MULTIPHOTON AND ABOVE-THRESHOLD IONIZATION OF MAGNESIUM
USING HIGH-INTENSITY Ti:SAPPHIRE LASER PULSES

DISSERTATION

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

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*****

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ABSTRACT

In this work we investigate the photoionization processes of magnesium through the interaction of high-intensity Ti:Sapphire laser pulses and a generated beam of magnesium atoms. Typical laser parameters are intensities of $10^{12}$ to $10^{14}$ W/cm$^2$, pulse widths of 120 fs, and carrier wavelengths of 780 to 830 nm. Observation and analysis of the laser-atom interaction is performed by detection of ions and free electrons created by the laser field, and measuring their flight time over a known distance. The resulting ion yields and photoelectron spectra are studied for their dependences on the peak field intensity, field ellipticity, carrier frequency, and electron ejection angle from the interaction region.

We observe that the population and subsequent ionization of bound excited states is a dominant process for the photoionization of magnesium. Using mass spectrometry of the ions and linearly polarized light we observe increased ionization rates of the neutral and significantly enhanced ionization yields of doubly charged ions over that expected for sequential ionization of structureless atoms. For circularly polarized light we observe non-resonant multiphoton ionization of the neutral and a persistent enhanced ionization "knee" structure for the double ion.
Using high-resolution photoelectron spectroscopy we observe intensity dependent resonant population of specific intermediate excited states of the neutral and their subsequent photoionization in the laser field. Various participating states are identified using angular momentum selection rules, partial yields, and angular distributions. Several unexpected results are observed and discussed, including: the lack of an elastic rescattering plateau, peaks which do not correspond to expected resonant processes, and order-to-order variations in the above-threshold ionization photoelectron spectra. We also demonstrate that by varying the laser field ellipticity and carrier frequency we can experimentally control the population of these intermediate steps in the photoionization process.
This work is dedicated to my mother,

Genevieve Gillen
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<th>Description</th>
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<tr>
<td>ABI</td>
<td>above barrier ionization</td>
</tr>
<tr>
<td>ADK</td>
<td>Ammosov, Delone, and Krainov tunneling model</td>
</tr>
<tr>
<td>Ar</td>
<td>argon</td>
</tr>
<tr>
<td>ATI</td>
<td>above-threshold ionization</td>
</tr>
<tr>
<td>a.u.</td>
<td>atomic unit</td>
</tr>
<tr>
<td>BSI</td>
<td>barrier suppression ionization</td>
</tr>
<tr>
<td>CP</td>
<td>circular polarization</td>
</tr>
<tr>
<td>CPA</td>
<td>chirped pulse amplification</td>
</tr>
<tr>
<td>cw</td>
<td>continuous wave</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>fs</td>
<td>$10^{15}$ seconds</td>
</tr>
<tr>
<td>FV</td>
<td>full volume</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GW/cm$^2$</td>
<td>$10^9$ watts per centimeter squared</td>
</tr>
<tr>
<td>IP</td>
<td>ionization potential</td>
</tr>
<tr>
<td>KE</td>
<td>kinetic energy</td>
</tr>
<tr>
<td>kHz</td>
<td>$10^3$ cycles/sec</td>
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LBO  lithium triborate
LP   linear polarization
MCPs micro-channel plates
Mg   magnesium
mG   0.001 Gauss
mJ   0.001 Joule
MPI  multiphoton ionization
MPPD maximum ponderomotive probing depth
MS   mass spectrometry
Nd:YLF yttrium lithium fluoride rod doped with neodymium
Nd:YVO₄ yttrium vanadate rod doped with neodymium
NS   non-sequential
PES  photoelectron spectrum
PTA  picosecond timing analyzer
QWP  quarter-wave plate
RV   restricted volume
SAE  single active electron
TFP  thin film polarizer
Ti:Sapphire sapphire rod doped with titanium³⁺ ions
TOF  time of flight
TW/cm² 10¹² watts per centimeter squared
Uₚ   ponderomotive energy
CHAPTER 1

INTRODUCTION

1.1 Historical Background

Electromagnetic radiation is one of the fundamental media of interactions between units of matter. It is also one of the only modes of transporting and transferring energy from one place to another. Thus, better understanding of how matter responds to various frequencies and intensities of electromagnetic radiation is of central importance to physics as well as many other scientific and engineering fields. The quantized nature of matter and energy allows each unique atom and molecule to have a unique response to incident electromagnetic radiation. The mapping of how each type of matter absorbs or emits radiation as a function of frequency has been studied for over 100 years. For most of this time variations in the intensity of the applied light field only resulted in a linear response from an ensemble of atoms or molecules. Each individual atom or molecule would have a binary response to the light, either absorbing a photon or not. An ensemble of atoms or molecules would then reflect the probability of a photon being absorbed. The probability of absorption depends linearly on the intensity of the light.
If the photon density is high enough, the cross section for simultaneous absorption of more than one photon is no longer negligible. During the last 30 years, technological developments in lasers have allowed scientists to begin exploring the regime where matter will react nonlinearly with the intensity of the applied light field. These advances in laser technology have given rise to many new fields of study including nonlinear optics, multiphoton physics, multiphoton microscopy, and numerous other fields.

