the presence of intense laser fields, the simultaneous absorption of multiple photons becomes possible. Typical multiphoton ionization spans the range from $10^{12}$ to $10^{14} \text{ W/cm}^2$, beyond which tunneling processes become non-negligible. A traditional problem of strong field photoionization in focused laser beams has been the spatial signal averaging over all intensities present within the focal volume.

This dissertation describes the development of \textit{Intensity-Selective-Scanning} (ISS), a novel method of time-of-flight spectroscopy that allows for observation of multiphoton ionization with unprecedented precision and intensity control. By scanning the laser-produced ionization region across a small pinhole, specific peak intensities can be spatially selected. The complexity of a Gaussian focal volume can be reduced to a 'slice' which has only a one-dimensional radial intensity dependence. In addition, ISS yields excellent signal-to-noise ratios and it provides signal gain for low intensity effects due to the volume increase of the diverging laser beam. Using this novel technique, several new phenomena in atomic strong field ionization have been observed.

For the first time, the clear evolution through parity-allowed resonances at the 8- and subsequent 9-photon levels has been unambiguously measured and modeled. Calculated photoelectron spectra demonstrate the validity of the transient resonance model near the saturation intensity. Furthermore, prominent structure in the hot electron production in
high intensity short pulse photoionization of xenon has been observed. It is shown in this dissertation that most of the photoelectrons with kinetic energies from 0 - 50 eV result from resonant processes at intensities up to 1.9x10^{14} \text{ W/cm}^2. While those new structures appear to be due to resonances, they cannot be attributed to traditional Rydberg transient resonances.

In addition, strong field multiple ionization, producing up to quadruple ions in xenon, has been observed via ISS. The presented ion spectra show spatially resolved sequential ionization, leading to a hole-burning into the xenon single ion distribution in favor of double ion production. ISS is an important tool in extracting real ionization rates because the volumetric scaling is easier to deconvolve and the intensity distribution is simplified to a radial dependence.

In summary, advances in kilohertz repetition rate lasers and exploitation of the ISS technique are revealing new physics in the field of high intensity photoionization to extend our knowledge further toward the tunneling regime and thereby bridging the gap between multiphoton and tunneling ionization.
Gewidmet an meine Eltern,
Horst und Christel Hansch
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Studies of high intensity, ultra short pulse laser interactions with Prof. Linn D. Van Woerkom
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>viii</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xiii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xiv</td>
</tr>
<tr>
<td>List of Abbreviations</td>
<td>xix</td>
</tr>
</tbody>
</table>

1. Introduction
   1.1 Historical Background                                               1
   1.2 Strong Field Ionization
      1.2.1 Multiphoton Ionization                                          2
      1.2.2 The Ponderomotive Energy                                       5
      1.2.3 Long versus Short Pulse Ionization                             7
      1.2.4 The Simpleman’s Model                                           12
   1.3 Experimental Setup
      1.3.1 Time-of-Flight Spectroscopy                                    17
      1.3.2 Laser System                                                   19
      1.3.3 Mode-locking                                                   20
      1.3.4 Spectrometer                                                   23
      1.3.5 Detection                                                      25
      1.3.6 TOF Data Conversion                                            26

   2.1 Introduction                                                      28
   2.2 Design                                                            29
   2.3 Experimental Results                                              32
   2.4 Discussion                                                        37
   2.5 Conclusion                                                        39
3. Intensity-Selective-Scanning: A New Method of Photoelectron Spectroscopy ..........40
  3.1 Introduction .....................................................................................................40
  3.2 The Curse of Spatial Averaging .........................................................................41
  3.3 Traditional Intensity Variation ...........................................................................43
  3.4 ISS Intensity Variation .......................................................................................44
  3.5 Experimental Results and Discussion ..............................................................51
  3.6 Conclusion .......................................................................................................57

4. High Resolution Transient Resonances in Above Threshold Ionization of Xenon.... 58
  4.1 Introduction .....................................................................................................58
  4.2 Experimental Results and Discussion ...............................................................58
  4.3 Conclusion .......................................................................................................64

5. High Intensity Photoelectron Spectra of the Noble Gases ............................................65
  5.1 Introduction .....................................................................................................65
  5.2 Experimental Results and Discussion ...............................................................66
  5.3 Conclusion .......................................................................................................68

6. Resonant Hot-Electron Production in Above-Threshold Ionization .......................75
  6.1 Introduction .....................................................................................................75
  6.2 Theory ...............................................................................................................76
  6.3 Experimental Results and Discussion ...............................................................76
  6.4 Conclusion .......................................................................................................86

7. High Order Resonances in Above Threshold Ionization of Noble Gases ...............87
  7.1 Introduction .....................................................................................................87
  7.2 Experimental Results and Discussion ...............................................................89
  7.3 Theoretical Model ...............................................................................................96
  7.4 Conclusion .......................................................................................................100

8. Spatially Dependent Multiphoton Multiple Ionization ........................................101
  8.1 Introduction .....................................................................................................101
  8.2 Experimental Approach ....................................................................................104
  8.3 Experimental Results and Discussion ...............................................................107
  8.4 Theoretical Model ............................................................................................112
  8.5 Conclusion .......................................................................................................116
9. Conclusion ........................................................................................................................117
  9.1 ISS and Strong Field Photoionization ..............................................................117
  9.2 Future Studies ....................................................................................................119

Appendices ...............................................................................................................................120
  A. Time-to-Energy Conversion .............................................................................120
  B. Time-to-Mass Conversion ................................................................................123
  B. Gaussian Laser Beams ......................................................................................126

List of References ...................................................................................................................130
LIST OF TABLES

Table 1.1. Relevant laser intensity ranges for strong field ionization. ....................... 13

Table 7.1. Zero-field energy levels for f- and g-states. $U_p$ is the ponderomotive
shift required to attain transient resonances of Xe($^{2P}_{3/2}$) states with 800 nm
light, and $I_R$ is the corresponding resonance intensity. The f-state energy
levels are taken from Ref. [77]. ................................................................. 95

Table 7.2. Coupling strengths $V_R$ and the corresponding resonance intensities $I_R$
for each resonance used in fitting the spectral data in Fig. 7.1 ......................... 99
LIST OF FIGURES

Figure 1.1. (a) MPI and ATI produce photoelectrons with kinetic energies equal to the photon level minus ionization potential. (b) Harmonic photons are generated with frequencies equal to odd integer multiples, $m$, of the fundamental.................................................................................................................3

Figure 1.2. "A schematic of the ATI process for xenon irradiated by intense 1064 nm light. The energy scale is the kinetic energy of the free electron. Only the absorption from the dominant $P_{3/2}$ core is shown." With a pulse duration of 100 ps this spectrum is a typical example of long pulse ATI. From Ref. [11]. ......4

Figure 1.3. Schematic energy level diagram showing ac-Stark shifted xenon Rydberg states as a function of intensity. Using 800 nm photons, ATI resonances occur first at the minimum 8-photon level but also at higher orders (9-photon resonances, etc.) [38]...................................................................................9

Figure 1.4. (a) Schematic energy level diagram showing the difference between short and long pulse ionization according to Eq. 1.3 (short) and Eq. 1.4 (long). $E_n$ refers to a Rydberg state with principal quantum number $n$. (b) Temporal intensity evolution and shifting energy levels for a Gaussian laser pulse [39].........................................................................................................................10

Figure 1.5. Photoelectron spectrum of xenon with 120 fs, 800 nm pulses at an intensity of $3 \times 10^{13}$ W/cm². The substructure within each ATI order results from 8-photon Rydberg state resonances with the f-series. Dotted lines mark the long pulse limit for each ATI order........................................................................11

Figure 1.6. An electron's motion depends on the phase at which it is liberated [31, 40, 41]. (a) No collision occurs if ionized before the peak of the field, e.g. at 0.15 rad before the peak, (b) the electron revisits the core without impact if ionized at the peak of the field, (c) multiple collisions can occur if ionized after the peak of the field, e.g. at 0.15 rad after the peak, (d) the maximum impact collision occurs if ionized at 0.297 rad after the peak of the field [13]. All cases assume ionization with zero initial kinetic energy. ..................14

Figure 1.7. "Normalized photoelectron spectra of helium over larger dynamic range as a function of $U_p$." From Ref. [54]. .................................................................15

Figure 1.8. An electron liberated at a phase of 0.297 rad after the peak of the electric field is first being accelerated away from the atom, but later returns and encounters a collision with a maximum kinetic energy of 3.17 $U_p$ [13]..............16
Figure 1.9. Ti:Sapphire amplification system. From Ref. [55].

Figure 1.10. Schematic setup of a time-of-flight photoelectron spectrometer. Knowing the flight length, $L$, and measuring the TOF, $t$, the kinetic energy can be determined via $E = \frac{1}{2} m_e (L/t)^2$.

Figure 1.11. "(a) Inhomogeneously broadened Doppler gain curve of the 6328 Å Ne transition and position of allowed longitudinal mode frequencies. (b) Intensity versus frequency profile of an oscillating He-Ne laser. Six modes have sufficient gain to oscillate." From Ref. [69, 70].

Figure 1.12. Xenon ion mass spectrum taken at approx. $10^{13}$ W/cm$^2$. Most of the recorded ions are Xe$^+$ ions. The different Xe isotopes can be resolved. The background signal is very low and consists mainly of water, nitrogen and hydrocarbons in the range 20-45 amu.

Figure 1.13. Spectrometer setup. Photoelectrons and ions are produced at the center of the 6-way cross. The flight tube is shielded with μ-metal. The conical anode at the end of the tube houses the microchannel plate detector. The dashed cross marks the laser focal region.

Figure 2.1. Schematic cross section of the time-of-flight spectrometer. The detail box shows a typical electron trajectory through the ellipsoidal grids.

Figure 2.2. Xenon energy level diagram with 6-photon absorption.

Figure 2.3. TOF spectra of Xe taken with 100 mJ of 532 nm, 5 ns laser pulses. (a) The grid is turned off and the polarization is pointed down the flight tube. (b) The polarization is pointed at 90° and $V_R = -3.5$ V on the outer grid.

Figure 2.4. Kinetic energy distributions derived from TOF spectra in Fig. 2.3. See text for explanation of individual features. (a) straight TOF, (b) EMA spectrum. Note the different y-scales, indicating the large gain.

Figure 3.1. Schematic spatial distribution of temporal peak intensities in a Gaussian focus.

Figure 3.2. Schematic setup of time-of-flight spectrometer with ISS. The focusing lens can be moved via a translation stage to scan the ionization volume across the pinhole at the front of the flight tube. MCP, microchannel plates.

Figure 3.3. Specific slices of the laser focus can be selected via ISS. The outer contours show the 1/e-points of the laser field. The inner lines around the slices are iso-intensity contours.

Figure 3.4. The 1/e E-field halfwidth can be measured with an imaging system. The solid line indicates the calculated contour according to Eq. 3.2, with a measured minimum beam radius of $r_0 = 45$ microns. The left hand side of the focus is used for scanning the intensity in our experiments since there is an excellent match with the theoretical profile. From Ref. [81].
Figure 3.5. Intensity contours for which (a) the photoelectron signal is dominated by ionization at the peak intensity (traditional TOF spectroscopy), and (b) the same intensity range as in (a) can be selected through ISS at a much higher peak intensity, resulting in signal gain due to the larger volume.

Figure 3.6. Volumetric gain for the ISS technique versus traditional TOF spectroscopy for $I_0 = 7 \times 10^{13}$ W/cm$^2$, $\Delta z = 2$ mm, and $z_0 = 4.5$ mm.

Figure 3.7. Photoelectron spectra of xenon at intensities ranging from $6 \times 10^{12}$ to $7 \times 10^{13}$ W/cm$^2$ obtained via ISS. The scans are presented on a vertical log-scale and vertically separated. The lowest intensity scan is presented at the bottom and the intensity increases upward. See text for full explanation.

Figure 3.8. Photoelectron spectra of xenon taken with circularly polarized 800 nm light. The top scan is recorded with the full ionization volume. The bottom three scans are ISS spectra from different parts of the laser focus.

Figure 4.1. Low intensity photoelectron spectra showing the evolution of 8-photon resonance structure in xenon using 800 nm light at intensities of (a) 0.66, (b) 0.77, (c) 0.91, (d) 1.20, (e) 1.47, (f) 1.85, (g) 2.39, (h) 2.75, (i) 3.20x10$^{13}$ W/cm$^2$. All curves are vertically shifted and normalized to a common maximum amplitude. The vertical lines at the top indicate the observed f-Rydberg states.

Figure 4.2. High resolution photoelectron spectrum of xenon showing the first ATI order at an intensity of 2.5x10$^{13}$ W/cm$^2$.

Figure 4.3. Photoelectron spectrum of xenon showing the 1st-7th ATI-order at an intensity of 4.5x10$^{13}$ W/cm$^2$.

Figure 5.1. Photoelectron spectra of helium with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) 1.7, (4) 1.4x10$^{14}$ W/cm$^2$.

Figure 5.2. Photoelectron spectra of neon with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) 1.7x10$^{14}$ W/cm$^2$.

Figure 5.3. Photoelectron spectra of argon with 800 nm, 120 fs pulses at intensities of (1) 6.3, (2) 4.0, (3) 2.6, (4) 1.7, (5) 1.4, (6) 1.1x10$^{14}$ W/cm$^2$.

Figure 5.4. Photoelectron spectra of krypton with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) 1.7, (4) 1.4, (5) 0.85, (6) 0.60x10$^{14}$ W/cm$^2$.

Figure 5.5. Photoelectron spectra of xenon with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) 1.7, (4) 1.4, (5) 0.85, (6) 0.60, (7) 0.40x10$^{14}$ W/cm$^2$.

Figure 5.6. Molecular photoelectron spectra with 800 nm, 120 fs pulses at intensities of (1) 3.4, (2) 2.6, (3) 1.7, (4) 1.4, (5) 1.1x10$^{14}$ W/cm$^2$. 

xvi
Figure 6.1. Photoelectron spectrum of xenon with 800 nm, 120 fs pulses at 1.51x10^14 W/cm^2.

Figure 6.2. Photoelectron spectra of xenon with 800 nm, 120 fs pulses at (1) 1.51, (2) 1.63, (3) 1.74, (4) 1.82, (5) 1.88, (6) 1.90x10^14 W/cm^2.

Figure 6.3. Photoelectron spectra of xenon with 800 nm, 120 fs pulses at (a) 1.26, (b) 1.44, (c) 1.51, (d) 1.63, (e) 1.74, (f) 1.78, (g) 1.82, (h) 1.86, (i) 1.88x10^14 W/cm^2.

Figure 6.4. Photoelectron spectra taken with different wavelengths.

Figure 6.5. Possible scenarios for producing hot electrons via multiple excitations.

Figure 7.1. Photoelectron spectra showing the transition from 8- to 9-photon resonances in xenon using 800 nm light at intensities between 1.66x10^13-4.68x10^13 W/cm^2. All curves are vertically shifted and normalized to a common maximum amplitude. (----- = experiment; ------ = calculations).

Figure 7.2. Resonance peak amplitudes as a function of laser intensity. Vertical lines show the 8- and 9-photon resonance threshold intensities for each state.

Figure 7.3. Resonance peak amplitudes vs. intensity. Vertical arrows show the 8- and 9-photon resonance threshold intensities for each state. Symbols are experimental data, solid lines are Gaussian volume contours for f- and g-states.

Figure 7.4. "Schematic diagram of the level crossing model with the ground state dressed by m photons labeled state 2, and the excited state subjected to the ac-Stark shift labeled state 1. (a) Positions in space where the local intensity equals the resonance intensity and quadratic time dependence is needed. (b) Positions at smaller (r, z) where the resonance intensity is passed on the rising and falling edges, requiring only the linear time dependence." From Ref. [39].

Figure 8.1. Xenon ion yields for various intensities > 10^14 W/cm^2. The yields for charge states up to Xe^8+ increase monotonically with intensity. After saturation is reached, each curve continues to grow as I_0^3/2. From Ref. [125].

Figure 8.2. Schematic setup of time-of-flight spectrometer with ISS. The focusing lens can be moved via a translation stage to scan the ionization volume across the pinhole at the front of the flight tube. A static potential of +1100 V accelerates ions toward the detector.

Figure 8.3. Schematic intensity contours. Low intensities occupy a much larger volume than high intensities in comparison to the ISS technique.

Figure 8.4. Xenon ion spectra recorded using (a) traditional method of exposing entire focal volume vs. (b) selecting a 500 µm window with ISS at the minimum beam waist.
Figure 8.5. (a) Ion signal of Xenon with 800 nm, 120 fs pulses as a function of z,
(b) same signal displayed vs. local on-axis peak intensity ........................................110

Figure 8.6. Calculated volumes for saturated ionization for single and double ions.
The model predicts the single ion yield to decrease as the intensity increases
due to the creation of higher charge states. ..........................................................114

Figure 8.7. Schematic cross-section of the laser focus near its waist. At
sufficiently high peak intensities, double-ions are produced in the center, thus
burning a hole into the single-ion population. This leads to a depletion of
single-ions and may cause higher yield for the higher charge states...............115

Figure C.1. "Notation for a lowest-order Gaussian beam diverging away from its
waist." From Ref. [56] ..........................................................................................127

Figure C.2. "Spreading of a TEM_{0,0} mode". From Ref. [128] .................................128
LIST OF ABBREVIATIONS

ATI ................. Above Threshold Ionization
CPA .................. Chirped Pulse Amplification
cw ..................... continuous wave
EMA .................. Ellipsoidal Mirror Analyzer
HOHG ................ High Order Harmonic Generation
ISS ................... Intensity-Selective-Scanning
MCP .................. Microchannel plates
MPI .................. Multiphoton Ionization
PMA .................. Parabolic Mirror Analyzer
TOF .................. Time-of-flight
CHAPTER 1

INTRODUCTION

1.1 Historical Background

The interaction between electromagnetic radiation and matter has historically been one of the most important means of unraveling the laws of nature. In 1905, Albert Einstein contributed to the foundation of quantum mechanics by postulating that electromagnetic waves are streams of energy quanta, or photons, of energy $E = h \nu = hc/\lambda$. Using this revolutionary concept, Einstein explained the photoelectric effect [1], for which he received the 1921 Nobel Price.