The goal of this work is to investigate the response of a "two electron" atom to laser intensities in the range of 10 to 100 TW/cm². Ion yield measurements and collection of high-resolution photoelectron spectra are the methods used in this work to record the response of magnesium atoms to high-intensity laser light. Ion yields and photoelectron spectra will be presented as a function of various laser field intensities, angular orientations, ellipticities, and carrier frequencies. There have been only a limited number of high intensity experimental investigations using alkaline earth elements as the target element. To date there have not been any published experimental results of ion yield curves and high-resolution photoelectron spectra of magnesium for the frequencies, intensities and laser field parameters that are used in this work.

1.2 Intense Laser – Matter Interactions

When matter is exposed to an intense laser field various outcomes can occur. Some of these possible outcomes are illustrated in figure 1.1. Once an atom, molecule or material has absorbed one or more photons, three general events can happen. First, the matter can reradiate the energy absorbed by emitting a single photon. Scattering, or the absorption and subsequent emission of a single photon, has been a field of study for more
than a century. Some macroscopic media, i.e. nonlinear optical crystals, can simultaneously absorb 2 or more photons and emit a single photon of higher frequency resulting in doubling, tripling, etc. of the incident laser frequency. Because of angular momentum selection rules, atoms can only absorb odd numbers of photons and return to the ground state emitting a single photon. This atomic response results in harmonic generation [1, 2]. Harmonic generation can occur either below or above the ionization limit of the atom. Another possible outcome is the atom or molecule can be excited to a metastable state where it will remain for a short time and collisionally transfer the energy absorbed to another atom or molecule.

Figure 1.1 Various single and multiple photon laser-matter processes.
The final possible outcome is that the atom or molecule can be ionized. When this occurs, the energy absorbed is split between the energy necessary to free the electron and the kinetic energy carried away by the electron. Albert Einstein first explained single photon ionization of matter in 1905 as the photoelectric effect [3]. The perplexing issue, at the time, was the fact that the kinetic energy of the freed electrons was independent of the intensity of the light. If the intensity of the incident light was increased, the number of electrons increased but the kinetic energy of each electron remained the same. The kinetic energy of the freed electrons only changes if the frequency of the incident light is varied. This confusion was clarified by Einstein's idea that a quantized particle of light was responsible for the ionization of each electron and the kinetic energy of the electron was the difference between the energy of the incident particle and that necessary to remove it. The energy of the incident photons is linearly dependent upon the frequency of the radiation, thus increasing or decreasing the radiation frequency results in an increase or decrease in the kinetic energy of the electrons. Nearly 60 years passed until photoionization was observed for multiphoton absorption [4, 5].

Since the focus of this work is the response of magnesium, only high-intensity laser-atom interactions will be presented and discussed. As the laser intensity is gradually increased, various ionization mechanisms can turn on or off. Table 1.1 illustrates some different multiphoton and ionization processes that can occur for atoms and their rough intensity ranges. The intensity ranges included in the table are intended to give a general order of magnitude. The intensity ranges for the various ionization mechanisms in Table 1.1 have definite overlap regions where more than one mechanism can be a significant means of ionization. The actual turn-on intensity for each
mechanism is highly dependent upon the atom and the properties of the laser field. For a particular atom these intensity regimes can be more accurately defined, somewhat, by considering the binding energies of the atomic states and frequency of the laser field. But, even for specific atomic species and laser field characteristics, the transition from one mechanism to another is not precisely defined, and identification of which mechanism is responsible or dominant is still a difficult challenge. Each of the mechanisms of table 1.1, and what factors they are dependent upon will be discussed in the next chapter.

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<th>General Intensity Range (W/cm²)</th>
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<tr>
<td>Nonresonant Multiphoton Ionization</td>
<td>10⁶ to 10¹³</td>
</tr>
<tr>
<td>Resonant Multiphoton Ionization</td>
<td>10¹² to 10¹⁴</td>
</tr>
<tr>
<td>Tunneling Ionization</td>
<td>10¹³ and up</td>
</tr>
<tr>
<td>Barrier Suppression Ionization</td>
<td>10¹⁴ and up</td>
</tr>
</tbody>
</table>

Table 1.1. Various high-intensity ionization mechanisms and the general intensity ranges where they become non-negligible.
CHAPTER 2

THEORY

2.1 Nonresonant Multiphoton Ionization

Nonresonant multiphoton ionization (MPI) occurs when a ground state atom absorbs just enough photons in order to free an electron. Similar to the photoelectric effect, the kinetic energy carried away by the electron is the difference between the total energy absorbed and that necessary to ionize it, or

$$KE = n\hbar\omega - IP,$$  \hspace{1cm} (2.1)

where \(n\) is the number of photons absorbed and \(IP\) is the ionization potential. Nonresonant MPI becomes a non-negligible process when the \(n^{th}\) power of the laser intensity, or photon density, approaches the same order of magnitude as the generalized cross section of absorbing that many photons. Cross sections for multiphoton processes are very small; for example, the 2-photon cross section for cesium has been measured to be \(6.7 \times 10^{50} \text{ cm}^4\text{s}\), and the 4-photon cross section to be \(7.5 \times 10^{-109} \text{ cm}^8\text{s}^3\) \([6]\).