The photoelectric effect refers to the emission of electrons off a metal surface when irradiated with light. While the electric current is proportional to the light intensity striking the metal, the maximum electron kinetic energy is independent of the intensity of the incident light. This puzzling observation was explained by Einstein. An electron emitted from a metal surface exposed to light receives its energy from absorbing a single photon. When the intensity of the light of a given frequency is increased, more photons strike the surface per unit time, but the energy absorbed by each electron is unchanged. In leaving the metal, an electron must do an amount of work, $\phi$, equal to its binding energy in the metal. The resulting kinetic energy is given by the famous Einstein photoelectric equation

$$\frac{1}{2}mv^2 = h\nu - \phi.$$  \hspace{1cm} (1.1)
1.2 Strong Field Ionization

1.2.1 Multiphoton Ionization

In contrast to the traditional photoelectric effect, strong field multiphoton ionization (MPI) describes the absorption of many photons in order to ionize atoms or molecules. Otherwise, it is identical to the photoelectric effect and thus builds on Einstein's ideas. Today, photoelectron spectroscopy continues to be an extremely valuable experimental tool in many areas of Physics, Chemistry and Materials Research to investigate the structure of atoms and molecules [2]. The development of ultrashort pulsed laser sources [3] has been crucial in obtaining intensities with field strengths greater than one atomic unit [4].

When an atom is exposed to intense radiation (>10^{12} W/cm^2), the simultaneous absorption of many photons becomes probable. As the light intensity is increased the dominant ionization process occurs via multiphoton ionization and subsequent above threshold ionization (ATI) [5-10]. MPI refers to the minimum number of photons required to exceed the ionization limit, while ATI, which was first observed by Agostini et al. [5] in 1979, is characterized by the absorption of additional photons in the continuum. The corresponding (long pulse) photoelectron kinetic energy spectra exhibit peaks which are separated by the photon energy, as shown in Fig. 1.1(a) and Fig. 1.2 [11].

The second dominant strong-field laser-atom interaction is high order harmonic generation (HOHG) [12-17]. HOHG refers to the temporary excitation of an electron via multiple photon absorptions, but instead of escaping from the atom the electron recombines and emits a single harmonic photon, as shown in Fig. 1.1(b). Gas phase atoms and molecules can generate harmonics with odd integer multiples of the fundamental frequency. Even integer multiple harmonics cannot be produced due to the inversion symmetry [18]. Both processes, ATI and HOHG in gases, can be modeled by the motion of a single active electron driven by the strong oscillating electric field and interacting with the parent ion when revisiting its vicinity, as described later.
Figure 1.1. (a) MPI and ATI produce photoelectrons with kinetic energies equal to the photon level minus ionization potential, (b) Harmonic photons are generated with frequencies equal to odd integer multiples, \( m \), of the fundamental.
Figure 1.2. "A schematic of the ATI process for xenon irradiated by intense 1064 nm light. The energy scale is the kinetic energy of the free electron. Only the absorption from the dominant $P_{3/2}$ core is shown." With a pulse duration of 100 ps this spectrum is a typical example of long pulse ATI. From Ref. [11].
1.2.2 The Ponderomotive Energy

An excellent discussion of the role of ponderomotive forces in strong field ionization has been presented in Ref. [19]. Briefly, when a free electron is placed in a high intensity laser field, it undergoes a wiggle motion due to the oscillating electric field. This wiggle motion gives the electrons a time-averaged kinetic energy, or ponderomotive energy, \( U_p \), given by Eq. 1.2 (in MKS units) [20].

\[
U_p = \frac{e^2 E^2}{4m\omega^2},
\]

where \( e \) is the electron charge, \( m \) is the electron mass, \( E \) is the electric field strength, and \( \omega \) is the laser frequency.

In order to ionize an atom, sufficient energy must be available to both overcome the zero-field ionization potential and provide the ponderomotive energy. This means that the effective ionization potential increases by \( U_p \) [9]. This increase is called ac-Stark shift [21-24]. It affects the ionization limit as well as the energy of high lying Rydberg states, since Rydberg electrons have large Kepler orbits and are therefore similar to free electrons [25]. Low-order perturbation theory yields also a shift of the ground state, which is proportional to the static polarizability times the intensity [26]. However, the shift of the ground state is small and can generally be neglected [27]. The ponderomotive shift of atomic Rydberg states can lead to multiphoton resonances, which are responsible for extremely nonperturbative behavior of multiphoton ionization [28, 29], as discussed in section 1.2.3. When using circularly polarized light, MPI resonances with ac-Stark shifted states are forbidden [30]; nevertheless, ponderomotive effects can be observed for non-resonant ionization, too, as shown in chapter 3.
It should be noted that ponderomotive forces can give substantial amounts of energy to liberated electrons. For 800 nm photons at an intensity of $10^{14}$ W/cm$^2$, the ponderomotive energy equals 5.98 eV. It scales linearly with intensity and quadratically with the laser wavelength. At higher intensities or longer wavelengths the ponderomotive energy can easily exceed the ionization potential of most atoms and molecules [31, 32].

Furthermore, the wiggle motion of an electron is complicated by the presence of both electric and magnetic forces in the laser field, and it is affected by spatial and temporal intensity inhomogeneities in a laser focus [33]. The actual electron trajectory is not a one-dimensional oscillation, but instead similar to a "figure-8" [30]. In addition, most mathematical treatments of the wiggle motion consider only the ponderomotive force and neglect the Coulomb force between an electron and its parent ion. Calculations by Brabec et al. [34] have shown an enhancement by more than an order of magnitude for multiphoton double ionization of helium due to Coulomb focusing of the electron wave packet.
1.2.3 Long versus Short Pulse Ionization

In 1987, Freeman et al. discovered that short laser pulses generate complex substructure in the photoelectron spectra [35]. A short pulse has a duration shorter than the escape time of an electron out of the focal volume of the exciting laser. The observed structure is due to atomic Rydberg states [36] that come into transient resonances with certain harmonics of the incident laser field.

In the presence of strong fields, both the ionization limit and most atomic Rydberg levels shift up by the ponderomotive energy, $U_p$ [37]. The ionization rate becomes strongly enhanced whenever a Rydberg state shifts into resonance with specific photon harmonics, as shown in Fig. 1.3. It should be noted that ATI can also occur due to high order resonances [38], as presented in chapter 7. At the instant a resonance occurs, a transient state with initial energy $E_i$ above the ground state produces a photoelectron with kinetic energy [33]

$$E = m\hbar \omega - IP - (n\hbar \omega - E_i) ,$$

(1.3)

where $IP$ is the field-free ionization potential relative to the ground state, $n$ indicates the harmonic at which the resonance occurs, and $m (>n)$ is the total number of photons absorbed during the ionization. Short pulses produce photoelectrons with final kinetic energies equal to the instantaneous kinetic energies at the moment of ionization, according to Eq. 1.3. The various Rydberg state resonances occur at different specific intensities and produce different kinetic energies, which account for the substructure within each ATI order [35]. This expression is valid in the limit where the atomic levels shift ponderomotively and the small shift of the ground state is neglected [27]. In the short pulse case each photoelectron experiences an energy deficit $(n\hbar \omega - E_i)$, characteristic of the particular Rydberg state with which the resonance occurs.
In the long pulse limit, on the other hand, electrons regain the initial kinetic energy deficit by accelerating out of the ponderomotive potential of the focal region. Their final kinetic energy is independent of the specific Rydberg resonance and only depends on the total number of absorbed photons, according to Eq. 1.4 [33].

\[
E = m\hbar\omega - IP
\]  

(1.4)

The difference in final kinetic energy between short and long pulse ionization is furthermore shown in Fig. 1.4(a). The ponderomotive shift of the ionization limit and the Rydberg states follows a Gaussian temporal profile, as indicated in Fig. 1.4(b).

Figure 1.5 shows a typical short pulse ATI spectrum of xenon. In contrast to long pulse ATI spectra, Fig. 1.5 shows clearly how each ATI order breaks up into a group of individual peaks, due to different Rydberg state resonances. The dashed lines represent the corresponding long pulse limits. Since photoelectrons cannot regain their initial energy deficit \((n\hbar\omega-E_i)\) under short pulse conditions, all peaks move toward lower kinetic energies with respect to their long pulse limit. Therefore, resonances with the lowest lying Rydberg states cause the largest shift.
Figure 1.3. Schematic energy level diagram showing ac-Stark shifted xenon Rydberg states as a function of intensity. Using 800 nm photons, ATI resonances occur first at the minimum 8-photon level but also at higher orders (9-photon resonances, etc.) [38].
Figure 1.4. (a) Schematic energy level diagram showing the difference between short and long pulse ionization according to Eq. 1.3 (short) and Eq. 1.4 (long). $E_n$ refers to a Rydberg state with principal quantum number $n$. (b) Temporal intensity evolution and shifting energy levels for a Gaussian laser pulse [39].
Figure 1.5. Photoelectron spectrum of xenon with 120 fs, 800 nm pulses at an intensity of $3 \times 10^{13}$ W/cm$^2$. The substructure within each ATI order results from 8-photon Rydberg state resonances with the f-series. Dotted lines mark the long pulse limit for each ATI order.
1.2.4 The Simpleman's Model

After the pioneering MPI/ATI studies, the research efforts of the community have shifted to studying the behavior of atoms in laser fields intense enough to reach the tunneling regime. Much attention has been paid to the production of hot electrons with kinetic energies as high as several hundred eV [31]. These efforts gave rise to the development of the semi-classical Simpleman's theory (or quasistatic model) [31, 40, 41], which describes the ionization as a two-step process: (1) An electron is liberated into the continuum with no drift velocity, (2) its subsequent motion is governed classically by the oscillating optical electric field. The probability of ionization as a function of electric field strength can be determined using dc tunneling theory [31]. The ionization probability is highest at the peak of the field. Depending on the instantaneous phase [42-45] of the electric field when an electron is ejected into the continuum, it may escape directly or revisit the atomic core, as shown in Fig. 1.6.

The resulting cycle-averaged photoelectron kinetic energy distribution has a cutoff at 2 $U_p$ for short pulses, where $U_p$ refers to the ponderomotive potential [9, 41]. However, experiments by Walker et al. [46] and Paulus et al. [47] show a sudden change in slope at 2 $U_p$. The production of hot electrons leads to kinetic energies greater than 10 $U_p$ [48]. Nevertheless, experimental results demonstrate that more than 98% of all detected photoelectrons fall between 0-2 $U_p$ (see Fig. 1.7) and can be adequately explained by the Simpleman's model.

So far, the occurrence of photoelectrons with kinetic energies above 2 $U_p$ has been attributed either to electrons being born with nonzero kinetic energy, or to backscattering of outer-shell electrons coherently driven by the field such that they encounter a collision with their parent ions [49-51], as shown in Fig. 1.8. Electrons born with zero kinetic energy can have a maximum collision energy of 3.17 $U_p$ [13]. Recent calculations have shown...
that classically backscattered electrons can achieve up to 10 $U_p$ kinetic energy in a monochromatic field [49].

The semi-classical Simpleman's model has been very successful in describing the essential physics behind much of high harmonic generation. However, for ATI the model predicts a maximum kinetic energy of 2 $U_p$ and must be modified to include backscattering in order to create hot electrons. Recently, new hot electron structure, which appeared in addition to that due to backscattering, has been observed [52, 53]. These observations are discussed in chapters 5 and 6. In summary, Table 1.1 presents the dominant ionization behavior of atoms and molecules for different high intensity ranges.

<table>
<thead>
<tr>
<th>$10^{10}$ - $10^{12}$ W/cm$^2$</th>
<th>MPI starts</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&gt; 10^{13}$ W/cm$^2$</td>
<td>everything ionizes</td>
</tr>
<tr>
<td>$&gt; 10^{14}$ W/cm$^2$</td>
<td>treat E-field classically</td>
</tr>
</tbody>
</table>

Table 1.1. Relevant laser intensity ranges for strong field ionization.
Figure 1.6. An electron's motion depends on the phase at which it is liberated [31, 40, 41]. (a) No collision occurs if ionized before the peak of the field, e.g. at 0.15 rad before the peak, (b) the electron revisits the core without impact if ionized at the peak of the field, (c) multiple collisions can occur if ionized after the peak of the field, e.g. at 0.15 rad after the peak, (d) the maximum impact collision occurs if ionized at 0.297 rad after the peak of the field [13]. All cases assume ionization with zero initial kinetic energy.
Figure 1.7. "Normalized photoelectron spectra of helium over larger dynamic range as a function of $U_p$." From Ref. [54].
Figure 1.8. An electron liberated at a phase of 0.297 rad after the peak of the electric field is first being accelerated away from the atom, but later returns and encounters a collision with a maximum kinetic energy of 3.17 $U_p$ [13].
1.3 Experimental Setup

1.3.1 Time-of-Flight Spectroscopy

A typical time-of-flight (TOF) experiment consists of a pulsed laser system (see Fig. 1.9 [55]), a vacuum chamber, and detection electronics. The pulses are focused into the vacuum chamber and ionize the target gas which fills the chamber. Ions and photoelectrons are produced which drift along the flight tube and strike the detector. Electrons are liberated in the absence of external electric or magnetic fields, whereas a static electric potential is used to accelerate ions toward the detector. Each laser pulse that leaves the interaction region is registered by a photodiode, which starts the trigger of a multichannel analyzer (MCA). The MCA measures the arrival time, or time-of-flight. Finally, the TOF data are converted to kinetic energy (for electrons) or atomic mass distribution (for ions). The entire experimental setup is schematically shown in Fig. 1.10.

![Diagram of Ti:Sapphire amplification system](image)

Figure 1.9. Ti:Sapphire amplification system. From Ref. [55].
Figure 1.10. Schematic setup of a time-of-flight photoelectron spectrometer. Knowing the flight length, $L$, and measuring the TOF, $t$, the kinetic energy can be determined via $E = \sqrt{2m_e(L/t)^2}$. 

18
1.3.2 Laser System

Most of the spectra presented in this dissertation have been obtained using a Positive Light, Inc. Ti:Sapphire laser system, as shown in Fig. 1.9 [55]. An argon ion laser pumps a cw mode-locked Ti:Sapphire oscillator, which produces a train of ultrashort laser pulses at a repetition rate of 80 MHz. These pulses are then directed into the Spitfire amplifier where they are stretched, amplified, and recompressed. The spitfire is pumped with a frequency doubled Nd:YLF laser at 527 nm.

Because time and spectral variation are related by a Fourier transform, there is a fundamental relationship between the temporal laser pulse width, $\tau$, and its frequency bandwidth, $\Delta \nu$. For a Gaussian pulse this relationship is $\Delta \nu \cdot \tau > 0.44$ [56]. Therefore, a large gain bandwidth is required in order to amplify femtosecond pulses. Titanium-doped Sapphire (Ti:Sapphire) [57] is used as the gain medium since it has a high stimulated emission cross section (high gain), and it has large gain-bandwidth, which supports extremely short pulses [58-65]. Using the entire Ti:Sapphire bandwidth, the theoretical minimum pulse width is 3 fs [57]. Currently, the shortest actual pulses have a width of 4-5 fs [65].

Ultrashort laser pulses are amplified using Chirped Pulse Amplification (CPA) [66-68]. Femtosecond pulses cannot be amplified directly since their intensity would destroy the gain medium. Therefore, they are first stretched in their pulse duration up to several hundred picoseconds, thus dramatically reducing the peak intensity. The stretched pulses are then amplified and finally recompressed to their original duration. The stretching occurs by using optical components that delay certain frequencies relative to others. Diffraction gratings or prisms can be arranged such that, for example, higher frequency (bluer) light travels a longer optical distance than lower frequency (redder) components. The resulting pulse is stretched in time and is referred to as positively chirped, since it has a positive group velocity dispersion (negatively chirped refers to the opposite frequency
After amplification, the pulse is compressed in a way that is the reverse of stretching, where the leading frequency components are delayed relative to those trailing, such that the pulse is compressed back to near its original pulse width.

Ultimately, the Spitfire produces 120 fs, 800 nm plane-polarized output pulses with an energy of 700 μJ per pulse. Using a 25 cm focal length lens, intensities up to \(4 \times 10^{14}\) W/cm\(^2\) can be achieved inside the interaction chamber. The pulse repetition rate is 1 kHz. The shot-to-shot TEM\(_{00}\) mode intensity fluctuations are less than 5%. Most of the data presented in this dissertation have been acquired with at least one million laser shots per spectrum, which takes 17 minutes. The high count rate yields a very low statistical error, which indicates that most of the observed features are well above the statistical noise.

1.3.3 Mode-locking

"Mode-locking is a standard technique for generating ultrashort laser pulses. The basic idea is that many modes are locked in phase. For each transverse mode, a laser resonator usually supports a number of longitudinal modes, which are separated in frequency by [69]

\[
\omega_{q+1} - \omega_q = \frac{\pi c}{l} = \omega = 2\pi v, \quad (1.5)
\]

where \(l\) is the cavity length and \(c\) is the speed of light. In order to produce short pulses, the laser resonator must support a large number (\(10^4-10^5\)) of longitudinal modes. Therefore, a large gain-bandwidth, as given with Ti:Sapphire, is a basic requirement for choosing a laser medium. The number of allowed modes is limited by the mode spacing, \(v\), and the bandwidth, \(\Delta v\), over which the laser gain exceeds the loss of the resonator, as shown in Fig. 1.11 [69, 70]" [71].
Figure 1.11. "(a) Inhomogeneously broadened Doppler gain curve of the 6328 Å Ne transition and position of allowed longitudinal mode frequencies. (b) Intensity versus frequency profile of an oscillating He-Ne laser. Six modes have sufficient gain to oscillate." From Ref. [69, 70].
The electric field of a multimode oscillation can be described by Eq. 1.6, where $E_n$ is the degeneracy and $\phi_n$ the phase of the $n^{th}$ mode. For simplicity all amplitudes are assumed to be equal to unity. Mode locking results if all $\phi_n=0$. In the case of $N$ oscillating modes with $E_n=1$ and equal amplitudes, Eq. 1.6 simplifies to Eq. 1.7. The average laser output power is given in Eq. 1.8. It is proportional to $E(t)E^*(t)$ [69].

$$E(t) = \sum_n E_n \exp\left[i\left((\omega_0 + n\omega)t + \phi_n\right)\right]$$ \hspace{1cm} (1.6)

$$E(t) = \sum_{-\frac{2K}{\Delta\omega}}^{\frac{2K}{\Delta\omega}} \exp\left[i(\omega_0 + n\omega)t\right] = \exp[i\omega_0 t] \frac{\sin(N\Delta\omega/2)}{\sin(\Delta\omega/2)}$$ \hspace{1cm} (1.7)

$$P(t) \propto \frac{\sin^2(N\Delta\omega/2)}{\sin^2(\Delta\omega/2)}$$ \hspace{1cm} (1.8)

Equation 1.8 indicates that mode locking produces a train of pulses, which are separated by $T = 2\pi/\omega = 2l/c$. Furthermore, the individual pulse width is given by $\tau = 2\pi/\Delta\omega = 1/\Delta v$. This shows that the pulse length is inversely proportional to the laser gain lineswidth, which supports the use of Ti:Sapphire as the laser medium.
1.3.4 Spectrometer

The TOF tube is inside a stainless steel vacuum chamber. In order to minimize the earth's magnetic field, several layers of μ-metal surround the entire flight tube, resulting in a residual magnetic field of ∼10-30 milligauss. The target gases enter via a leak valve and backfill the entire chamber. Photoionization spectra are typically recorded at pressures between $10^{-8}$-$10^{-5}$ torr. In order to keep impurities at a minimum, the target gas is cleaned via a molecular sieve [72] before entering the chamber. The sieve traps moisture and most organic molecules. After baking the chamber at greater than 100 °C, a background pressure of $2\times10^{-10}$ torr can be achieved. Figure 1.12 illustrates the absence of major contaminants in our ion spectra. The vacuum chamber with TOF setup is shown in Fig. 1.13.

![Xenon ion mass spectrum](image)

**Figure 1.12.** Xenon ion mass spectrum taken at approx. $10^{13}$ W/cm². Most of the recorded ions are Xe⁺ ions, followed by some Xe double ions. The different Xe isotopes can be resolved. The background signal is very low and consists mainly of water, nitrogen and hydrocarbons in the range 20-45 amu.
Figure 1.13. Spectrometer setup. Photoelectrons and ions are produced at the center of the 6-way cross. The flight tube is shielded with μ-metal. The conical anode at the end of the tube houses the microchannel plate detector. The dashed cross marks the laser focal region.
1.3.5 Detection

For detecting the photoelectrons a custom 50 Ω conical anode was attached to a chevroned pair of micro channel plate (MCP) detectors. The conical anode acts as a wave guide to maintain a 50 Ω impedance from the MCP to a coaxial connector. The acceptance angle of the detector is 3°. The analog signal was recorded by a multichannel scaler, triggered by a photodiode, which detected the laser pulses as they left the vacuum chamber after passing through the ionization region (see Fig. 1.10). The data in chapter 5 were recorded with a Multichannel Scaler/Averager (Stanford Research Systems SR430). This counting device recorded pulses coming from the MCP detector in successive 5 ns time bins. The other data presented in this dissertation have been recorded via a constant-fraction-discriminator, time-to-amplitude converter and subsequent multichannel analyzer. For practical purposes, a bin size of 80 ps is sufficient to yield good energy resolution over the range 0-50 eV. It should be noted that the line width of the laser is about 7 nm at a center wavelength of 800 nm. This corresponds to an energy uncertainty of 13 meV. Therefore, the absorption of, for instance, 8 photons results in an energy spread of \( \sqrt{8} \times 13 \text{ meV} = 37 \text{ meV} \). This leads to a time-of-flight uncertainty of about 40 ps for 50 eV electrons.
1.3.6 TOF Data Conversion

Photoelectron kinetic energy spectra can be obtained by converting time-of-flight data to kinetic energy using

\[ E = \frac{1}{2} m_e \frac{L^2}{(t + t_0)^2} + E_0. \]  

(1.9)

where \( t_0 \) is the time offset due to the detection electronics and \( E_0 \) is a contact potential offset. It is required that the probability of detection within a certain time interval must equal the probability of detection within the corresponding energy interval.

\[ P(t)dt = P(E)dE \]  

\[ (1.10) \]

There are two ways to convert from time to energy, while satisfying Eq. 1.10. The first method is to plot the recorded signal versus a modified energy axis, given by Eq. 1.9. Then, the signal has to be multiplied with the Jacobian of the time-to-energy transformation. The Jacobian in this particular case is given by

\[ \left| \frac{dt}{dE} \right| = \left| \frac{1}{dE/dt} \right| = \left| \frac{1}{\frac{d}{dt} \left( \frac{1}{2} m_e \frac{L^2}{t^2} \right)} \right| = \frac{1}{m_e \frac{L^2}{t^3}} = \frac{t}{2E}. \]  

(1.11)

This method is adequate if overall counting statistics are good, and many events per time bin have been recorded. The Jacobian weighting factor accounts for the fact that low energy electrons are spread out over a large time range, while a large range of high energy electrons fall within a narrow time range. However, this technique is inappropriate if counting statistics are low, or if the resolution is high enough, so that only a few events are
counted per time bin. In that case, it is better to perform data rebinning, where a specific
energy bin size, $\Delta E$, is defined and the recorded TOF signal is redistributed into the new
ergy bins. Each data point is assigned to a particular energy bin, based on its
corresponding time-of-flight. The sum of all counting events per energy bin yields the
correct kinetic energy distribution. Of course, rebinning is the more universal approach,
which is also valid for cases of high statistics. The major difference between the Jacobian
transformation and rebinning is that rebinning is computationally more demanding and time
-consuming, but it gives the more accurate transformation. The routine used for our TOF-
to-energy rebinning procedure is included in Appendix A.

Similarly, ion spectra are usually recorded as a function of time-of-flight and later
converted to charge per mass, $q/m$. A TOF spectrometer can differentiate only between
ions with different $q/m$. All ions are accelerated by the same potential difference, $V$, and
hence their kinetic energy equals $qV$. Using a Jacobian transformation yields quick
conversion and is sufficient if the counts rates are high. The Jacobian factor is given in
Eq. 1.12. Otherwise, time-to-mass rebinning produces a more accurate conversion but
requires more computing. A routine for rebinning ion TOF signal to $q/m$ is presented in
Appendix B.

\[
\left| \frac{dt}{dm} \right| = \left| \frac{1}{dm/dt} \right| = \left| \frac{1}{\frac{d}{dt}\left(\frac{2qVt^2}{L^2}\right)} \right| = \frac{1}{2qVt^2/L^2} = \frac{t}{2m} \tag{1.12}
\]
2.1 Introduction

The goal of this work was to develop a high efficiency time-of-flight spectrometer with reasonable resolution. The problems of traditional time-of-flight analyzers are a small acceptance solid angle (low collection efficiency) and space charge if the ionization rate is too high. These problems have been dealt with using strong magnetic [73] or static electric fields [74, 75]. The *Ellipsoidal Mirror Analyzer* (EMA) [76] addresses these problems by accepting a large solid angle of 8.4 str (67% of the sphere). Given the high collection efficiency, the EMA does not require a high ionization rate and space charge problems can be avoided. On the other hand, the EMA resolution becomes sensitive to extended electron sources. When focusing a laser into a collection of atoms or molecules photoelectrons are formed not only near the focal point but also along the line of propagation of the laser. This creates photoelectrons throughout a volume bounded by the overlap of the laser beam and the particles. Electrons created in any part of the region that is in the line-of-sight of the detector contribute to the kinetic energy spectrum. For straight TOF an extended source poses fewer problems, since the change in path length is small. The line source is most extended for single photon ionization. In case of multiphoton ionization the ionization region is more closely localized; however, extended source problems are still of concern.
As will be shown, the Ellipsoidal Mirror Analyzer allows the possibility of detecting only those electrons created in a small region around the focal point, thus not producing a degradation in resolution due to otherwise significant changes in path length. The design of the Ellipsoidal Mirror Analyzer is related to the concept of the Parabolic Mirror Analyzer (PMA) [75]. The PMA was based on paraboloidal grids and demonstrated good energy resolution for high order multiphoton processes. The parabolic mirror images a point into a parallel beam, whereas the ellipsoidal mirror images point to point. The converging electron beam rather than a parallel beam is the advantage of the EMA. Focusing the electron beam makes the signal less sensitive to stray fields, thus yielding a higher gain for the EMA than the PMA.

2.2 Design

The EMA works as an electron-optical mirror, consisting of two closely spaced grids. The inner grid has an ellipsoidal shape, while the outer grid is designed to maintain a constant separation, $d$, of 1 mm. The inner grid is at ground potential and the outer one has a negative retarding potential, $V_R$. Thus, the ionization region is field free, except for small leakage fields. An ellipsoid has two focal points and the sum of the distances from any point on the ellipsoid to the two focal points is constant. By focusing a pulsed laser onto focus 1 of the ellipsoid, $F_1$ in Fig. 2.1, photoelectrons are generated and stream radially outward in a specific angular distribution. Many of these electrons propagate through the inner grid, are reflected by the retarding electric field between the two grids and are refocused onto the second focal point, $F_2$, where the detector is placed. The total path length is the same (to first order in kinetic energy) for all photoelectrons coming from $F_1$ independent of their kinetic energy or emission angle. The additional path length inside the retarding field is negligible (see section 2.3). In that case, electrons with the same kinetic energy also have the same time-of-flight. Photoelectrons that are generated at other points
along a possible line source are not reflected exactly toward the second focal point. Those electrons, which would otherwise lead to spectral broadening, could be blocked by positioning an aperture in front of the detector. The elimination of these undesired photoelectrons reduces the error, $\Delta L/L$, in flight distance, maintaining the energy resolution.

In principle, it is also possible to obtain information about the original angular electron distribution by placing a position-sensitive detector some distance behind the aperture. Every point on the detector would correspond to a particular initial direction of emission. However, this design has not been investigated yet.

The retarding potential, $V_R$, has to be chosen such that the photoelectrons penetrate sufficiently deeply into the $E$-field between the grids. This insures that the deflection occurs in the region where the field is most homogeneous. The retarding $E$-field is created by individual wires and not continuous conducting surfaces, so in the region very close to a single wire the field acts as an electrostatic lens. Therefore, the wire separation has to be small compared to the grid spacing, yet the grid spacing must be small relative to the curvature of the ellipsoid to ensure an almost homogeneous $E$-field in the reflection region. A grid gap of 1 mm works well, given an opening diameter of the grids of 50 mm.

The grids were made out of stainless steel woven wire mesh (40 wires/cm, diameter=25 μm). The mesh was tightly stretched over a Delrin mold of ellipsoidal shape. The wire diameter was reduced to approximately 18 μm by electroetching in a solution of phosphoric acid. Afterwards, chromium was electroplated onto the mesh to increase the diameter back to about 25 μm. Due to the bimetal joint, the grids became very rigid and free-standing, maintaining their ellipsoidal shape during UHV baking procedures. Finally, the electroplated mesh was spot welded onto a stainless steel ring which was bolted onto the flight tube assembly.
Figure 2.1. Schematic cross section of the time-of-flight spectrometer. The detail box shows a typical electron trajectory through the ellipsoidal grids.
2.3 Experimental Results

Frequency-doubled 532 nm light from a Nd:YAG laser at a pulse repetition rate of 10 Hz was used to characterize the mirror. The output pulses were plane polarized and had a duration of 5 ns with an energy of 100 mJ per pulse. The beam was focused with a 25 cm focal length lens through holes cut into the grids, as shown in Fig. 2.1, yielding an intensity near $10^{13}$ W/cm² in the focus. Xenon was chosen as the target gas because of its relatively low ionization potential. Given the 532 nm light (hv=2.34 eV), a minimum absorption of 6 photons is required for liberating photoelectrons, as shown in Fig. 2.2. Due to above threshold ionization, the photoelectron kinetic energy spectrum consists of peaks separated by the photon energy. Xenon has two ionization limits due to spin-orbit splitting at 12.127 eV and 13.433 eV above the ground state, leaving the remaining ion in a Xe II(2P₃/₂) or Xe II(2P₁/₂) state, respectively [77]. Therefore, a given number of photons creates a pair of peaks, separated by the spin-orbit splitting of 1.306 eV.

![Xenon energy level diagram with 6-photon absorption.](image)

Figure 2.2. Xenon energy level diagram with 6-photon absorption.
For multiphoton ionization the emission of photoelectrons is the strongest along the
direction of polarization. Therefore, in order to objectively compare straight TOF with the
EMA the polarization was pointed down the flight tube (0°) for straight TOF with the grid
temperature off, and pointed perpendicularly (90°) when using the grids. Spectra were gathered
at a xenon pressure of 2x10⁻⁶ torr. At that pressure, a very good signal-to-noise ratio was
obtained, yet the pressure was still low enough to avoid space charge effects.

Figure 2.3 shows typical time-of-flight spectra obtained by counting electrons from
10⁵ laser shots. The time-of-flight, t, is given by

\[ t = L \sqrt{\frac{m_e}{2E}} \left[ 1 + 4 \left( \frac{d}{L} \right) \frac{E}{eV_R} \cos^3 \alpha \right], \tag{2.1} \]

where \( E \) is the electron kinetic energy, \( L \) the total flight distance (0.5 m), \( V_R \) the retarding
potential, and \( \alpha \) the angle of incidence into the grids. The correction term on the right hand
side of Eq. 2.1 is dominated by the time that the electrons spend in the gap between the grids.
For our measurements this term was negligible. Figure 2.4 was obtained by converting
Fig. 2.3 from time-of-flight to kinetic energy.

Comparing Figs. 2.3(a) and 2.3(b), we see a gain in electron count rate of 36 between
the EMA and straight TOF for the 1.85 eV peak at \( V_R=3.5 \) V. The gain for 0.55 eV,
2.88 eV and 4.18 eV electrons is 11, 31, and 19, respectively. The gain varies as a
function of electron kinetic energy and retarding grid voltage \( V_R \). We observe the highest
gain for electrons of a specific kinetic energy when the grid voltage equals the kinetic
energy divided by the electron charge, e.g. the EMA yields the highest gain for 5 eV
electrons if \( V_R \) is close to 5 V.
Furthermore, we obtain good energy resolution with the EMA. By measuring peak widths we identified energy resolutions of 37 meV (6.7%), 51 meV (2.8%), 71 meV (2.5%), and 169 meV (4.0%) for the 0.55 eV, 1.85 eV, 2.88 eV, and 4.18 eV photoelectrons, respectively. The EMA is able to retain the same resolution as we detect with straight time-of-flight, which proves the high quality of the reflecting grids.
Figure 2.3. TOF spectra of Xe taken with 100 mJ of 532 nm, 5 ns laser pulses. (a) The grid is turned off and the polarization is pointed down the flight tube. (b) The polarization is pointed at 90° and $V_R=-3.5$ V on the outer grid.
Figure 2.4. Kinetic energy distributions derived from TOF spectra in Fig. 2.3. See text for explanation of individual features. (a) straight TOF, (b) EMA spectrum. Note the different y-scales, indicating the large gain.
2.4 Discussion

Given a straight flight distance of 48 cm from the ionization region to the 27 mm diameter detector, a solid angle of approximately $2.5 \times 10^{-3}$ str is accepted for straight TOF. The grids on the other hand cover about 67% of the full sphere, which leads to a 3400 times larger solid angle than straight TOF. However, the maximum theoretical gain for MPI of xenon is significantly less than 3400 since the angular distribution is far from isotropic. Based on earlier studies by Freeman et al. [11], a $\cos^{10\theta}$ dependence for the angular distribution of our MPI source is assumed. It is estimated that a maximum fraction of 0.25% of all emitted photoelectrons can be detected with the straight TOF analyzer when the polarization is pointed toward the detector. Given the particular size and geometry of our grids, it is estimated that about 50% of all photoelectrons are emitted into the grids when the laser polarization is at 90° relative to the direct flight path. In this case, electrons strike the inner grid at angles of incidence $\alpha$ (see Fig. 2.1) between 30° and 60°. An average incident angle of $\alpha=45^\circ$ is used for estimating the grid transmission ($\alpha=45^\circ$ reflections correspond to electrons emitted exactly along the direction of polarization). Considering the wire thickness and separation, the mesh has an open area of 80%. Electrons entering the grid gap at $\alpha=45^\circ$ and penetrating twice through the inner grid experience an effective transmission of $(80% \times \cos45^\circ)^2 = 32%$. Therefore, we expect a gain of approximately 64. A more sophisticated estimate would require integrating over the exact angular distribution and the angle-dependent transmission.

The gain of 36 for 1.85 eV electrons (Fig. 2.3(b)) is an excellent result considering that low energy electrons are very sensitive to residual fields. The highest gain occurs for the 1.85 eV electrons because they have a more isotropic angular distribution than any of the higher energy electrons. For ATI the angular spread of emitted photoelectrons peaks about the direction of polarization. The higher the number of absorbed photons, the smaller the opening angle of the angular spread. This results in a higher gain for the lower
energy electrons. A comparison between Figures 2.3(a) and 2.3(b) clearly shows this tendency. The reason why the highest gain is not seen for the 0.55 eV electrons is that they are the slowest, thus most affected by fringe electric fields and any residual magnetic field. For the same reason, the 0.55 eV energy resolution does not reproduce the expected value. Otherwise, our experimental resolution reaches the limit imposed by the 5 ns bin width of the multichannel analyzer.