The ionization rate for any \(N\)-photon process is given by

$$W = \sigma_N I^N,$$ \hspace{1cm} (2.2)
where $\sigma_N$ is the N-photon cross section, and $I$ is the intensity [7]. The units of $\sigma_N$ are in $\text{cm}^{2N}\text{s}^{-N-1}$, and the units of intensity are in photons per square centimeter per second. For lower order processes, say $N = 2$ to 4, comparison between experiment and theory can be made for the ionization cross section [6, 8]. For higher order MPI processes, equation 2.2 is more commonly used to identify only the order of the multiphoton process and apply fits to ionization yield graphs. An example of three very different order processes and their expected intensity ranges is illustrated in figure 2.1 [7]. Note that the slope of the line represents the order of nonlinearity.

![Figure 2.1](image)

Figure 2.1 N-photon MPI rates for cesium, xenon, and helium for 1.06 $\mu$m laser radiation [7].
2.2 DC and AC Stark Shifts

When an atom is exposed to a very weak electric field, where the influence of the electric field of the laser on the bound electron(s) is much, much weaker than that of the coulomb core, no change in the energy levels of the bound states will occur. But, if the amplitude of the electric field is increased then the influence of the applied field can become non-negligible, and perturbation theory can be applied. In order to determine the actual shift to bound atomic states in a more quantitative manner a semi-classical approach is necessary. In the semi-classical approach, the laser field is treated as a macroscopic classical plane wave, and the electron is treated as a quantum mechanical wave function. The energy shifts of bound atomic states for an atom exposed to a DC electric field can be found by applying the quantum mechanical time-independent perturbation theory. The new Hamiltonian for the electron becomes

\[ H = H_o + H' = \left( \frac{P^2}{2m} + V \right) + (eEz), \tag{2.3} \]

where \( H_o \) is the unperturbed Hamiltonian, \( H' \) is the perturbation due to the DC electric field, \( V \) is the potential due to the core, \( E \) is the magnitude of the electric field, and \( P, m, \) and \( e \) are the electron's momentum, mass and charge, respectively. The energy shift to each state can be found through either a first or second order correction, depending upon the state's parity, and degeneracy. The details of these calculations can be found in any quantum mechanics textbook.

If the electric field applied to the atom is that of an oscillating laser field the quantum mechanical treatment and calculation of the energy shifts of the bound states
becomes more complicated. If the electric field, \( \vec{E} \), or the vector potential, \( \vec{A} \), is written as

\[
\vec{E} = \vec{E}_0 \sin(\omega t) \quad \text{or} \quad \vec{A} = \frac{\vec{E}_0 c}{\omega} \cos(\omega t),
\]

then the interaction Hamiltonian is

\[
H' = \frac{E}{\omega} \cos(\omega t) \hat{p}_y + \frac{E^2}{2\omega^2} \cos^2(\omega t).
\]

Working through second order perturbation theory we find that the energy correction for any state is (in atomic units) [9]

\[
\Delta E = \frac{E^2}{4\omega^2} \left[ 1 - \sum \tilde{J}_{fi} \frac{\omega_n^2}{(\omega_n^2 - \omega^2)} \right],
\]

where \( \Delta E \), known as the AC Stark Shift, is the energy shift of the state, \( E_0 \) and \( \omega \) are the amplitude and frequency of the laser field, and \( \tilde{J}_{fi} \) and \( \omega_n \) are the oscillator strength and the energy difference between the initial and final states. The summation is over any possible final state of the electron. (For a more detailed treatment of the Stark shifts see reference [10] or Appendix E of reference [9].) From equation 2.6 we see that the energy correction for any state has two different terms. The first term is a constant, i.e. independent of the initial state or its relationship to any other state, and will be discussed further in the following section. The second term in the energy correction depends upon how well the laser frequency couples the state of interest to all possible atomic transitions.

The effect of the second term of the energy shift can be analyzed in two extreme cases. First, let us consider a deeply bound state, such as the ground state of an atom.
For photons whose energies are much less than the ionization energy, the ground state will be much farther than one photon energy away from all other states forcing $\omega_\text{f} \gg \omega$, for all final states. The second term then becomes the sum over all oscillator strengths, which is 1, making the total energy shift zero. The other extreme case is that for a Rydberg state that is near the ionization limit and very closely spaced to an infinite number of other states. In this case $\omega_\text{f} \ll \omega$, forcing the denominator to $-\omega^2$ and the numerator to zero. Thus the total shift of a higher excited state is just the first term in equation 2.6. For intermediate cases the Stark shift can be stronger or weaker depending upon the coupling strengths, or positive or negative depending upon which side of an atomic resonance the laser is tuned.

2.3 Ponderomotive Shifting

In section 2.2 we discussed the AC Stark shift for an electron bound to an atom. In this section we will discuss the AC Stark shift of a free electron, or the ponderomotive shift. If we use the same classical approach for the laser field

$$\vec{E} = E_0 \cos(\omega t) \hat{x},$$  \hspace{1cm} (2.7)

and treat the electron now as a classical free charged particle, instead of a quantum mechanical wave function, then we can write the electron's equation of motion as

$$m \ddot{x} = \vec{F} = e\vec{E} = eE_0 \cos(\omega t) \hat{x}.$$  \hspace{1cm} (2.8)

The instantaneous kinetic energy of the electron is then

$$KE = \frac{m}{2} (\dot{x})^2 = \frac{e^2 E_0^2}{2m\omega^2} \sin^2(\omega t) + KE_0.$$  \hspace{1cm} (2.9)
The first term is the time dependent kinetic energy of the electron due to the laser field and the second term is whatever initial kinetic energy the electron had before the laser field turned on, or the moment it was ionized. The ponderomotive energy, $U_p$, is defined as the time-averaged AC Stark shift of a free electron with no initial kinetic energy, or

$$U_p = \langle KE \rangle = \frac{E^2}{4\omega^2}.$$  \hspace{1cm} (2.10)

Equation 2.10 is written in atomic units where $e=m=1$. Closer inspection of equation 2.6 shows that the constant term for the AC Stark shift of any state is that of the ponderomotive shift. Equation 2.10 can be written in a more useful form of

$$U_p = 9.3208 \times 10^{-2} \, I \lambda^2,$$ \hspace{1cm} (2.11)

where $I$ is in units of W/cm$^2$ and $\lambda$ is in units of nm. Some examples of ponderomotive potentials are illustrated in table 2.1. Since $U_p$ is the minimum energy that a free electron can have, the amount of energy necessary to ionize a bound electron must include the ponderomotive energy if that electron is to be classified as a free electron. Thus, the ionization limit shifts ponderomotively with the laser field, and linearly with the laser intensity, or

$$IP \rightarrow IP(I) = IP_0 + U_p(I) = IP + 9.3208 \times 10^{-2} \, W/cm^2.$$ \hspace{1cm} (2.12)

As discussed in the previous section, Rydberg states that are relatively weakly bound will also shift ponderomotively, or very close to it.
<table>
<thead>
<tr>
<th>Wavelength</th>
<th>$10^{12}$ W/cm$^2$</th>
<th>$10^{13}$ W/cm$^2$</th>
<th>$10^{14}$ W/cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 nm</td>
<td>0.06 eV</td>
<td>0.6 eV</td>
<td>6 eV</td>
</tr>
<tr>
<td>400 nm</td>
<td>0.015 eV</td>
<td>0.15 eV</td>
<td>1.5 eV</td>
</tr>
</tbody>
</table>

Table 2.1. Some values for the ponderomotive potential for given laser intensities and wavelengths.

### 2.4 Resonant Multiphoton and Above Threshold Ionization

The important result of AC Stark shifts for atoms exposed to intense laser fields is that the energy levels of bound atomic states, that previously were stationary for lower intensities, have now become functions of intensity. Figure 2.2 is a calculated energy level diagram for magnesium $f$ states as a function of intensity. The energy shift of the ionization limit is ponderomotive, and the shift of each of the $f$ series states is assumed to be ponderomotive for this illustration. Thus, the energy of each state is

$$E_i(I) = E_{i_0} + U_p(I) \tag{2.13}$$

Figure 2.2 also displays the energy levels of 5, 6 and 7 photons above the non-shifted ground state. As the intensity of the applied field increases, shifting states can move into a resonance with a particular number of photons at a particular intensity. The occurrences of these types of resonant population of excited states are known as Freeman resonances [11].
Figure 2.2 Intensity dependent f states of magnesium due to ponderomotive shifting.
During a Freeman resonance, the probability of population transferring from the ground state to that specific excited state is significant, and the energy of that state has become

$$E_i = E_{io} + U_p = n\hbar\omega \quad .$$  

(2.14)

From figure 2.2 we can see that if the lowest \(f\) state, the \(4f\) state, shifts ponderomotively it will shift into resonance with a 5-photon absorption from the ground state at an intensity of just over 15 TW/cm\(^2\), and a 7-photon resonance at 67 TW/cm\(^2\). Due to angular momentum selection rules the \(f\) states are not accessible from the ground state for any even number of photon absorption.

Once an excited state becomes populated it can quickly ionize by either multiphoton ionization (MPI) or above-threshold ionization (ATI). Resonant MPI is similar to nonresonant ionization in that the electron absorbs just enough photons to ionize; only now the electron is ionized from an excited state that has been populated because it has been tuned to a resonant transition, instead of ionizing from the ground state. However, we are in the multiphoton regime and the probability of an electron absorbing more than one photon simultaneously is significant. An excited state can easily absorb more photons than necessary to ionize it leading to resonant ATI.