Another interesting feature in Fig. 2.3(b) is the signal cut-off at 400 ns. Due to the grid voltage of -3.5 V, electrons with more than 6 eV kinetic energy are not reflected, but instead penetrate through the outer grid and are not detected. The reason 4.18 eV electrons can be seen is that they do not enter the retarding field normally but at about 45°. In order to increase the count rate of higher energy photoelectrons, $V_R$ would have to be increased at the expense of detecting fewer of the slow electrons. The maximum count rate for a given energy range can be attained whenever the electrons penetrate halfway into the retarding field between the two grids. Then the reflection occurs where the field is most homogeneous.

Figure 2.3 reveals several other interesting effects. For straight TOF, compared to the EMA signal, the higher energy peaks are shifted toward shorter times-of-flight whereas the 0.55 eV peak appears at a longer TOF. This is the result of two competing effects. Straight TOF has a shorter flight distance of 48 cm as opposed to 50 cm for the EMA, but it also requires an energy offset, $E_0$, near 220 meV, due to retarding contact potentials. The EMA on the other hand has additional fields present when a voltage is applied to the grids, resulting in a smaller energy offset near 160 meV. Therefore, fast electrons have a shorter straight TOF due to the shorter distance, while the contact potential does not affect their TOF very much. Slow electrons, however, experience a significant decrease in speed and therefore appear at later times in straight TOF.
In addition, Fig. 2.3(b) shows a small peak at 600 ns close to the main 1.85 eV signal. It arises from those 1.85 eV electrons that strike the detector directly without being reflected by the grids. Therefore, they appear at a slightly shorter TOF. After the transfer to a kinetic energy spectrum, the small straight TOF peak appears at a slightly higher energy because the conversion assumes a path length of 50 cm for the entire spectrum. Furthermore, there is a peak at 450 ns that does not correspond to a xenon ionization. It arises from laser reflections inside the chamber that hit the outer grid and ionize the chromium coating which has a low work function of 4.5 eV. Those electrons are then accelerated by \( V_R = -3.5 \) V and appear at a TOF corresponding to 3.5 eV.

### 2.5 Conclusion

The Ellipsoidal Mirror Analyzer is a novel time-of-flight spectrometer that uses an electrostatic field to reflect and focus electrons with a very high collection efficiency. This versatile spectrometer analyzes single and multiphoton ionization processes and operates over a wide energy range. For 1.85 eV photoelectrons produced by ATI of xenon, a maximum gain of 36 with a resolution of 51 meV (2.8%) has been demonstrated. Given the high collection efficiency it is possible to avoid space charge effects while maintaining a high electron detection rate. The application of the EMA is most useful when recording photoelectron data at a low repetition rate, or whenever the observed process occurs with low probability.
CHAPTER 3

INTENSITY-SELECTIVE-SCANNING:
A NEW METHOD OF PHOTOELECTRON SPECTROSCOPY

3.1 Introduction

Traditional time-of-flight analyzers have small acceptance solid angles, low collection efficiencies, and may encounter space charge problems if the ionization rates are too high. In the past, several methods have been developed to enhance the low collection efficiency by applying strong magnetic [73] or static electric fields [75, 76]. While some of these approaches yield signal gains of close to 40 [76], it should be noted that either the environment of the ionization region or the electron flight path are affected by the presence of magnetic or electric fields and could result in perturbations compared to spectra obtained under field-free conditions.

The goal of this work was to develop a method of high precision time-of-flight spectroscopy applicable to a wide range of intensities with good resolution and high count rates. This novel technique, Intensity-Selective-Scanning (ISS) [78], allows the study of any multiphoton ionization process by combining high repetition rate laser technology and the optical properties of focused laser beams. In particular, it can be used for short pulse resonance-enhanced MPI studies, as will be demonstrated in this chapter. Typical high order MPI (requiring greater than 5 photons to ionize) spans the range from $10^{12}$-$10^{14}$ W/cm², beyond which tunneling processes become non-negligible. This chapter is concerned with the low end of this high intensity range.
3.2 The Curse of Spatial Averaging

The spatial and temporal intensity distribution in a Gaussian focus is given by Eq. 3.1 [56], where \( I_0 \) is the intensity at the spatial and temporal peak, \( r_0 \) is the minimum waist size and \( \tau \) is the temporal 1/e-halfwidth of the electric field. The \( z \)-dependent waist is given by Eq. 3.2 [56], where \( z_0 \) is the Rayleigh range given by \( z_0 = \pi r_0^2 / \lambda \) [56]. Figure 3.1 displays the spatial distribution of the temporal peak intensities in a Gaussian laser focus, given by Eq. 3.1.

\[
I(r, z, t) = I_0 \left( \frac{r_0}{\omega(z)} \right)^2 \exp \left[ -2 \left( \frac{r}{\omega(z)} \right)^2 - 2 \left( \frac{t}{\tau} \right)^2 \right]
\]  

\[
\omega(z) = r_0 \sqrt{1 + \left( \frac{z}{z_0} \right)^2}
\]  

It is apparent that a large range of intensities is present within the focus. When observing an entire focal volume the associated photoelectron spectrum results from a convolution of both volume and ionization rate. The ionization rate is typically highest for the peak intensity located at the minimum beam waist. However, the volume occupied by the highest intensities is very small. In contrast, much larger volumes are occupied by low intensities, which are often still sufficient to ionize the targets. By detecting photoelectron or ion signals from the whole focal volume, such measurements represent the spatial average over all available intensities. This can become particularly problematic when trying to study very high intensity phenomena. Sensitive measurements can be adversely affected by a large portion of low-intensity signal from the large volume focal periphery.
Figure 3.1. Schematic spatial distribution of temporal peak intensities in a Gaussian focus.
3.3 Traditional Intensity Variation

In order to study multiphoton ionization over a range of different intensities the absolute peak intensity, $I_0$, has to be changed to the desired level, when using the traditional approach of exposing the full focal volume. To change the overall laser intensity, filters or auxiliary optics are typically inserted into the beam. This, however, can disturb the quality of the laser beam due to interactions such as self-phase modulation [18, 79, 80]. In addition, the actual laser peak intensity must be measured experimentally after each change, which can introduce a large relative error for the chosen intensities. Depending on the availability of certain filters, or the accuracy of a $\lambda/2$-wave-plate for changing the intensity, traditional TOF spectroscopy usually does not allow changing the intensity in very fine steps. The biggest problem is that the overall beam quality may fluctuate too much, due to the use of additional optical components. A small change in the laser pulse width can cause dramatic fluctuations in the average laser intensity, which is given by $I = \frac{E}{A \cdot \tau}$, where $E$ is the pulse energy, $A$ is the beam cross section area, and $\tau$ is the temporal pulse width.

Furthermore, it is extremely difficult to study low-intensity ionization phenomena ($I_0 < 10^{13}$ W/cm$^2$) when detecting the full volume. For a Gaussian focus, the volume experiencing an intensity between $I_0$ and $I_0 - \Delta I$ is given by

$$V(\Delta I, I_0) = \pi z_0^2 \left\{ \frac{4}{3} \left( \frac{\Delta I}{I_0 - \Delta I} \right)^{1/2} + \frac{2}{9} \left( \frac{\Delta I}{I_0 - \Delta I} \right)^{3/2} - \frac{4}{3} \tan^{-1} \left( \frac{\Delta I}{I_0 - \Delta I} \right)^{1/2} \right\}^{3/2} \tag{3.3}$$

Although the volume $V(\Delta I, I_0)$ increases slightly as $I_0$ is reduced, for fixed $\Delta I$, typical ionization rates associated with low intensity phenomena decrease more rapidly so that the resulting overall signal still vanishes relatively fast. The relevant ionization volume at the minimum beam waist is simply too small to detect low intensity signal.
3.4 ISS Intensity Variation

Instead of exposing the entire ionization region to the time-of-flight detector, a pinhole at the front of the flight tube, as shown in Fig. 3.2, drastically reduces the relevant ionization volume which is in the line-of-sight of the detector. The scanning is performed by moving the focusing lens via a translation stage outside of the interaction chamber. The complex geometry of a Gaussian focal volume can be simplified to different slices, as shown in Fig. 3.3, which have essentially only a one-dimensional radial intensity dependence.

By scanning the ionization region across the pinhole, intensity-selective observation of MPI in a field-free region becomes possible without changing the characteristics of the focused laser beam. This ensures consistent pulse energies and temporal widths. The peak intensity within a spatially selected part of the laser focus can be varied by selecting different slices along the z-axis (the direction of propagation of the laser beam) as shown in Fig. 3.3. For any selected z-position the local on-axis peak intensity can be obtained via Eq. 3.4 [56] as

\[
I(r = 0,z) = \frac{I_0}{1 + z^2/z_0^2}.
\]  

Therefore, an evolution of intensities can be studied with extremely high precision and intensity control. Moving the lens with a micrometer allows changing the observed intensity reproducibly in very small steps. Knowing the beam profile and the Rayleigh range, \(z_0\), great relative accuracy can be achieved for successive intensity positions, as opposed to the traditional full volume technique. The actual beam profile, as shown in Fig. 3.4 [81], has been measured with an imaging system and a CCD camera. The laser beam intensity can be calculated from the measured 1/e-halfwidths, and allows for a self-consistent check of our intensity calibration.
Figure 3.2. Schematic setup of time-of-flight spectrometer with ISS. The focusing lens can be moved via a translation stage to scan the ionization volume across the pinhole at the front of the flight tube. MCP, microchannel plates.
Figure 3.3. Specific slices of the laser focus can be selected via ISS. The outer contours show the 1/e-points of the laser field. The inner lines around the slices are iso-intensity contours.
Figure 3.4. The 1/e E-field halfwidth can be measured with an imaging system. The solid line indicates the calculated contour according to Eq. 3.2, with a measured minimum beam radius of $r_0=45$ microns. The left hand side of the focus is used for scanning the intensity in our experiments since there is an excellent match with the theoretical profile. From Ref. [81].
With ISS, high-intensity effects can be observed more accurately and spatially resolved. The full volume often produces significant low-intensity signal, so that the contributions from the laser peak intensity may get washed out. ISS allows the observer to zoom in on the minimum beam waist, while blocking out most of the large-volume weak-field signal.

Similarly, the same restricted ISS geometry also allows for improved observation of low-intensity signals. Low intensities can be selected by moving the pinhole away from the beam waist along the $z$-direction, while maintaining the same absolute $I_0$. As the focused laser beam diverges from its waist the volume occupied by lower intensities increases rapidly and leads to a significant low-intensity signal gain over traditional methods. This approach differs from traditional TOF photoelectron spectroscopy by blocking out the otherwise strong high intensity signal.

Figure 3.5 shows the relative volumes occupied by intensities between some $I$ and $I-\Delta I$ for two cases: (a) $I_0$ is lowered to match $I$ (traditional method), and (b) $I_0$ is kept high while the desired intensity range in $z$ is selected (ISS). The observed ionization volume in Fig. 3.5(b) can be derived similarly to Eq. 3.3. The gain achieved by ISS is the ratio between the volume occupied by the selected ISS intensity range (given by $z$, $I_0$ and pinhole size $\Delta z$) compared to the volume one would observe by decreasing $I_0$ accordingly. The theoretical gain is shown in Fig. 3.6 for $I_0=7\times10^{13}$ W/cm$^2$, $\Delta z=2$ mm and a Rayleigh range of 4.5 mm.
Figure 3.5. Intensity contours for which (a) the photoelectron signal is dominated by ionizations at the peak intensity (traditional TOF spectroscopy), and (b) the same intensity range as in (a) can be selected through ISS at a much higher peak intensity, resulting in signal gain due to the larger volume.
Figure 3.6. Volumetric gain for the ISS technique versus traditional TOF spectroscopy for $I_0 = 7 \times 10^{13}$ W/cm$^2$, $\Delta z = 2$ mm, and $z_0 = 4.5$ mm.
Under the above conditions an expected maximum gain of 15 occurs at an intensity near $10^{12}$ W/cm$^2$ and then rapidly increases to over 100 at lower intensities. At higher absolute intensities, $I_0$, the gain for any intensity will rise even more. This calculation yields the surprising result that low intensity phenomena are best studied using the highest intensity lasers while selectively observing regions away from the beam's minimum waist.

Furthermore, Intensity-Selective-Scanning yields better signal-to-noise ratios and the effects of extended signal sources are minimized. The simplified geometry also allows the direct extraction of ionization rates because the volumetric scaling is easier to deconvolve. The well-known problem of spatially averaging over a large intensity range can be reduced. Instead, observation of a radial one-dimensional intensity distribution is now possible, providing much more reliable data for comparison with theoretical MPI models [82-84].

3.5 Experimental Results and Discussion

We have recorded photoelectron spectra of xenon using a 1 kHz Ti:Sapphire laser system, generating 120 fs, 800 nm plane-polarized output pulses with an energy of 700 μJ per pulse. Based on a measured 1/e-radius for the electric field of 45 μm an absolute intensity of $I_0=7\times10^{13}$ W/cm$^2$ at the minimum beam waist was achieved inside the interaction chamber. The kilohertz repetition rate allowed acquiring a minimum of $3\times10^5$ laser shots per spectrum at a xenon pressure between $5\times10^{-7}-3\times10^{-5}$ torr.

Figure 3.7 shows photoelectron kinetic energy spectra for the intensity range $6\times10^{12} - 7\times10^{13}$ W/cm$^2$. The scans are plotted on a vertical log-scale and vertically separated for better comparison. Via ISS we have observed a very clean evolution of the xenon Rydberg state series. As the selected intensity is slowly stepped up, one can follow the successive appearance of additional Rydberg states whenever the corresponding threshold intensities are overcome. The ability to resolve the Rydberg states this well, and the excellent signal-to-noise ratio shown in Fig. 3.7, demonstrate the feasibility of Intensity-Selective-
Scanning. The fluctuations in the wings of the bottom ten scans are at the noise level of a few counts per bin. A full quantitative analysis of the observed transient resonances is presented in chapters 4 and 7.

Furthermore, Fig. 3.7 illustrates the dynamic range of ISS. Twenty-six scans have been taken over more than one order of magnitude in intensity. The step size for translating the focusing lens was $\Delta z=1 \text{ mm}$, which means that a much lower stepsize is still possible (e.g. 50 $\mu\text{m}$). The trade-off lies between intensity step-size and overall data collection time. If ISS is applied with a very small $\Delta z$ stepsize, while a few million laser shots per scan are desired, then the total time to cover a large intensity range may be many hours. On the other hand, ISS offers the possibility to zoom in on certain intensities and follow closely how small intensity variation affect the spectra. This is especially important in cases where phenomena occur within a narrow intensity window [52].

Given 800 nm photons (1.55 eV), the first parity-allowed multiphoton resonances are the 8-photon f-series Rydberg states. The bottom scans on Fig. 3.7 show that the lowest intensity of $6 \times 10^{12}$ W/cm$^2$ suffices to ac-Stark-shift high lying Rydberg states above the 10f-state into resonance. As the intensity is increased, the entire f-series develops and eventually saturates. Suddenly, within only two scans, the 9-photon g-state resonances start appearing (9th scan from the top), as extensively discussed in chapter 7. This shows the importance of having the control of following the turn-on of specific features. By using a potentially more coarse and less reproducible full-volume technique, effects with sudden turn-on may be missed entirely or may be hard to trace. Furthermore, ISS reduces the volume dependence of the signal, and better quantitative analysis is possible. Effects that occur at higher intensities are not washed out by low-intensity, large volume signal. The favorable volumetric behavior contributes to the clarity of the emerging higher order resonances.
Figure 3.7. Photoelectron spectra of xenon at intensities ranging from $6 \times 10^{12} - 7 \times 10^{13}$ W/cm$^2$ obtained via ISS. The scans are presented on a vertical log-scale and vertically separated. The lowest intensity scan is presented at the bottom and the intensity increases upward. See text for full explanation.
Another example of the advantages of ISS is illustrated in Fig. 3.8, which shows photoelectron spectra obtained with circularly polarized light. Previous experiments [30, 85, 86] have shown that the short pulse ionization process depends sensitively on the laser polarization. ATI spectra vary for different degrees of ellipticity of the polarization, with linear and circular polarization being the two extremes.

Linear polarization produces ATI spectra that exhibit substructure within each ATI order due to transient resonances. In contrast, circular light practically does not permit ionization via intermediate states, given the angular momentum selection rules [87]. However, direct multiphoton ionization into the continuum is possible, although the cross section for circular light is smaller. The resulting spectra show broad peaks that are separated by the photon energy, but no clear substructure within each ATI order can be detected. These nonresonant ATI bumps shift ponderomotively with intensity. As shown by Bucksbaum et al. [30] nonresonant ATI structure vanishes when the ponderomotive shift exceeds the ATI separation of the photon energy. Then, different parts of the laser focus experience different shifts such that the spatial average over the entire focal volume produces a fairly smooth photoelectron spectrum which does not show any ATI peaks any more. Therefore, nonresonant ATI peaks can only be seen for low peak intensities when using traditional TOF spectroscopy.

In contrast, using ISS and circular 800 nm light we have been able to clearly observe nonresonant ATI peaks for large ponderomotive shifts. The top spectrum in Fig. 3.8 has been recorded with the traditional method of exposing the whole laser focus to the detector. It reproduces Bucksbaum's observation of a structureless photoelectron spectrum due to spatial averaging. The bottom three scans show ISS spectra that are taken under the same laser conditions as the full view scan. By selecting slices of the focal volume the spatial averaging is drastically reduced so that nonresonant ionization at high peak intensities can be observed. Scanning the focus at different positions yields similar ATI spectra, except
they are shifted toward higher or lower kinetic energy depending on the local ponderomotive potential within the selected slice. The three ISS spectra illustrate how different parts of the laser focus yield slightly shifted kinetic energy spectra for circular light at large intensities. It becomes clear that the conventional technique of spatially averaging over these different contributions results in a loss of information. The ISS spectra shown in Fig. 3.8 are only representative scans. Recording spectra of adjacent ISS slices over the entire focal volume and adding the recorded scans yields the same structureless spectrum as the full view scan in Fig. 3.8.