Evidence of population of excited states and subsequent ionization by one or more photons can be seen by looking at the kinetic energy distribution of electrons ejected from the atoms in the laser focus. If an atom starts in the ground state and encounters a Freeman resonance to an excited state, its energy is now that of equation 2.14. If the
electron is then ionized from state $i$ by absorbing $m$ more photons, its kinetic energy will be

$$KE(i) = E_i(I) + m\hbar\omega - IP(I)$$  \hspace{1cm} (2.14)

Now, substituting in Equation 2.13 and equation 2.12 we find

$$KE(I) = (E_{i_o} + U_p(I)) + m\hbar\omega - (IP_o + U_p(I)),$$  \hspace{1cm} (2.16)

or

$$KE(I) \rightarrow KE = m\hbar\omega - E_b,$$  \hspace{1cm} (2.17)

where $E_b$ is the binding energy of the electron, or $E_b = IP_o - E_{i_o}$. Examining equation 2.17 we see that the kinetic energy of each electron is no longer a function of the laser intensity, but rather the atomic state from which it was ionized. If $m$ is equal to the minimum number of photons necessary to ionize the atom, then the kinetic energy of those electrons is in the MPI order and any value of $m$ above this corresponds to ATI photoelectrons. Thus, by examining the kinetic energies of ionized electrons, the intermediate bound states that were populated can be identified. Figure 2.3 is an example photoelectron spectrum that clearly illustrates the occurrence of Freeman resonances and subsequent ionization, and the bound states involved [9].
Figure 2.3 MPI and ATI photoelectron spectra for argon illustrating resonant multiphoton population of $f$ series states and subsequent ionization [9].
2.5 MPI and ATI for Non-ponderomotively Shifted States

Ponderomotive shifting is only a special case of AC Stark Shifting, as discussed in section 2.3. The fact that some atomic states may exist that do not shift ponderomotively does not come as a big surprise. Many theoretical models of numerous types of atoms predict atomic states that shift non-ponderomotively [12-14]. Even though predictions of such states is very common among calculations, experimental observation of non-ponderomotively shifted atomic states subject to intense laser fields is quite rare and hard to identify. If an atomic state shifts non-ponderomotively then equation 2.13 becomes

\[ E_i(I) = E_{io} + \Delta E(I) \]  \hspace{1cm} (2.18)

where \( \Delta E \) is the AC Stark Shift for state \( E_{io} \) for the laser intensity \( I \). The actual value of \( \Delta E \) can theoretically be either greater than or less than \( U_p \), have a positive or negative value, or even both for a given state as a function of intensity.

The simplest case of a non-ponderomotively shifted state is that of a state that shifts linearly with the laser intensity and with a value that is some constant factor of \( U_p \), or

\[ E_i(I) = E_{io} + \alpha U_p(I) \]  \hspace{1cm} (2.19)

where \( \alpha \) is the constant factor of \( U_p \). Now substituting equation 2.19 into equation 2.14 we get

\[ KE(I) = E_i(I) + m\hbar \omega - IP(I) = \left( E_{io} + \alpha U_p(I) \right) + m\hbar \omega - \left( IP_o + U_p(I) \right) \]  \hspace{1cm} (2.20)

which can be rewritten as

\[ KE(I) = m\hbar \omega - E_b(I) \]  \hspace{1cm} (2.21)
where the binding energy of the state, $E_b$, is now a function of intensity, or

$$E_b(I) = IP_o - E_\omega + [1 - \alpha]U_p(I). \quad (2.22)$$

Once again, if the state shifts ponderomotively then $\alpha = 1$ and the kinetic energy of the freed electron is not a function of intensity and is simply that of equation 2.17.

Now we will predict what signature to look for in a photoelectron spectrum, in order to identify a non-ponderomotively shifting atomic state that is populated by a Freeman resonance and then subsequently photoionizes. First, the threshold intensity must be reached in order for a Freeman resonance to occur. The threshold intensity will occur when

$$E_t(I) = E_{io} + \alpha U_p(I) = n\hbar\omega. \quad (2.23)$$

Thus a Freeman resonance to a non-ponderomotively shifted state will occur at an intensity of

$$I_{np} = \frac{1}{\alpha} I_p. \quad (2.24)$$

$I_{np}$ and $I_p$ are the threshold intensities necessary to shift a non-ponderomotively and ponderomotively shifting states into resonance, assuming that they have equal initial binding energies.

Identification of a non-ponderomotively shifted state in terms of the kinetic energies observed in a photoelectron spectrum is not as easy as it is for its ponderomotively shifted counterpart. A ponderomotively shifted state's kinetic energy will occur exactly at $n\hbar\omega - E_{ib}$ for each MPI and ATI order regardless of the intensity of the field at the time of ionization, because $E_b$ is a constant. The kinetic energy of an
electron from a non-ponderomotively shifted state, on the other hand, is now a function of the intensity of the field at the time of ionization.

One special case of non-ponderomotively shifted states is a state that ionizes rapidly with respect to the time evolution of the field intensity. For this case, the observed binding energy in the photoelectron spectrum will be constant and comparable in growth, width and shape to that of a non-ponderomotively shifted state, but shifted to a different kinetic energy value. The state will also have a corresponding shift of the threshold intensity for which the Freeman resonance occurs. For example, if $\alpha<1$ the peak in the PES will be shifted to lower energy, but would have the same turn-on characteristics of a more deeply bound state that does shift ponderomotively. Thus, inspection of a peak in the PES using its energy position and turn on intensity, a non-ponderomotively shifted state is indistinguishable from a ponderomotively shifted state with a different original binding energy. The only odd feature about a non-ponderomotively shifted state is that its position in the PES is different than that which is expected for a state with its original binding energy.