Intensity-Selective-Scanning shows how important new insight can be gained from spatially resolving the focal volume. In the case of circularly polarized light we are able to observe nonresonant ATI peaks with larger ponderomotive shift than can be observed by traditional means. Using ISS we have gained new perspectives on several other high intensity ionization phenomena, as will be shown in the following chapters, where the ionization process depends strongly on the spatial distribution of intensities within the focus.
Figure 3.8. Photoelectron spectra of xenon taken with circularly polarized 800 nm light. The top scan is recorded with the full ionization volume. The bottom three scan are ISS spectra from different parts of the laser focus.
3.6 Conclusion

We have developed a novel method of time-of-flight photoelectron spectroscopy that allows observation of multiphoton ionization with extremely high precision for both high and low probability events. Intensity-Selective-Scanning embraces the use of high repetition rate lasers to build up fast statistics, ultrashort pulses to generate high intensities, and a pinhole to select specific intensity regions of the Gaussian focal volume. Furthermore, this technique allows studying angular photoelectron distributions and it minimizes the effects of extended electron sources. ISS capitalizes on the volume increase of the intensity distribution as one moves away from the minimum Gaussian beam waist. This technique presents a new way of observing fundamental laser-matter interactions. The applications of ISS are very broad, ranging from high precision studies of fundamental laser-matter interactions to analyses in chemistry and materials research.

In summary, the key features of the ISS technique are:

- Very precise peak intensity control while maintaining optimal overall beam quality.

- Enhanced detection of high-intensity effects.

- Enhanced detection of low-intensity effects due to the volumetric growth of the diverging laser beam.

- Improved signal-to-noise ratio.

- Reduction of complex intensity distribution to a 1-dimensional radial dependence within a selected window.
CHAPTER 4

HIGH RESOLUTION TRANSIENT RESONANCES IN
ABOVE THRESHOLD IONIZATION OF XENON

4.1 Introduction

Since the discovery of transient resonances, most above threshold ionization phenomena at low kinetic energies have been considered sufficiently well understood. In contrast, we have observed low energy phenomena [52] demonstrating that some of the details of multiphoton and above threshold ionization remain unclear. The purpose of this chapter is to present the evolution of low kinetic energy, high resolution photoelectron spectra of xenon to illustrate the limits of traditional ATI theory. We have used 800 nm light to record high resolution photoelectron spectra displaying high lying Rydberg resonances that can be resolved up to the 9f-state. Furthermore, we have observed clear Rydberg structure up to the 7th ATI-order.

4.2 Experimental Results and Discussion

Figure 4.1 displays the evolution of f-series Rydberg states in the photoelectron spectra of xenon at various intensities over the range $6 \times 10^{12} - 2 \times 10^{13}$ W/cm$^2$. Using 800 nm photons, and given the xenon ionization potential of 12.127 eV, the first parity-allowed transient resonances occur with the 8-photon level. At an intensity of $6.6 \times 10^{12}$ W/cm$^2$ (Fig. 4.1(a)), only the highest lying Rydberg states can be shifted into resonance. As the intensity increases, from Fig. 4.1(a) toward 4.1(i), more ponderomotive

58
energy becomes available to also shift the lower lying f-states into resonance. This trend leads to a nice sequence of spectra showing the onset of each of the individual low-lying Rydberg states down to the 4f-state. The successive appearance of the observed resonances confirms, at least in the low kinetic energy range, the traditional model of ponderomotively shifting Rydberg states into resonance with harmonics of the laser field. The f-states clearly dominate the spectra, while only small p-state contributions can be observed. This is due to the 3-fold p-degeneracy compared to the 7-fold f-state degeneracy, which goes as \((2l+1)\).

The excellent agreement between the recorded f-states and their theoretical positions is furthermore shown in Fig. 4.2. It shows the first ATI-order at an intensity of \(2.5 \times 10^{13} \) W/cm\(^2\). Given our high resolution, we are capable of resolving Rydberg states as high as the 9f. Beyond that, the density of higher lying Rydberg lines approaches our experimental bin size of about 10 meV at 3 eV kinetic energy. Furthermore, it is apparent that only remnants of p-state resonances appear in the spectrum.
Figure 4.1. Low intensity photoelectron spectra showing the evolution of 8-photon resonance structure in xenon using 800 nm light at intensities of (a) 0.66, (b) 0.77, (c) 0.91, (d) 1.20, (e) 1.47, (f) 1.85, (g) 2.39, (h) 2.75, (i) $3.20 \times 10^{13}$ W/cm$^2$. All curves are vertically shifted and normalized to a common maximum amplitude. The vertical lines at the top indicate the observed f-Rydberg states.
Figure 4.2. High resolution photoelectron spectrum of xenon showing the first ATI order at an intensity of $2.5 \times 10^{13}$ W/cm$^2$. 
Figure 4.3 shows a photoelectron spectrum of xenon taken at $4.5 \times 10^{13}$ W/cm$^2$. The time resolution is 80 ps/bin, yielding an energy resolution of 0.2 meV for 1 eV electrons, and 0.6 meV for 10 eV electrons. We have observed very clear Rydberg structure out to kinetic energies as high as 12 eV. This result is remarkable since it shows Rydberg state resonances that correspond to an absorption of up to 16 photons. For each ATI order, Fig. 4.3 shows the corresponding Rydberg series, starting with the $n=4$ state and converging toward the ionization limit (bold line) at higher kinetic energy. As recently observed, at sufficiently high intensity, higher-order ATI resonances become dominant and yield enhanced ionization rates [38]. At an intensity of $4.5 \times 10^{13}$ W/cm$^2$ the observed Rydberg structure results from resonances with the next highest parity-allowed 9-photon level. As demonstrated in chapter 7, this strong-field behavior leads to a dominance of the g-states. The kinetic energy range in Fig. 4.3 displays the 1$^\text{st}$ to 7$^\text{th}$ ATI orders. All of them show unambiguously the 5g-, 6g-, 7g- and 8g-lines, even within the highest order around 12 eV. Above 12 eV kinetic energy, no clear Rydberg resonances can be identified due to the degrading resolution as well as the occurrence of additional resonant structure, which has not yet been explained. Figure 4.3 does not extend to show higher energy structures, since those are the subject of chapter 6.
Figure 4.3. Photoelectron spectrum of xenon showing the 1^{st} - 7^{th} ATI orders at an intensity of 4.5 \times 10^{13} \text{ W/cm}^2.
4.3 Conclusion

We have shown a very clean intensity-evolution of low kinetic energy transient resonances in xenon, obtained via Intensity-Selective-Scanning. Our high resolution spectra show that traditional ATI resonances can be clearly observed at least up the 7th ATI-order. Other recent experiments [52] have shown that new resonance phenomena appear at higher kinetic energies above 12 eV, as will be discussed in chapter 6. Using 800 nm light for ionizing xenon, we have demonstrated that traditional above threshold ionization is valid for at least the first 7 ATI-orders, up to 12 eV.
CHAPTER 5

HIGH INTENSITY PHOTOELECTRON SPECTRA
OF THE NOBLE GASES

5.1 Introduction

The purpose of this chapter is to present a survey of photoelectron spectra of several noble gases, displaying the appearance of hot electrons beyond the $2 \, U_p$ point. Recent experiments [47, 50] have shown that the high energy part of strong field photoelectron spectra exhibits a change in slope and a tail, somewhat similar to the plateau and abrupt cutoff known from high order harmonic generation (HOHG). While the HOHG plateau extends to $3.17 \, U_p$ [13, 88], the photoelectron tail has a cutoff around $10 \, U_p$, as discussed in chapter 1. The main spectral characteristics of HOHG appear to be understood at the current experimental level, whereas the mechanism leading to ATI is more complex and has not yet been fully explained. Theoretical models [51, 89-93] have improved the understanding of ATI; however, some of the details of the process remain unclear.

The hot electron part of the spectra for some gases shows structure that cannot be explained by the Simpleman's theory alone. Due to equipment constraints the presented spectra have relatively low energy resolution in the high energy range. Nevertheless, qualitative features have been identified that led into the more detailed studies presented in chapter 6.
5.2 Experimental Results and Discussion

In order to reach intensities up to $4 \times 10^{14}$ W/cm$^2$ inside the interaction chamber, the initial laser beam diameter was enlarged by a factor of 3 via a telescope so that tighter focusing can be achieved. Using a Multichannel Scaler/Averager, the analog signal is recorded in successive 5 ns-time bins. The given instrumental resolution does not allow observation of any MPI structure above 20 eV kinetic energy; however, it accurately provides the envelope of the photoelectron energy distribution.

Figures 5.1 - 5.5 show photoelectron spectra over different intensities for helium, neon, argon, krypton and xenon. The intensities ranged from $4 \times 10^{13}$ to $4 \times 10^{14}$ W/cm$^2$. All five spectra show similar overall characteristics: Most electrons are emitted in the kinetic energy range below 20 eV, consisting of ATI structure and transient resonances [35]. At intermediate energies the spectra exhibit Simpleman's behavior up to the 2 $U_p$ point at which the slope changes. The ponderomotive potential scales linearly with intensity and is 0.598eV at our wavelength of 800 nm and an intensity of $10^{13}$ W/cm$^2$. The high energy regions above 2 $U_p$ account for a few percent of the total emitted electrons and are the focus of this chapter. Each target gas exhibits a hot electron tail that extends out to about 10 $U_p$. This tail has been attributed to elastic electron backscattering [51, 94], as discussed in section 1.2.3. Although generally similar, our spectra exhibit specific differences between the gases for the energy range 20-60 eV. In particular:

1. A prominent spectral feature in xenon is located at about 35 eV which shifts to slightly higher kinetic energy and broadens at increasing laser peak intensity (Fig. 5.5).

2. Krypton exhibits two features at approximately 30 eV and 55 eV (Fig. 5.4). The structures appear less prominent than in xenon and are less sensitive to laser intensity changes.
Argon shows multiple modulations, in particular bumps at 40 eV and 65 eV (Fig. 5.3). No shift in these structures can be observed as a function of intensity.

Neon exhibits one feature at 35 eV and a second one near 60 eV (Fig. 5.2).

Helium spectra exhibit no prominent features above 20 eV (Fig. 5.1).

It is apparent that the structures for all noble gases, except helium, persist as a function of intensity and are not artifacts at a single intensity. The Simpleman's model predicts a smooth, structureless signal fall-off due to its inherent classical nature. When taking a quantum mechanical point of view, the spectra include the repetitive photon structure underneath the envelope. However, no bumps and shoulders in the envelope can be explained by straight MPI or Simpleman's/backscattering behavior.

The helium photoelectron spectra in Fig. 5.1 exhibit no strong peaks or shoulders. The low energy regions of the spectra follow the Simpleman's model very well and the higher energy portions do not exhibit any strong features. The absence of any bumps could potentially be correlated with the absence of inner shells in helium, as opposed to the other noble gases.

As mentioned earlier, the xenon bump near 35 eV shifts to slightly higher energies as the laser intensity increases. The shift is possibly due to ponderomotive effects. The bump appears to shift linearly with peak ponderomotive potential according to $\Delta E = \alpha U_p$, where $\Delta E$ is the shift from a zero-field position near 35 eV. The slope $\alpha$ for the xenon peak is about 0.75. In contrast, the hot electron modulations in neon, argon and krypton do not shift nearly as much as in xenon. They remain at almost constant kinetic energy. At higher intensities above $1.7 \times 10^{13}$ W/cm$^2$ the 2 $U_p$ cutoff extends beyond 20 eV. At that point, some of the observed hot electron features start vanishing since they get swallowed by the Simpleman's background. This can be observed for all noble gases.
Finally, Fig. 5.6 shows a survey of several molecular photoelectron spectra. Due to the additional degrees of freedom, molecular strong field ionization is more complex than atomic behavior and has thus not been studied as extensively in the past [95-100]. The three molecules CH$_3$F, SF$_6$ and N$_2$ show general behavior similar to atomic photoelectron spectra. The majority of all emitted electrons appear below about 20 eV, and all three gases show the typical 10 $U_p$ cutoff due to backscattering. There are some differences in the very low energy MPI falloff. The SF$_6$ spectra seem to drop more rapidly than either CH$_3$F or N$_2$. Moreover, except for some modulations in the lowest intensity scan in SF$_6$, none of the scans show any prominent features in the hot electron tail. Apparently, the high energy bumps seen in the noble gases are a unique atomic phenomenon, even though some of the studied gases have similar ionization potentials ($IP_{(SF_6)}=15$ eV, close to Ar) and the Simpleman's motion that leads to backscattering primarily depends on the field and phase at the time of ionization.

5.3 Conclusion

We have recorded strong field photoelectron spectra of the noble gases and a few molecules. All exhibit multiphoton resonances at low kinetic energies, a Simpleman's falloff at 2 $U_p$ and a hot electron backscattering tail out to 10 $U_p$. However, differences have been seen in the envelopes of the atomic spectra in the energy range 20-60 eV. There are several modulations and bumps in those regions that cannot be explained by backscattering alone. These observations have led to further studies, with higher resolution, which are presented in chapter 6.
Figure 5.1. Photoelectron spectra of helium with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) 1.7, (4) $1.4 \times 10^{14}$ W/cm$^2$. 
Figure 5.2. Photoelectron spectra of neon with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) $1.7 \times 10^{14}$ W/cm².
Figure 5.3. Photoelectron spectra of argon with 800 nm, 120 fs pulses at intensities of (1) 6.3, (2) 4.0, (3) 2.6, (4) 1.7, (5) 1.4, (6) $1.1 \times 10^{14}$ W/cm².
Figure 5.4. Photoelectron spectra of krypton with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) 1.7, (4) 1.4, (5) 0.85, (6) 0.60x10^{14} W/cm^2.
Figure 5.5. Photoelectron spectra of xenon with 800 nm, 120 fs pulses at intensities of (1) 4.0, (2) 2.6, (3) 1.7, (4) 1.4, (5) 1.1, (6) 0.85, (7) 0.60, (8) 0.40x10^14 W/cm².
Figure 5.6. Molecular photoelectron spectra with 800 nm, 120 fs pulses at intensities of (1) 3.4, (2) 2.6, (3) 1.7, (4) 1.4, (5) $1.1 \times 10^{14}$ W/cm$^2$. 
CHAPTER 6

RESONANT HOT-ELECTRON PRODUCTION IN
ABOVE-THRESHOLD IONIZATION

6.1 Introduction

The purpose of this chapter is to present photoelectron kinetic energy spectra showing prominent features at high kinetic energies that cannot be explained by Simpleman/rescattering theory or traditional ATI via Rydberg state resonances. Using Intensity-Selective-Scanning, three new and unexplained effects have been seen in xenon [52]:

1. We observe narrow dominant structures near 20 eV in the photoelectron kinetic energy spectra that indicate resonant ionization even at intensities as high as $1.9 \times 10^{14} \text{ W/cm}^2$ and ponderomotive potentials above 10 eV.

2. We find broader peaks near 35 eV comprised of at least two separate series of ATI peaks that do not shift with laser intensity.

3. The structures appear within a very narrow intensity range between $1.2 \times 10^{14}$-$1.9 \times 10^{14} \text{ W/cm}^2$.

Similar effects are also observed in argon and krypton in different kinetic energy regions. These measurements represent a new level of resolution and signal-to-noise ratio for high intensity photoelectron studies.
6.2 Theory

Narrow structures in the photoelectron kinetic energy spectrum have been routinely seen for low kinetic energies and short pulse excitation. In 1987, the pioneering efforts of Freeman et al. [35] showed that in the limit of short laser pulses, where the photoelectron does not sample the spatial gradients of the laser focus, the resulting electron spectrum shows dramatic structure. As explained in chapter 1, this structure arises from the ac-Stark shift of the atomic levels producing multiphoton resonances with harmonics of the laser field. Each ATI order breaks up into a series of narrow peaks corresponding to resonances with different Rydberg states. Each peak appears at a fixed kinetic energy corresponding to the precise intensity at which the atomic level shifts into resonance with the laser. The principal implication of the ac-Stark shifted resonance model is that photoelectron kinetic energies are fixed due to the multiphoton resonance occurring at a single laser intensity for each resonance. Thus, any electron energy structure that does not shift with laser intensity must be due to some type of resonant process.

6.3 Experimental Results and Discussion

We have recorded high resolution spectra over the intensity range near $10^{14}$ W/cm$^2$ in fine intensity steps using Intensity-Selective-Scanning. The time resolution is 150 ps/bin, yielding an instrumental energy resolution of 0.4 meV for 1 eV electrons and 65 meV at 30 eV. Given the uncertainty of a photon’s energy the absorption of ~20 photons generates an energy spread of about 25 meV (see chapter 1). Thus, our device resolution is adequate.

Our data show surprising structure within each ATI order for kinetic energies up to 50 eV. Furthermore, we see additional substructure near 20 eV, which does not appear in the 35-50 eV range. If these features resulted from nonresonant ionization, they would
have to shift to lower kinetic energies as the peak intensity increased. In contrast, our measurements show that no such shift occurs and that the hot electron features appear over a small intensity range, indicating a resonant ionization process. Traditional Rydberg transient resonances account unambiguously for the low energy photoelectron structure found in experiments using linearly polarized light. For 800 nm light, Rydberg state resonances yielding kinetic energies up to the 2 \( U_p \) point can be clearly identified. Recently, the envelope of the electron signal beyond 2 \( U_p \) has been attributed to inelastic backscattering. Very little attention, however, has been paid to the ATI structure in the region above 2 \( U_p \) [49].