If a non-ponderomotively shifted state does not ionize rapidly with respect to the time evolution of the field intensity, the kinetic energies observed in a photoelectron spectrum can be harder to identify. The worst-case scenario is that the lifetime of the excited state before it subsequently ionizes samples all of the intensities of the field from the point of the Freeman resonance to the peak of the laser field. For this situation the expected kinetic energy distribution is that of

$$\Delta KE = \left| (m\hbar \omega - E_b(I_p)) - (m\hbar \omega - E_b(I_{\text{max}})) \right|,$$

(2.25)
or
\[ \Delta KE = \left| \alpha U_p \left( I_{\text{max}} \right) - \alpha U_p \left( I_r \right) \right| . \] (2.26)

So the spread in kinetic energies of ionized non-ponderomotively shifted states can be quite broad for even a single non-ponderomotively shifted state.

Thus, if \( \alpha \) is positive and the lifetime of the excited state before ionization is long, then the signature in the photoelectron spectrum would be a sharp edge on the high kinetic energy side with a "tail" on the low kinetic energy side with a width up to that of equation 2.26. If \( \alpha \) is negative then the sharp edge will be on the low kinetic energy side with a smooth distribution to the higher kinetic energy side with a width of up to that of equation 2.26.

2.6 Nonresonant ATI from the Ground State

Nonresonant ATI from the ground state is a special case of ATI from a non-ponderomotively shifted state where the shifting factor, \( \alpha \), is equal to zero. This form of ionization becomes the dominant mechanism for atoms that are comprised of only a single deeply bound state. Although this might seem to be a purely theoretical model atom and not fully applicable to physical atoms, it is discussed in sections 4.3 and 5.4 how magnesium, and nearly any atom, can resemble a completely structureless atom for particular choices of laser field parameters.

If an atom contains no accessible excited states then it is impossible for a Freeman resonance to occur, and all ionization becomes a transition from a stationary ground state to the continuum, over a shifting ionization potential. If we substitute an initial state
energy, $E_{io}$, and a shift factor, $\alpha$, of zero into equations 2.21 and 2.22, we find that the expected kinetic energy becomes $KE = m\hbar \omega - (IP_o + U_p)$. For nonresonant ionization from the ground state of the atom, the kinetic energy of the ionized electron has become a function of the ponderomotive potential, which in turn is a function of the intensity. Incorporating the temporal and spatial averaging over a single, focused laser pulse, the range of kinetic energies within each ATI order is dependent upon the range of values of the ponderomotive potential, resulting in a distribution of detected kinetic energies for each ATI order, instead of a single, stationary well-defined peak. How these effects of nonresonant ATI from the ground state of an atom manifest themselves into observed ion yields and photoelectron spectrum will be discussed in sections 4.3 and 5.4, respectively.

### 2.7 Tunneling and Barrier Suppression Ionization

Another dominant mechanism for ionization of atoms subject to intense laser radiation is that of tunneling ionization. Resonant MPI and ATI occurs when the electric field of the laser "wiggles" the potential barrier of the coulomb core with a frequency that is much higher than the ionization rate. Tunneling ionization occurs when the potential of the electron in the laser field becomes comparable to the potential due to the core. When this occurs the laser field distorts the combined potential to the point where the energy of a previously bound state is now bound and unbound, separated by a new potential barrier as depicted in figure 2.4.

Treating the laser field classically and the electron quantum mechanically, as a wave function, tunneling ionization rates can be quantitatively calculated. The ionization rate is then the rate of "leakage" of wave function out of the bound section of the
Figure 2.4  (a) A bound electronic state in the potential due to the core, (b) a state which is both bound and unbound in the combined potential of the core and maximum laser field.

potential. The parameters that the tunneling ionization rate depends upon are the amplitude of the laser field, the depth of the initial energy state in the coulombic well, and the frequency of the laser field's oscillation. The most widely used tunneling ionization model used is that developed by Ammosov, Delone and Krainov [15], commonly referred to as ADK tunneling. The full expression for the ADK tunneling rate from a bound state with angular quantum numbers \( l \) and \( m \), core charge \( Z \), and quantum defect \( n^* \), exposed to a laser field, \( F \), is

\[
W = (2l + 1) \left( \frac{3F_{n^*}^3}{\pi Z^3} \right)^{1/2} \left( \frac{Z^2}{4\pi n^*} \right)^{3/2} \left( \frac{2e}{n^*} \right)^{2n^*} (l + |m|)! \\
\times \left( \frac{2Z^3}{F n^*} \right)^{2n^* - |m| - 1} \frac{2^{1-|m|}[|m|!(l - |m|)!]}{\exp \left( - \frac{2Z^3}{3n^*^{3/2} F} \right)}
\]

for linear laser field polarization, where

\[
n^* = \frac{Z}{\sqrt{2E_b}},
\]

and \( E_b \) is the binding energy of that state. For circular polarization the rate is
\[ W_{\text{circular}} = W_{\text{linear}} \left( \frac{\pi Z^3}{3 F n \ *^3} \right)^{\frac{1}{2}}. \tag{2.29} \]

The frequency of the laser field is absent from the ADK approximation because it is an adiabatic model. The ADK approximation assumes that the time scale of the oscillating laser field is much larger than the movement or response of the electron. As the model steps through time it calculates the instantaneous DC tunneling rates for each step, and averages the set of instantaneous ionization rates for a whole laser cycle.