Figure 6.1 shows a high resolution photoelectron kinetic energy spectrum of xenon from 2-50 eV. The spectrum consists of three basic regions: (i) 2-11 eV with well defined Rydberg structure, (ii) 11-28 eV with narrow structure appearing as a function of intensity, and (iii) 28-50 eV with prominent bumps comprised of a number of ATI orders appearing as the intensity increases. It should be noted that the overall envelope of the electron signal does not monotonically decrease as predicted by various theoretical models. Although some calculations produce modulations in the spectrum for various kinetic energies [47, 93, 101] the experimentally observed signal enhancement between 15-50 eV is at least an order of magnitude larger than any current model predicts.
Figure 6.1. Photoelectron spectrum of xenon with 800 nm, 120 fs pulses at $1.5 \times 10^{14} \text{ W/cm}^2$. 
Figure 6.2. Photoelectron spectra of xenon with 800 nm, 120 fs pulses at (1) 1.51, (2) 1.63, (3) 1.74, (4) 1.82, (5) 1.88, (6) 1.90 x 10^{14} \text{ W/cm}^2.
Figure 6.3. Photoelectron spectra of xenon with 800 nm, 120 fs pulses at (a) 1.26, (b) 1.44, (c) 1.51, (d) 1.63, (e) 1.74, (f) 1.78, (g) 1.82, (h) 1.86, (i) 1.88x10^{14} W/cm^2.
Figure 6.4. Photoelectron spectra taken at different wavelengths.
The low kinetic energy region in Fig. 6.1 consists of clear ac-Stark shifted Rydberg states which can be identified up to 13 eV. The structure consists of the g-states coming into 9-photon-resonance with the laser field [38]. Although the basic photoionization processes producing these electrons is believed to be understood, there are in fact many subtleties that are unexplained. This fine structure continues at higher kinetic energies; however, it becomes extremely difficult to make assignments due to rapid variation in amplitude of the fine structure for different ATI orders.

Figure 6.2 shows the intermediate energy region of the spectrum. The well ordered Rydberg structure gives way to a series of narrow peaks that cannot be simply identified with atomic levels. One of the difficulties in the hot electron portion of the spectrum is calibrating the energy scale from the measured time-of-flight data. Small variations in the time offset have dramatic effects in the higher kinetic energies. This notwithstanding, we are unable to link the high energy structures to the low kinetic energy f- or g-states or other Rydberg series. It is interesting to note the region between 20 and 30 eV, where the photoelectron structure almost vanishes, but reappears at higher energies. This is possibly a manifestation of the interference involving returning portions of the ionized wavepacket.

The high energy portion of the kinetic energy spectrum is shown in Fig. 6.3. At intensities between 1.26-1.74 x 10^{14} W/cm^2, the envelope of the spectra exhibits a bump, centered around 34 eV. Overall, there is a large modulation depth and the individual peaks are separated by the photon energy. Although we have sufficient resolution, no fine structure is detected within the ATI orders. The peaks in the range 28 - 40 eV increase in amplitude as the intensity rises but they do not shift in energy. As they grow, shoulders develop on the higher energy side. At intensities above 1.74 x 10^{14} W/cm^2 the peaks below 36 eV appear to saturate while signal for the higher energy electrons grows rapidly,
indicating the enhancement of a second series of peaks. These peaks seem to rise out of the 
shoulders that developed in the first bump. While the peaks within each bump are exactly 
separated by the photon energy, there is an energy shift of about 0.5 eV between the two 
series. This supports the observation that at least two distinguishable series develop as the 
intensity increases. The intensity regime above 1.74x10^{14} W/cm^2 also corresponds to the 
appearance of the intermediate kinetic energy peaks as shown in Fig. 6.2. At the highest 
intensities, there are statistically significant small peaks between the dominant structure 
around 46 eV. This may be the onset of an additional series of peaks different from the 
first two.

No explanation exists for the observed structures. Clearly, a resonant process must be 
dominant since the individual peaks do not shift with laser intensity. A traditional measure 
of the relative dominance of tunneling versus multiphoton effects is given by the Keldysh 
parameter $\gamma = \sqrt{IP/2U_p}$ [82], where IP is the ionization potential and $U_p$ is the 
ponderomotive potential. For xenon and the intensity range considered here we have 
0.734 \leq \gamma \leq 0.897, placing our experiment very slightly in the tunneling regime ($\gamma<1$). 
Within the limits of our energy calibration Rydberg states of the ion cannot be aligned with 
the measured structures. The saturation intensity for ionizing neutral xenon with 800 nm 
and 100 fs pulses is approximately 8x10^{13} W/cm^2 [102]. Although our measurements are 
above the saturation intensity, ion yield measurements made in our laboratory show that 
double ionization is not prominent [103]. Although the number of double ions is small, it 
is still possible that portions of the photoelectron spectrum arise from double ionization.

Finally, the excitation wavelength was changed in order to determine how the high 
energy peaks shifted. The laser was tuned 0.04 eV above and below the original photon 
energy of 1.55 eV. The kinetic energy region near 34 eV amounts to an absorption of 
about 22 photons. When using wavelengths tuned to the blue and red of 800 nm this 
yields a shift in kinetic energy of about 0.88 eV if the electrons come from a process that
involves the absorption of many photons. The measured shift in this region is about 1 eV, as shown in Fig. 6.4, which is in agreement with our estimate. Thus, it appears that the hot electrons are related to the direct absorption of many photons.

Current models utilizing the Simpleman/rescattering ideas rely upon electrons produced with zero initial kinetic energy. This scenario is valid in the tunneling regime and has been successful in describing results in helium [102]. The hot electrons are produced when electrons born at specific phases backscatter off the ion core and gain more energy from the laser. It is evident from our data that the Simpleman/rescatter picture cannot explain the hot electron substructure or the observed enhancements.

Two key issues must be resolved: First, a process must be found that describes the resonant production of structure at high electron energies. Second, a mechanism for enhancing specific kinetic energy regions must be found. We propose two possible scenarios for the production of narrow features at high energies. The first involves multiple excitations as illustrated in Fig. 6.5. The issue of the fine structure could be dealt with through a combination of multiple excitations of the atom in the intense field. For example, an outer electron may be shelved in a Rydberg state and survive to higher intensities [104]. While the first electron remains far from the core, a remaining outer shell electron can absorb a modest number of photons and be excited to the family of doubly excited states that exists in the heavier noble gases converging on the first double ion limit. Subsequent autoionization will produce narrow features in the kinetic energy range from 10-20 eV. Recall that this is the region marked by narrow features that cannot be assigned to traditional Rydberg resonances. In any event it seems likely that a process involving additional electrons from outer or inner shells is occurring.
Figure 6.5. Possible scenarios for producing hot electrons via multiple excitations.

The enhancement between 30 and 50 eV could be due to a similar process. The difference is that an inner shell excitation must be invoked in order to produce energies this high. One possible scenario involves the excitation of one of the 5s electrons in Xenon. The $5s \rightarrow 5p$ excitation requires about 11 photons at 800 nm. As mentioned earlier, the enhancement in this high energy region is made up of at least two different peak series. Both features turn on very rapidly as soon as threshold intensities of $1.20 \times 10^{14}$ and $1.74 \times 10^{14}$ W/cm² are reached for the bumps centered around 34 and 42 eV, respectively. In addition, the onset of very sharp strong features in the 20 eV region coincides with the growth of the 42 eV bump. Both of these features could be due to double ionization effects since the intensities are above the saturation point for single ionization. Since the described features appear in such a narrow intensity window it required very fine intensity control as obtained via ISS to observe the effects.
The second proposed scenario is the inclusion of nonzero initial energies in the Simpleman's model. Then it is possible to generate high energy electrons by scattering in the field (or quantum mechanically to absorb more photons). If, for example, 5-10 eV electrons created via traditional Rydberg resonances scatter in the laser field, specific energies could be "amplified" to produce narrow structures at higher kinetic energies.

6.4 Conclusion

We have observed for the first time prominent structure in the hot electron production in high intensity short pulse photoionization of xenon. We have shown that most of the photoelectrons with kinetic energies from 0 - 50 eV result from resonant processes at intensities up to $1.9 \times 10^{14}$ W/cm$^2$. In particular, the kinetic energy regions near 20 eV and 35 eV show an enhancement in electron production. It is clear that a resonant process must be involved due to the lack of kinetic energy shifts with laser intensity. The amplitudes of the structures change rapidly with intensity and turn on at different specific intensities. While those new structures appear to be due to resonances, they cannot be attributed to traditional Rydberg transient resonances. We propose that the mechanism involves coupling to other valence or inner shell electrons.
CHAPTER 7

HIGH ORDER RESONANCES IN
ABOVE THRESHOLD IONIZATION OF NOBLE GASES

7.1 Introduction

We have measured and modeled the clear evolution of higher order ac-Stark shifted multiphoton resonances in xenon. This marks a significant advance in showing that strong optical field ionization remains multiphoton in character at higher intensities near saturation. Furthermore, a simple Landau-Zener model is sufficient to understand the basic principles and extract coupling strengths. The remarkable quality of our data illustrates the unambiguous evolution through parity-allowed resonances at the 8- and subsequent 9-photon levels.

When atoms are placed in a fixed frequency nonresonant intense laser field, the absorption of multiple photons beyond the ionization limit becomes possible. Multiphoton resonances can occur due to light induced changes in the atom, as discussed in chapter 1. A decade after the first observation of transient resonances [35] for large initial detunings and ultrashort pulse durations, interesting physics is still emerging. The purpose of this chapter is to directly verify the validity of the transient resonance model for laser intensities large enough to access higher order resonances. We present a complete, high precision intensity evolution of multiphoton ionization leading to higher order resonances and extract coupling strengths and lifetimes. We are able to model these novel features by extending
Landau-Zener curve crossing theory to include both 8- and 9-photon transitions. Even in the nonperturbative intensity regime the model demonstrates that the essential physics of the ionization process remains multiphoton in character.

Between the early studies of low intensity multiphoton ionization [33] and the current efforts of studying tunneling ionization [105-108], little quantitative work has been done investigating the details of ionization in the intermediate intensity range. In particular, there is little experimental work testing the accepted transient resonance model at higher laser intensities. Experimentally, there have only been a few measurements indicating higher order resonances [109, 110]. Other experiments [111, 112] were limited in the intensity range and therefore not able to follow the unambiguous emergence of specific higher order resonances. Theoretical electron spectra and ion yields have been calculated for intensities high enough to observe higher order resonances [113, 114].

We have observed a significant enhancement in the ionization rate when reaching higher order 9-photon resonance intensities in xenon. Using a 3-dimensional calculation we show that the transient resonance model is valid and supports the new observed spectral features. The following effects are observed: (1) The clear evolution from 8- to 9-photon resonances. (2) A huge rise in photoelectron signal at the 9-photon resonance intensities. (3) The 9-photon peaks are narrower than the 8-photon peaks.

As shown in chapter 1, the various Rydberg state resonances produce different kinetic energies, which account for the substructure within each ATI order. Given the resonant nature of this process, photoelectron peaks corresponding to specific transient resonances appear in the kinetic energy spectra and they do not shift with absolute laser intensity. Therefore, the appearance or absence of certain resonances is a good indicator of the overall laser intensity [115]. However, as the intensity increases, other effects may play an important role in determining the photoelectron yield. For example, the large number of photons involved (>8) and the high intensity ac-Stark shifts of bound levels could create
coupling between states, leading to non-ponderomotive energy shifts. Calculations have shown this to be the case although experimental demonstration remains weak [113, 116, 117]. Thus, it is not obvious that the simple resonance model first proposed by Freeman et al. [35] is valid at higher intensities. We show that in spite of the high intensity and many possible couplings the process remains simple in nature and is dominated by the higher angular momentum states.

7.2 Experimental Results and Discussion

Figure 7.1 shows the first ATI order of the photoelectron kinetic energy spectra for the intensity range $1.63 \times 10^{13} - 4.68 \times 10^{13}$ W/cm$^2$. The structure is similar for the other ATI orders; however, differences appear above 12 eV, as discussed in chapter 6. Each curve is normalized to a common maximum amplitude for better comparison of relative effects. The scans have been taken at intensities of (a) 1.66, (b) 1.98, (c) 2.52, (d) 2.85, (e) 3.23, (f) 3.73, (g) 4.12, (h) $4.68 \times 10^{13}$ W/cm$^2$. The unprocessed vertical scale increases by a factor of 100 in going from Fig. 7.1(a) to 7.1(h).

We are able to clearly resolve transitions due to states with $n=4,...,10$. However, Rydberg resonances above $n=10$ cannot be identified due to the orbital period being larger than the laser pulse duration. In this case a wavepacket is launched that does not return to the core until after the laser pulse has passed. The emergence of the 8-photon 4f-resonance is clearly seen as the intensity increases from Fig. 7.1(a) to 7.1(b). As the intensity rises beyond the threshold for observing the 4f-state, the overall signal keeps rising, yet the 4f-resonance clearly becomes the dominant spectral feature. In Fig. 7.1(d) a broad feature appears below the 4f-state for intensities above $2.6 \times 10^{13}$ W/cm$^2$. Due to fine structure, the 7p-state splits into 6 levels with $J$-values ranging from 0 to 3 over an energy range of 0.11 eV in this region. Furthermore, the broadening of this peak toward lower energy indicates nonresonant contributions to the ionization.
Figs. 7.1(f)-(h) display the sudden emergence of the 6g- and higher lying Rydberg g-states once the ac-Stark shift brings them into 9-photon resonance. While the 8-photon 4f-state contribution remains fairly constant in Figs. 7.1(e)-(h), the effects of the 9-photon resonances at higher intensities increase dramatically and dominate the spectrum. The onset of these 9-photon resonances occurs at about $3.3 \times 10^{13}$ W/cm$^2$, and a similar evolution as with the 8-photon resonances starts over again. Due to the high angular momenta and small quantum defects, the f- and g-states appear at the same kinetic energy positions. At our highest intensities we measure a slight red-shift relative to the pure ponderomotively positioned states. Estimates using the measured spot size and ionization yields reveal that the observed small shift is most likely due to space charge.

The widths of photoelectron peaks depend on instrumental resolution, the laser bandwidth (inversely on pulse duration), and the short lifetime of the Rydberg states being ionized. We have measured the widths of the f- and g-states. While all of the g-states and high lying f-states have widths of about 40 meV, the 4f- and 5f-state have larger widths of 120 meV and 74 meV, respectively.

The instrumental resolution is 10 meV at 2.5 eV and the laser bandwidth is approximately 15 meV. For an 8-photon process this yields an inherent width of about 40 meV, indicating an upper limit on the natural width for the high lying f- and g-states. The 4f- and 5f-states, however, indicate the presence of ionization (lifetime) broadening. Deconvolving the widths using the experimental values we estimate widths of 113 meV and 62 meV for the 4f and 5f levels as 6 and 8 fs, respectively. This translates into a lifetime of 5.8 fs for the 4f-state and 10.5 fs for the 5-f state. Due to the higher angular momentum of the g-states and hence less penetration into the core region, the 9-photon features are expected to be narrower and more stable against ionization even though they appear at higher intensities.

90
Figure 7.2 displays the peak counts as a function of intensity for the specific kinetic energies associated with the degenerate hydrogenic Rydberg state resonances for the f- and g-states. These curves correspond to the amplitudes of the unscaled spectra in Fig. 7.1. When plotting the peak counts versus intensity, no Jacobian transformation has been performed in Fig. 7.2. The z-position of the ISS slice has been parameterized by the respective on-axis intensity. It should be noted that each data point reflects a constant Δz width of the slice of the focal volume. The Jacobian transformation from z-position to intensity of the data in Fig. 7.2 is shown in Fig. 7.3. All curves are displayed on a log-log plot. The individual graphs in Fig. 7.3 have the same amplitude scale. It is important to recall the difference between our ISS technique and full volume measurements. Traditionally, ionization signal increases with rising intensity due to volumetric growth. In contrast, the restricted ISS volume can result in a decrease in signal as higher intensities are selected. This effect is evident in the region from $1 \times 10^{13} - 3 \times 10^{13}$ W/cm$^2$ in Fig. 7.3, where the signal decreases as the Gaussian focal contour is followed. For comparison, the solid lines indicate the Gaussian intensity contours corresponding to each f- and g-state resonance intensity. The data follow the Gaussian contours extremely well.

Figures 7.2 and 7.3 show clearly the threshold behavior for each transient resonance as soon as the corresponding resonance intensity is reached. After a rapid rise the signal follows the volumetric behavior until the 9-photon resonance intensities become available. At that point, a dramatic jump in photoelectron signal is observed due to the onset of the g-states. Since $n=5$ is the lowest lying g-state, no higher order jump can be observed in the $n=4$ curve. The volumes occupied by intensities above the 9-photon resonance thresholds are clearly smaller than for the 8-photon resonances. Nevertheless, a huge rise in signal occurs when ionizing out of g-states. The g-state contours in Fig. 7.3 had to be scaled up by a factor of 300 to account for the increased ionization probability. Energy levels and intensity thresholds for 8- and 9-photon resonances are given in Table 7.1.
Figure 7.1. Photoelectron spectra showing the transition from 8- to 9-photon resonances in xenon using 800 nm light at intensities between $1.66 \times 10^{13}$ and $4.68 \times 10^{13}$ W/cm$^2$. All curves are vertically shifted and normalized to a common maximum amplitude. (— = experiment; ——— = calculations).
Figure 7.2. Resonance peak amplitudes as a function of laser intensity. Vertical lines show the 8- and 9-photon resonance threshold intensities for each state.
Figure 7.3. Resonance peak amplitudes vs. intensity. Vertical arrows show the 8- and 9-photon resonance threshold intensities for each state. Symbols are experimental data, solid lines are Gaussian volume contours for f- and g-states.
8-photon Resonances

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9-photon Resonances

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Table 7.1. Zero-field energy levels for f- and g-states. U_p is the ponderomotive shift required to attain transient resonances of Xe(^2P_{3/2}) states with 800 nm light, and I_R is the corresponding resonance intensity. The f-state energy levels are taken from Ref. [77]; the levels for g-states are assumed to be the same as for the f-states due the small quantum defect.
7.3 Theoretical Model

We have modeled the evolution of the 8- and 9-photon resonances using multiphoton Landau-Zener theory [39, 87, 112, 118, 119]. The ground state is dressed in energy with either 8 or 9 photons to create an avoided crossing with the time dependent energy levels of the Rydberg states. The ac-Stark shift of the Rydberg states is assumed to be purely ponderomotive. Transient resonances with a particular Rydberg state occur for all atoms in the focus, independent of their position in space, as long as the necessary threshold intensity is overcome. The ionization probability depends on the specific time each atom spends in a multiphoton resonance with the laser field. This resonance time varies throughout the focus due to the complex spatial intensity distribution [120]. Figure 7.4 shows the difference in resonance time for different local peak intensities. Figure 7.4(a) represents those points in space where the local peak intensity just reaches the required resonance intensity. In that case, the atom experiences a very long resonance time, due to the quadratic behavior of the temporal intensity profile at the peak. In contrast, Fig. 7.4(b) shows regions with higher local peak intensity, where resonances occur only on the rising and falling edge. The linear crossing between the ac-Stark shifted excited state and the ground state dressed by \(m\) photons results in a shorter resonance time, and thus lower ionization probability. As remarked by Van Woerkom et al. [39]: "It is this spatial variation of the 'resonance time' that produces a complex spatial distribution of the total ionization."