Barrier suppression ionization is a much simpler theory for ionization of atoms exposed to intense fields. If the field applied is strong enough, then the combined potential is distorted to the point where the energy level is completely unbound. This model is more effective for weakly bound states or very high field intensities. The ionization rate is then binary, with a probability of 1 if the barrier is suppressed far enough, and 0 if it is not. The calculation of the electric field intensity that is required to completely free some bound state, \( E_b \), is relatively straightforward. First, the combined potential, \( E \), as a function of radial distance in the direction of laser polarization can be written as

\[ E = -\frac{Z}{r} - Fr, \tag{2.30} \]

in atomic units, where \( Z \) is the charge of the coulomb core, and \( F \) is the amplitude of the electric field of the laser. Maximizing equation 2.30 as a function of \( r \), and substituting that expression back into equation 2.30 and solving for the laser field we get

\[ F_{\text{critical}} = \frac{E_b^2}{4Z}. \tag{2.31} \]
2.8 The Keldysh Parameter

For the vast majority of experiments conducted in the $10^{12}$ to $10^{16}$ W/cm$^2$ regime, it can be very difficult to determine with any level of certainty which of the possible ionization mechanisms is dominant. In many experiments there may well be more than one significant mechanism. The general sequence of which mechanism may be dominant as the intensity is increased is as follows: nonresonant MPI, resonant MPI and ATI, tunneling ionization, then barrier suppression ionization. The exact overlap of one or more mechanisms and in which intensity range each occurs is specific to the target species and laser field characteristics. Experiments that reside in the intensity range of $10^{13}$ to $10^{15}$ W/cm$^2$, such as all experiments in this work, are primarily in the MPI/ATI regime and the tunneling ionization regime. In 1965, L. V. Keldysh introduced what has become known as the Keldysh parameter, $\gamma$, that helps distinguish between these two regimes for these intensity ranges [16]. The Keldysh parameter is the ratio between the tunneling time of a bound electron of a given depth in the atomic well to the time of one optical cycle, or

$$\gamma = \sqrt{\frac{E_b}{2U_p}}$$

(2.32)

Thus a Keldysh parameter of $\gamma \ll 1$ is interpreted as residing in the tunneling regime, and $\gamma \gg 1$ in the multiphoton regime.
2.9 **Full Volume versus Restricted Volume**

One of the major challenges high-intensity experimentalists face when comparing experimental results to theoretical models and predictions is due to the geometry of focusing a Gaussian laser beam. The vast majority of theoretical models and publications present their results for a given *single* intensity. Physically, when a laser beam is focused a single intensity is not present, but rather a distribution of an infinite number of intensities with some maximal value in the center of the focal plane. A TEM\(_{00}\) laser profile will have a Gaussian intensity distribution in the x-y plane for a beam traveling in the z-direction, and a Lorentzian profile in the z-dimension or

\[
I(r, z) = I_o \left( \frac{\omega_o}{\omega(z)} \right)^2 e^{-2 \left( \frac{r}{\omega(z)} \right)^2},
\]

(2.33)

where the spot size for a given position on the axis of propagation is

\[
\omega(z) = \omega_o \sqrt{1 + \left( \frac{z}{z_o} \right)^2}.
\]

(2.34)

\(\omega_o\) is the minimum beam waist, and \(z_o\) is the Rayleigh range which is given by

\[
z_o = \frac{\pi \omega_o^2}{\lambda}.
\]

(2.35)

The Rayleigh range is defined as the distance along the z direction where the spot size is a factor of \(\sqrt{2}\) larger than \(\omega_o\). Typical parameters for all of the experiments conducted in this work are a spot size of \(\omega_o \approx 35\ \mu m\), and a Rayleigh range of \(z_o \approx 1.4\ cm\).
If the interaction region between the laser and the target atoms exposed to the detector is a "thin" slice, $\Delta z << z_o$, then we can assume that the intensity variation along the $z$ direction for the interaction volume exposed to the detector is negligible. Experiments utilizing this interaction region arrangement are referred to as "restricted volume" (RV) experiments. Thus signal received by the detector for RV experiments is a superposition of signals for an infinite number of different intensities that follow the Gaussian beam profile in the $x$-$y$ plane. This "spatial averaging" can make comparison between experimental results and theoretical predictions for a single intensity very challenging. If the distance in the $z$ direction that is exposed to the detector is larger than the Rayleigh range then the spatial averaging that the detector sees is not only over the Gaussian beam profile, but over the Lorentzian intensity profile along the axis of beam propagation as well. Experiments utilizing a much larger or unrestricted interaction region are referred to as "full volume" (FV) experiments.