The probability of a multiphoton transition to a particular Rydberg state via adiabatic passage is given by [39]

\[
P = 1 - e^{-2\pi V_R^2 \tau_c^2},
\]

(7.1)

where \(V_R\) is the coupling strength related to the transition matrix element and \(\tau_c\) is the resonance time. The coupling strengths depend on the laser intensity only through the
resonance intensity, $I_R$, at which the crossing occurs. Earlier efforts approximated the coupling strength as a multiphoton transition with a perturbative $(I_R)^n$-behavior, where $n$ is the number of photons to resonance [39, 121]. We have not restricted the coupling constants, but rather have varied each $V_R$ in order to model all of the observed resonances simultaneously. One set of $V_R$'s is selected to fit the relative photoelectron peak heights for one intensity slice. The entire evolution is determined from these values and a knowledge of the focal geometry in ISS. The ionization signal due to a single resonance is found by assuming instantaneous ionization from the Rydberg states once they are populated via Landau-Zener transition. Thus, the amplitudes for each resonance in a photoelectron spectrum are constructed by overlapping individual contributions from each state. Saturation effects due to rising and falling edge ionization are also included [39]. A full three-dimensional spatial integration is performed using the geometry of an ISS volume slice for each spectrum.
Figure 7.4. "Schematic diagram of the level crossing model with the ground state dressed by m photons labeled state 2, and the excited state subjected to the ac-Stark shift labeled state 1. (a) Positions in space where the local intensity equals the resonance intensity and quadratic time dependence is needed. (b) Positions at smaller (r, z) where the resonance intensity is passed on the rising and falling edges, requiring only the linear time dependence." From Ref. [39].
Calculated photoelectron spectra are shown in Fig. 7.1 along with the data. Our simple model matches the data extremely well. For simplicity, only the f- and g-states up to n=8 are included in the model. We have not included the p- or d-states since they are not the dominant series in the data. Furthermore, due to our small angular acceptance and the different angular distributions emanating from different resonances, we cannot compare the relative heights with lower angular momentum states. The calculated spectra for Figs. 7.1(g) and 7.1(h) have been red-shifted by approximately 20 meV to account for experimental space charge. Furthermore, each peak in the calculated spectra has an artificial Gaussian 1/e half width of 25 meV. Nonresonant processes have not been included in the calculation. The purpose of the calculation is to show the validity of the multiphoton curve crossing theory for higher order resonances. Future efforts are needed to correctly account for the intensity dependent widths. It is not necessary to invoke tunneling ionization or sophisticated resonance models to describe the ionization process at these intensities.

<table>
<thead>
<tr>
<th>State</th>
<th>$V_R(t^2)$</th>
<th>$I_R \times 10^{14}$ W/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>8f</td>
<td>5.60E-05</td>
<td>0.081</td>
</tr>
<tr>
<td>7f</td>
<td>7.60E-05</td>
<td>0.092</td>
</tr>
<tr>
<td>6f</td>
<td>0.00012</td>
<td>0.109</td>
</tr>
<tr>
<td>5f</td>
<td>0.00022</td>
<td>0.137</td>
</tr>
<tr>
<td>4f</td>
<td>0.00057</td>
<td>0.189</td>
</tr>
<tr>
<td>8g</td>
<td>0.00185</td>
<td>0.340</td>
</tr>
<tr>
<td>7g</td>
<td>0.00265</td>
<td>0.351</td>
</tr>
<tr>
<td>6g</td>
<td>0.0032</td>
<td>0.368</td>
</tr>
<tr>
<td>5g</td>
<td>0.0045</td>
<td>0.396</td>
</tr>
</tbody>
</table>

Table 7.2. Coupling strengths $V_R$ and the corresponding resonance intensities $I_R$ for each resonance used in fitting the spectral data in Fig. 7.1.
Table 7.2 shows the values of the coupling strengths and the corresponding resonance intensity for the states included in the model. The calculation cannot distinguish different functional forms for the couplings, \( V_R \). If the process proceeds via purely perturbative paths, then one would expect \((V_R)^2\) to follow an \( n^{th} \) order intensity power law where \( n=8 \) or 9 [122]. It is possible within the current model to fit the coupling strengths with an order of nonlinearity between 5 and 9. For any value of \( n \) in this range effective cross sections can be found which are consistent with nonresonant estimates [123].

7.4 Conclusion

The clear evolution through parity-allowed resonances at the 8- and subsequent 9-photon levels has been unambiguously measured and modeled for the first time. The probability for 9-photon ionization exceeds that for the 8-photon process by about two orders of magnitude. This is to be expected due to the 9-photon g-state resonances occurring at about a factor of 3-5 higher intensity. We have extracted coupling strengths for the f- and g-states up to \( n=8 \). Calculated photoelectron spectra demonstrate the validity of the transient resonance model near the saturation intensity. Advances in kilohertz repetition rate lasers and exploitation of the ISS technique are revealing new physics in the field of high intensity photoionization to extend our knowledge further toward the tunneling regime and thereby bridging the gap between multiphoton and tunneling ionization.
CHAPTER 8

SPATIALLY DEPENDENT MULTIPHOTON MULTIPLE IONIZATION

8.1 Introduction

One of the major difficulties plaguing strong field control efforts is the continuous distribution of intensities contained within a typical laser focal volume. Intensity dependent phenomena are blurred by the spatial averaging inherent in tightly focused geometries. This chapter presents measurements of multiple ionization coming from greatly reduced spatial extent. It is shown that the ionization results from spatial regions characterized by only a radial intensity dependence. The key features of the ISS measurements are: (1) Enhanced detection of high-intensity effects, (2) improved signal-to-noise ratio by blocking out low intensity regions in the focal volume, (3) reduction of complex intensity distribution to a 1-dimensional radial dependence within a selected window, (4) precise peak intensity control while maintaining good overall beam quality.

Given the sensitive intensity control, it is possible to measure the evolution of ionization rates for multiple charge states of atoms and molecules as a function of intensity, simplifying the effects of spatially averaging over a continuously changing ionization volume. Traditionally, ionization rates at different high intensities have been studied by changing the overall peak intensity of a focused laser beam. Ionization spectra have been regarded as being dominated by the strong field interaction near the absolute peak intensity at the minimum beam waist. As will be demonstrated in this chapter, a non-negligible
fraction of Xenon ions can be generated as far as several Rayleigh ranges away from the minimum beam waist. Typically, the entire ionization volume is exposed to the time-of-flight detector. For a given ion charge state the ion yield after saturation continues to rise as the intensity increases due to the growth of the entire focal volume [46, 124]. Figure 8.1 [125] shows full volume ion yields which continuously increase with rising intensity for each charge state. This makes it difficult to identify the onset of saturation intensities. Furthermore, the true ionization rates (intensity-dependent, not volume-dependent) can be extracted only by deconvolving the complicated Gaussian volume. Despite the low ionization rates at low intensities, the volume increase in a Gaussian focal volume causes a significant number of ions to be produced far away from the center of the beam.
Figure 8.1. Xenon ion yields for various intensities $>10^{14}\text{ W/cm}^2$. The yields for charge states up to $\text{Xe}^{8+}$ increase monotonically with intensity. After saturation is reached, each curve continues to grow as $I_{0}^{3/2}$. From Ref. [125].
8.2 Experimental Approach

Previously, Jones [126] demonstrated spatially-selective ion spectroscopy using a large unfocused beam and a large aperture. In contrast, the present work exploits a tight focusing geometry and a very small aperture. This allows studying a broader range of intensities under otherwise identical conditions, while the intensity distribution within a selected window is very well known.

We applied ISS to obtain the presented ion spectra. As demonstrated in chapter 3, intensity-selective TOF spectroscopy can be studied by combining high repetition rate laser technology and the optical properties of focused laser beams [78]. In order to avoid a spatially averaged ion signal, only a very small fraction of the ionization region is exposed to the detector. Unlike photoelectrons, ions must be accelerated toward the detector to record time-of-flight data [127]. Therefore, ionization occurs in the presence of a static electric field oriented such that ions are swept toward and electrons away from the detector, as shown in Fig. 8.2. The entire flight tube is at ground potential and the grid opposing the pinhole has a potential of +1100 V. By moving the focusing lens via a translation stage, the focal volume can be scanned across the pinhole exposing only a thin slice of the ionization region rather than the whole volume.

A telescope serves to enlarge the beam diameter so that an absolute intensity of \( I_0 = 4 \times 10^{14} \text{ W/cm}^2 \) can be reached inside the vacuum chamber. In the case of photoelectron spectroscopy only a small fraction of the emitted electrons are detected due to their angular distribution. In contrast, here all ions are swept toward the detector and a pressure of \( 6 \times 10^{-9} \text{ torr} \) sufficed to maintain good count rates while avoiding space charge.

Figure 8.3 shows the schematic scaling of several iso-intensity contours. The largest fraction of the total Gaussian focal volume is occupied by low intensities. In contrast, ISS selects a slice of the focal region where the volumetric weighting enhances high intensity regions by blocking most of the low intensity volume.
Figure 8.2. Schematic setup of time-of-flight spectrometer. The focusing lens can be moved via a translation stage to scan the ionization volume across the pinhole at the front of the flight tube. A static potential of +1100 V accelerates ions toward the detector.
Figure 8.3. Schematic intensity contours. Low intensities occupy a much larger volume than high intensities in comparison to the ISS technique.
8.3 Experimental Results and Discussion

Figure 8.4 shows xenon ion signal that has been converted from time-of-flight to atomic mass including proper scaling through the Jacobian of the time-mass transformation. A TOF spectrometer can only differentiate between ions with different q/m. Therefore, Xe\(^+\) ions are located at the neutral Xe mass around 132 amu, while Xe\(^{2+}\), Xe\(^{3+}\) and Xe\(^{4+}\) appear at 1/2, 1/3 and 1/4 the neutral mass, respectively. Each charge state shows a group of lines which correspond to the different isotopes of Xenon. The most prominent isotopes range from \(^{128}\text{Xe}\) to \(^{136}\text{Xe}\) and can be very well resolved. Figure 8.4 contrasts (a) the traditional method of exposing the full ionization volume vs. (b) Intensity-Selective Scanning, exposing only a slice at the minimum beam waist. Both spectra have been vertically normalized for comparison. It is apparent that the single ions dominate the spectrum in Fig. 8.4(a), followed by a significantly smaller fraction of double ions. The Xe\(^{3+}\) and Xe\(^{4+}\) counts on the other hand are close to the noise level and their contributions are almost negligible compared to Xe\(^+\). The reason Xe\(^+\) yields the maximum contribution is that single ions are generated within a much larger volume than any of the higher charge states. For absolute peak intensities, \(I_0\), that are greater than the saturation intensity to create Xe\(^+\), the spatial weighting factor grows as \(I_0^{3/2}\) [124]. The higher charge states are produced only near the core of the Gaussian focal volume since they require higher intensities. The volumetric weighting results in an enhancement of single ions. Furthermore, the large volume low-intensity regions of the laser focus introduce significant amounts of noise by ionizing contaminants with typically low ionization potentials. The spatial weighting makes it difficult for highly charged ions coming from small volumes to compete with these large volume noise contributions. This introduces significant uncertainties when trying to extract quantitative ionization rates for high charge states.
In contrast, Fig. 8.4(b) shows an ISS ion spectrum where the pinhole exposed only the peak intensity region at the minimum beam waist. Due to the spatial selectivity, the various charge states of xenon have different volumetric weightings and now the Xe$^{2+}$ ions dominate the spectrum, followed by Xe$^+$ and clearly enhanced contributions from Xe$^{3+}$ and Xe$^{4+}$. Since the overall count rates drop by limiting the view with the pinhole, only the relative signals are meaningful in terms of enhancements. Moreover, it should be noted that the ISS technique yields better isotope resolution and a reduction of noise such that Xe$^{3+}$ and Xe$^{4+}$ can unambiguously be identified. The single-ion signal is not as prominent any more since the contributions from low intensity regions far away from the core are blocked out. It should be noted that the MCP detector has different detection efficiencies for different charge states. All xenon ions have the same mass, but the higher charged ions are accelerated more and thus have more impact on the MCP. Therefore, higher charge states of the same isotope are detected with higher efficiency than low charge states. The data in Figs. 8.4 and 8.5 have not been corrected for the differences in detection efficiency, but it does not change the overall trend of the relative contributions.

Within the selected window in Fig. 8.4(b) the number of Xe$^+$ ions is saturated and sequential ionization starts depleting these single ions to produce Xe$^{2+}$ and higher charge states. By simplifying the complex overall intensity distribution to a slice which is approximately cylindrically symmetric and only has a radial intensity dependence, a much cleaner measurement of high intensity effects can be obtained. Particularly, low probability events can be observed by reducing the noise.
Figure 8.4. Xenon ion spectra recorded using (a) traditional method of exposing entire focal volume vs. (b) selecting a 500 μm window with ISS at the minimum beam waist.
Figure 8.5. (a) Ion signal of Xenon with 800 nm, 120 fs pulses as a function of $z$, (b) same signal displayed vs. local on-axis peak intensity.
The peak intensity within a spatially selected part of the laser focus can be varied by selecting different slices along the z-axis (the direction of propagation of the laser beam). Starting at the minimum beam waist the laser focus was scanned across the pinhole in 100 μm steps over a range of nearly 6 mm (~8 Rayleigh ranges). Figure 8.5(a) displays the number of detected ions for the various charge states as a function of z along the beam axis. In order to qualitatively demonstrate the trends, different detection efficiencies for different Xe charge states are not taken into account. For any selected z-position the local on-axis peak intensity can be obtained via Eq. 8.1 as [56]

\[ I(r = 0, z) = \frac{I_0}{1 + \frac{z^2}{z_0^2}}. \] (8.1)

Using \( I_0 = 4 \times 10^{14} \text{ W/cm}^2 \) and \( z_0 = 0.7 \text{ mm} \), the recorded evolution of ion counts from Fig. 8.5(a) can be converted to signal vs. local peak intensity as shown in Fig. 8.5(b). In addition to a more balanced volumetric weighting, ISS provides another important advantage: By moving along z, different peak intensities can be selected without changing the characteristics of the laser beam. Traditionally, the absolute intensity \( I_0 \) had to be changed when exposing the full volume. Inserting additional optics into the beam to control \( I_0 \) may result in affecting the overall beam quality and temporal width of the pulses. With ISS this problem can be avoided.

Fig. 8.5(b) shows that the highest number of Xe\(^+\) is not produced at the absolute peak intensity; instead it peaks near the saturation intensity of the double ions. When looking at the full volume the signal is characterized by a change in slope at the saturation intensities and a continued rise according to \( I_0^{3/2} \) [46], as shown in Fig. 8.1. By using ISS, the saturated volume stays nearly constant with no increase in the total number of atoms that can be ionized. When moving toward the center of the beam, higher intensities become available without increasing the spatial width of the observed slice. This leads to depletion.
of Xe\(^+\) and a sharp rise in Xe\(^{2+}\). At the same time, the rates for sequentially producing higher charge states rise as well. The analysis of ionization probabilities benefits significantly from the simplified geometry \[5\].

### 8.4 Theoretical Model

It is well known that for a Gaussian focus with absolute intensity, \(I_0\), the total volume occupied by intensities greater than some saturation intensity, \(I_s\), is given by \[1\]

\[
V(I_s, I_0) = \pi \sigma_0^2 \left\{ \frac{4}{3} \left[ \frac{I_o - I_s}{I_s} \right]^{1/2} + \frac{2}{9} \left[ \frac{I_o - I_s}{I_s} \right]^{3/2} - \frac{4}{3} \tan^{-1} \left[ \frac{I_o - I_s}{I_s} \right]^{1/2} \right\}. \tag{8.2}
\]

For absolute intensities \(I_0\) much greater than the saturation intensity \(I_s\) of a given charge state, Eq. 8.2 yields the familiar volume increase according to \(I_0^{3/2}\). It should be noted that, to be exact, the volume generating a given ion charge state equals the corresponding total \(V(I_s, I_0)\) minus the saturated volume of higher charge states. However, when exposing the full focal region this difference becomes negligible. For instance, the full saturation intensity contour will always be significantly larger for Xe\(^+\) than for Xe\(^{2+}\), etc.

For Intensity-Selective-Scanning on the other hand, one must consider the differences between consecutive saturation volumes due to their comparable size. The volume-slice that experiences intensities greater than some \(I_s\) is given by

\[
V_{iss}(I_s, I_0, I_{ol}) = \frac{1}{2} \pi \sigma_o^2 \Delta z \ln \left( \frac{I_{ol}}{I_s} \right), \tag{8.3}
\]
where $I_{Oz}$ is the local on-axis peak intensity at a given z-position according to Eq. 8.1, and $\Delta z$ is the pinhole diameter. Under the approximation that volumes with saturated intensities dominate the ion signal, Fig. 8.6 displays the calculated ion yields based on Eq. 8.3 with saturation intensities of $I_s(Xe^+) = 8 \times 10^{13}$ W/cm² and $I_s(Xe^{2+}) = 2 \times 10^{14}$ W/cm² and an absolute peak intensity of $I_p = 4 \times 10^{14}$ W/cm².

It is apparent that the effective volume producing single ions starts dropping as soon as the saturation intensity for double ions is reached. Moving in z toward the minimum beam waist increases the local peak intensity $I_{Oz}$ without increasing the total ionized volume. In fact, due to the bone-shaped intensity contours, as shown in Fig. 8.3, the total number of ionized atoms decreases slightly when reaching the core of the focus, as indicated by the dotted line in Fig. 8.6 which represents the total yield of all charge states. The volumetric model based on Eq. 8.3 captures the ionization process at the high intensity end sufficiently well. It clearly demonstrates how the production of double ions burns a hole into the total volume capable of generating single ions (see Fig. 8.7). The Xe^{3+} and Xe^{4+} signals have not been included in Fig. 8.6 since those charge states are clearly not saturated yet. Of course, the above model of saturated volumes cannot reproduce the low intensity features of our experimental data in Fig. 8.5(b). The tails below the saturation intensities arise from non-resonant ionization with low probabilities and traditionally follow an $I^n$-dependence, $n$ being the number of absorbed photons. For higher than single charge states non-sequential ionization also contributes.
Figure 8.6. Calculated volumes for saturated ionization for single and double ions. The model predicts the single ion yield to decrease as the intensity increases due to the creation of higher charge states.
Figure 8.7. Schematic cross-section of the laser focus near its waist. At sufficiently high peak intensities, double-ions are produced in the center, thus burning a hole into the single-ion population. This leads to a depletion of single-ions and may cause higher yield for the higher charge states.
8.5 Conclusion

We have observed strong field multiple ionization with a much more balanced volumetric weighting of the intensities producing up to quadruple ions in xenon. Intensity-Selective-Scanning yields a cleaner signal and better signal-to-noise ratios by blocking out large volume low intensity contributions. The observed peak intensities can be controlled very accurately by moving the pinhole along z. ISS is an important tool in extracting real ionization rates because the volumetric scaling is easier to deconvolve and the intensity distribution has been simplified to only a radial dependence.
CHAPTER 9

CONCLUSION

9.1 ISS and Strong Field Photoionization

In order to study the behavior of atoms and molecules in strong laser fields we have developed Intensity-Selective-Scanning, a novel method of time-of-flight spectroscopy. ISS embraces the use of high repetition rate lasers to build up fast statistics, ultrashort pulses to generate high intensities, and a pinhole to select specific intensity regions of the Gaussian focal volume. Although atoms in intense laser fields have been studied for nearly two decades, many details of the ionization process remain unclear. Using the ISS technique we have recorded exceptionally high quality photoelectron and ion data, revealing several new phenomena in atomic strong field photoionization.

We have shown a very clean intensity-evolution of low kinetic energy transient resonances in xenon. Using 800 nm light for ionizing xenon, it has been demonstrated that traditional above threshold ionization is valid for at least the first seven ATI-orders, up to 12 eV. Beyond this point, we have observed for the first time prominent structure in the hot electron production in high intensity short pulse photoionization. We have shown that most of the photoelectrons with kinetic energies from 0 - 50 eV result from resonant processes at intensities up to $1.9 \times 10^{14}$ W/cm$^2$. In particular, the kinetic energy regions near 20 and 35 eV show an enhancement in electron production. It is clear that a resonant process must be involved due to the lack of kinetic energy shifts with laser intensity.
The amplitudes of the structures change rapidly with intensity and appear at different specific intensities. While those new structures appear to be due to resonances, they cannot be attributed to traditional Rydberg transient resonances. We propose that the mechanism involves coupling to other valence or inner shell electrons.

Furthermore, the clear evolution through parity-allowed resonances at the 8- and 9-photon levels has been unambiguously measured and modeled for the first time. The probability for 9-photon ionization exceeds that for the 8-photon process by about two orders of magnitude. However, due to the small focal volume occupied by the highest intensities, it is difficult to observe the appearance of high order resonances with traditional techniques. The restricted ISS geometry has been essential in unambiguously showing the transition from 8- to 9-photon resonances. The high quality data allows for quantitative comparison between experiment and theory. We have extracted coupling strengths for the f- and g-states up to n=8. Calculated photoelectron spectra using a Landau-Zener model demonstrate the validity of the transient resonance model near the saturation intensity for low kinetic energies.

Finally, we have observed strong field multiple ionization, producing up to quadruple ions in xenon. By blocking out large volume contributions at low intensities, ISS yields cleaner signal and better signal-to-noise ratios than conventional TOF spectroscopy. Our spatial resolution revealed a hole-burning into the single ion distribution through sequential ionization and production of higher charge states at the core of the laser focus. A volumetric model has been presented which reproduces the qualitative features of the spatial distribution of xenon ions in the ionization volume.
9.2 Future Studies

Intensity-Selective-Scanning can be used to pursue many future directions. More work is necessary to understand the observed hot electron features in the noble gases. Although the novel ATI structure in xenon accounts only for a few percent of all emitted photoelectrons, it is a fascinating process that leads to the conversion from 1.55 eV photons to electron kinetic energies up to 30-40 eV. Similar hot electron features have been seen in argon and krypton; however, there are clear differences in the substructure of the observed hot electron enhancements. Studies of angular photoelectron distributions are under way to understand the important transition from MPI to tunneling.

Experimentally, the ISS setup could be modified to allow for even finer spatial resolution by replacing the 500 μm pinhole with a 10-50 μm slit. Coupled with a high repetition laser it is expected that the count rates will remain sufficiently high.

Furthermore, we expect ISS to unravel the complexity of molecular strong field ionization. Despite the additional degrees of freedom and the dissociation of molecules in intense light fields we have recorded molecular photoelectron spectra that reveal atom-like features. An interesting question is: When does a molecule look like an atom, and when does it behave differently? The ability to spatially resolve the laser focus might be crucial for understanding the complex photoelectron and ion spectra of molecules.
APPENDIX A

TIME-TO-ENERGY CONVERSION

The following is a procedure for the program *Igor Pro, Version 3*, for Macintosh computer. It converts TOF data to kinetic energy. This procedure creates a wave given by "name" and scales its x-axis using the energy limits from the time data. It rebins the data using constant width energy bins. The number of points in the wave is given by \((E_{\text{final}} - E_{\text{initial}})/\text{(energy bin size)}\), so it covers the same energy range as the converted time data.

\[
t_{\text{wave}} = \text{time data}
\]

name = name of new energy wave created....put in quotes......"name"

tbin = time bin size in nanoseconds

to = time offset in nanoseconds

l1 = TOF length in meters

eo = energy offset in eV

ebin = constant energy bin width in meV

y_scale = overall y-scaling factor to account for relative pressures and relative number of shots

elo = lower energy limit of integration range in eV


eh = upper energy limit of integration range in eV

Usage:  VAR := enbin(twave, name, tbin, to, l1, eo, ebin, y_scale, elo, ehi)

VAR is a variable to allow using the ":=" option for automatic updates. VAR will contain the integrated number of counts between elo and ehi in the new wave "name". If elo = ehi then VAR returns the value of the single bin that both elo and ehi fall into. Furthermore,
ehi can also contain the maximum energy value. Since many of our data sets contain more than 20,000 points, out to 300 eV, we would like to limit the number of points and hence the maximum energy. If elo=ehi, but not equal to zero, then ehi is the maximum energy in eV for the graph. This will typically reduce the number of points to about a few thousand and make it run faster.

Igor Pro time-to-energy rebinning procedure:

Function enbin(twave, name, tbin, to, ll, eo, ebin, y_scale, elo, ehi)
    wave twave
    Variable tbin, to, ll, ebin, eo, y_scale, elo, ehi
    string name
    Variable jj, ii, jimax, iimax, eb, nnn, lo, hi, int, enmax
duplicate/O twave eet, tt

eb=ebin/1000
	iimax=numpnts(twave)-1
	tt=(to+tbin*x)*1e-9
	eet=2.8469e-12*(ll/((to+tbin*x)*1e-9))^2+eo
	enmax=eet[0]

nnn=trunc((enmax-eet[iimax])/eb)
if((elo==ehi) %& (ehi != 0)) then
    enmax=ehi
    nnn=trunc((enmax-eet[iimax])/eb)
endif
make/n=(nnn)/d/o xen,en
en=0
xen=0
xen=eet[iimax]+x*eb
setscale/p x, eet[iimax], eb, "eV", en
jimax=nnn-1

ii=1
jj=1
do
    if(eet[iimax-ii] <= xen[jj]) then
        en[jj-1] += twave[iimax-ii]
        ii += 1
else
  en[jj-1] += twave[iimax-ii]*(xen[jj]-eet[iimax-ii+1])/(eet[iimax-ii]-eet[iimax-ii+1])
  jj += 1
if(eet[iimax-ii] < xen[jj]) then
  en[jj-1] += twave[iimax-ii]*(eet[iimax-ii]-xen[jj-1])/(eet[iimax-ii]-eet[iimax-ii+1])
else
  do
    en[jj-1] += twave[iimax-ii]*eb/(eet[iimax-ii]-eet[iimax-ii+1])
    jj += 1
  while((eet[iimax-ii] >= xen[jj]) & (jj < jjmax))
  en[jj-1] += twave[iimax-ii]*(eet[iimax-ii]-xen[jj-1])/(eet[iimax-ii]-eet[iimax-ii+1])
endif
endif
while((jj <= jjmax) & (eet[iimax-ii] <= enmax))
en=en*y_scale

lo=trunc((elo-xen[0])/eb)
hi=trunc((ehi-xen[0])/eb)

int=0
jj=lo+1

if((elo>ehi) | (lo<0) | (hi>=jjmax)) then
do nothing
else
  if (lo==hi) then
    int=en[lo]
  else
    int += en[jj-1]*(xen[jj]-elo)/eb
    if ((hi-lo) > 1) then
      do
        int +=en[jj]
        jj += 1
      while(jj < hi)
      int += en[jj]*(ehi-xen[jj])/eb
    endif
  endif
endif
duplicate/O en Sname
killwaves en,xen,eet, tt
return int
end
APPENDIX B

TIME-TO-MASS CONVERSION

The following is a procedure for the program Igor Pro, Version 3, for Macintosh computer. It converts TOF data to mass. This procedure creates a wave given by "name" and scales its x-axis using the mass limits from the time data. It rebins the data using constant width mass bins in amu. The number of points in the wave is given by \((m_{\text{final}} - m_{\text{initial}}) / (\text{mass bin size})\), so it covers the same mass range as the converted time data.

\[
\text{twave} = \text{time data} \\
\text{name} = \text{name of new mass wave created...put in quotes..."name"} \\
\text{tbin} = \text{time bin size in nanoseconds} \\
\text{to} = \text{time offset in nanoseconds} \\
\text{mbin} = \text{constant mass bin width in amu} \\
\text{mm} = \text{scaling factor to account for accelerating potential} \\
\text{y_scale} = \text{overall y-scaling factor to account for relative pressures and relative number of shots} \\
\text{mlo} = \text{starting mass of integration range in amu} \\
\text{mhi} = \text{ending mass of integration range in amu}
\]

Usage: \(\text{VAR} := \text{massbin(twave, name, tbin, to, mbin, mm, y_scale, mlo, mhi)}\)

VAR is a variable to allow using the "\(\text{:=}\)" option for automatic updates. VAR will contain the integrated number of points between \(mlo\) and \(mhi\) in the new wave "name". If \(mlo=mhi\) then VAR returns the value of the single bin that both \(mlo\) and \(mhi\) fall into.
Igor Pro time-to-mass rebinning procedure:

Function massbin(twave, name, tbin, to, mbin, mm, y_scale, mlo, mhi)

wave twave
Variable tbin, to, mbin, mm, y_scale, mlo, mhi
string name

Variable jj, ii, jjmax, iimax, nnn, int, lo, hi
duplicate/O twave mmt

iimax=numpnts(twave)-1
mmt=mm*(to+tbin*x)^2
nnn=trunc((mmt[iimax]-mmt[0])/mbin)
make/n=(nnn+1)/d/o xmass,mass
mass=0
xmass=0
xmass=mmt[0]+x*mbin
setscale/p x, mmt[0], mbin, "amu", mass
jjmax=nnn-1

ii=0
jj=1
do
if(mmt[ii] <= xmass[jj]) then
    mass[jj-l] += twave[ii]
    ii += 1
else
    mass[jj-1] += twave[ii-1]*xmass[jj]/(mmt[ii]-mmt[ii-1])
    jj += 1
if(mmt[ii] < xmass[jj]) then
    mass[jj-1] += twave[ii-1]*xmass[jj]/(mmt[ii]-mmt[ii-1])
else
    do
        mass[jj-1] += twave[ii]*mbin/(mmt[ii]-mmt[ii-1])
        jj += 1
    while(mmt[ii] >= xmass[jj])
    mass[jj-1] += twave[ii]*xmass[jj]/(mmt[ii]-mmt[ii-1])
    endif
    ii += 1
endif
while(jj <= jjmax) %& (ii<=iimax)
mass=mass*y_scale

lo=trunc((mlo-xmass[0])/mbin)
hi=trunc((mhi-xmass[0])/mbin)
int=0
jj=lo+1
if((mlo>mhi) || (lo<0) || (hi>=jjmax)) then
  do nothing
else
  if (lo==hi) then
    int=mass[lo]
  else
    int += mass[jj-1]*(xmass[jj]-mlo)/mbin
    if ((hi-lo) > 1) then
      do
        int += mass[jj]
        jj += 1
        while(jj < hi)
      endif
    endif
    int += mass[jj]*(hi-xmass[jj])/mbin
  endif
endif
duplicate/O mass $name
killwaves mass,xmass,mmt
return int
end
APPENDIX C

GAUSSIAN LASER BEAMS

Mathematically, Gaussian laser beams are the solutions to the paraxial equation [128], given by Eq. C.1, whose solutions are given by Eq. C.2.

\[
\nabla^2 \psi - i2k \frac{\partial \psi}{\partial z} = 0
\]  

(C.1)

\[
\frac{E(x,y,z)}{E_{m,p}} = H_m \left( \frac{\sqrt{2}x}{w(z)} \right) H_p \left( \frac{\sqrt{2}y}{w(z)} \right) \frac{w_0}{w(z)} \exp \left[ -\frac{x^2 + y^2}{w^2(z)} \right]
\]

\[
\times \exp \left[ -i \left( k z - (m + p) \tan^{-1} \left( \frac{z}{z_0} \right) \right) \right] \exp \left[ -i \frac{kr^2}{2R(z)} \right].
\]  

(C.2)

where \( H_m \) and \( H_p \) stand for the Hermite polynomials of \( m^{th} \) and \( p^{th} \) order.

\[
w(z) = w_0 \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]^{\frac{1}{2}}
\]  

(C.3)

\[
R(z) = z \left[ 1 + \left( \frac{z_0}{z} \right)^2 \right]
\]  

(C.4)

\[
w_0^2 = \frac{\lambda_0 z_0}{n \pi}
\]  

(C.5)

\( n \)= index of refraction, \( z_0 \)= Rayleigh range
The lowest order transverse electric and magnetic mode is TEM\(_{0,0}\), given by Eq. C.6.

\[
\frac{E(x, y, z)}{E_0} = \frac{w_0}{w(z)} \exp \left[ -\frac{x^2 + y^2}{w^2(z)} \right] \exp \left\{ -i \left[ k z - \tan^{-1} \left( \frac{z}{z_0} \right) \right] \right\} \exp \left[ -i \frac{kr^2}{2R(z)} \right] \tag{C.6}
\]

Eq. C.6 describes the complex amplitude of the TEM\(_{0,0}\) mode as a function of \(x\), \(y\), and \(z\) as the beam propagates in the \(z\)-direction. At \(z=0\) the beam focuses the most, and its wave front is planar. The further the beam propagates from there the more it diverges and approaches a spherical wave (⇒ curved phase fronts).

Figure C.1. "Notation for a lowest-order Gaussian beam diverging away from its waist." From Ref. [56].
Taking the absolute value of Eq. C.6 shows that the magnitude of the TEM$_{0,0}$ amplitude has a Gaussian profile (Eq. C.7). The envelope contours in Fig. C.1 and Fig. C.2 show where the amplitude has reached the 1/e-points of the on-axis value.

$$\left| \frac{E(x,y,z)}{E_0} \right| = \frac{w_0}{w(z)} \exp \left[ -\left( \frac{r}{w(z)} \right)^2 \right]$$

(C.7)

Figure C.2. "Spreading of a TEM$_{0,0}$ mode". From Ref. [128].
At the beam waist (z=0) the distance between the axis and the 1/e-point of the amplitude is called the minimum spot size, $w_0$. The Rayleigh range, $z_0$, characterizes the $z$-location where the spot size increased to $\sqrt{2}w_0$, and $2z_0$ is referred to as the confocal parameter. The intensity is proportional to the square of the electric field amplitude.

$$I \propto \langle \vec{E}\vec{E}^* \rangle$$ \hspace{1cm} (C.8)

Eqs. C.7 and C.8 yield:

$$I \propto \frac{w_0^2}{w^2(z)} \exp\left[-2 \frac{r^2}{w^2(z)} \right]$$ \hspace{1cm} (C.9)

Substituting Eq. C.3 in Eq. C.9 yields:

$$I \propto \frac{1}{1 + \left( \frac{z}{z_0} \right)} \exp\left[-2 \frac{\left( \frac{r}{w_0} \right)^2}{1 + \left( \frac{z}{z_0} \right)} \right]$$ \hspace{1cm} (C.10)
LIST OF REFERENCES

[4] An oscillating electric field with a strength of one atomic unit has a corresponding intensity of $3.51\times10^{16}$ W/cm$^2$.