An illustration of how FV and RV results can differ from that of a single intensity is seen in figures 2.5, 2.6 and 2.7. The theoretical model used for these figures is that of ADK tunneling ionization. The calculation is the following set of coupled differential equations for the time-dependent populations of the magnesium neutral, Mg, first ionic, $\text{Mg}^+$, and second ionic, $\text{Mg}^{2+}$, species:

\[ \frac{d}{dt} \text{Mg}(t) = -\Gamma_1 \text{Mg}(t) \]  
(2.36)

\[ \frac{d}{dt} \text{Mg}^+(t) = \Gamma_1 \text{Mg}(t) - \Gamma_2 \text{Mg}^+(t) \]  
(2.37)

\[ \frac{d}{dt} \text{Mg}^{2+}(t) = \Gamma_2 \text{Mg}^+(t), \]  
(2.38)
where $\Gamma_1$ and $\Gamma_2$ are the intensity dependent ADK tunneling ionization rates given by equation 2.27. Figure 2.5 shows the time-dependent population of the three different species of magnesium, as well as a normalized temporal intensity profile of the laser pulse. The cross section of the laser pulse is assumed to be that of a single intensity. The Gaussian profile of the laser intensity is due to the time evolution of the pulse. The laser characteristics used for figure 2.5 are an intensity of 280 TW/cm$^2$, and a temporal FWHM of 120 fs. This intensity was chosen because it is much higher than the ADK calculation of the saturation intensity for Mg$^+$ of 50 TW/cm$^2$. The saturation intensity is defined as the intensity where the ionization rate is 1. A few important features this figure illustrates are the following: (1) the population of the neutral state begins to be depleted relatively early in the pulse, (2) the population of the first ionic species initially increases, then decreases as these ions are then ionized again, (3) the decrease in the first ionic species corresponds with the increase of the doubly charged ions. Below the saturation intensity for Mg$^+$ the only substantial ionic species present after the pulse has passed by is that of Mg$^+$. Above the saturation intensity there are always more Mg$^{2+}$ ions than Mg$^+$ ions.

If we take the Mg$^+$ and Mg$^{2+}$ populations after each mono-intensity pulse passes by, and then plot these final populations as a function of the pulse intensity, we get figure 2.6, which would be an expected ion yield curve graph for pulses that were comprised of only a single intensity. Notice how the yield of the single ionic species increases until saturation occurs then its population is depleted by the creation of doubly charged ions.

Signal detected for an actual laser pulse described by equation 2.33 will yield results that can differ greatly than those expected for calculations for single intensity profile. Figure 2.7 shows what an ion yield curve would look like for an experiment that
Figure 2.5  An example of time-dependent populations of the magnesium neutral, first ionic and second ionic species for a 120-fs, single intensity laser pulse using ADK tunneling ionization rates.
Figure 2.6. ADK ion yield curve for magnesium for laser pulses comprised of a single intensity.
Figure 2.7. Calculated ADK ionization yield curves spatially weighted for either a FV or RV interaction region.
uses either a RV or FV interaction region. The largest difference between figures 2.6 and 2.7 is the expected yield for each species above their respective saturation intensities. For mono-intensity pulses, the Mg\textsuperscript{+} yield decreases above the saturation intensity. For RV the Mg\textsuperscript{+} yield flattens out to a constant value, and for FV continues to increase following an I\textsuperscript{3/2} dependence.

The spatial distribution of intensities for a focused Gaussian beam, described in equation 2.33, can be thought of as a series of concentric volumetric shells. These shells all have angular symmetry around the axis of propagation. Each "shell" contains intensities in some small range from \(I\) to \(I+\Delta I\), with some maximal intensity \(I_0\). For RV, equation 2.33 simplifies to

\[
I(r) = I_0 e^{-\frac{r^2}{\sigma_z^2}},
\] (2.39)

for some \(\Delta z << z_0\). Now the volumetric shells have the shape of an annulus with a volume of [9]

\[
\Delta V = \pi \Delta z \sigma_z^2 \ln \left( \frac{I + \Delta I}{I} \right).
\] (2.40)

Notice that equation 2.40 is independent of \(I_0\). The "flattening out" of the Mg\textsuperscript{+} yield for RV is due to the fact that once \(I_0\) is greater than the saturation intensity the volume of intensity that creates Mg\textsuperscript{+} remains constant. As the intensity is increased the radial location of the annulus increases with a corresponding decrease in its width to maintain a constant volume. This explanation does not account for the behavior of the Mg\textsuperscript{2+} ions, as observed in figure 2.7. For the model used, Mg\textsuperscript{2+} is the highest charged species that can
be created. Thus once an Mg\(^{2+}\) ion is created, it will not further ionize regardless of how high the intensity gets, making the ionization volume for the double ions a solid disk shape (instead of an annulus) that follows

\[ \Delta V = \pi \Delta z \omega_z^2 \ln \left( \frac{I_o}{I} \right). \]  

(2.41)

whose volume continues to increase with increasing \(I_o\) as the radial location of the saturation intensity for the production of Mg\(^{2+}\) ions increases.

In addition to the radial symmetry and growth of the ionization volume, FV experiments also have a \(z\)–dimensional distribution and intensity dependent growth. The volumetric shell for FV experiments is shaped like that of a angularly symmetric peanut shell or [9]

\[
\Delta V = \pi \omega_o^2 \left\{ \frac{4}{3} \left[ \frac{I_o - (I + \Delta I)}{(I + \Delta I)} \right]^{\frac{1}{2}} + \frac{2}{9} \left[ \frac{I_o - (I + \Delta I)}{(I + \Delta I)} \right]^{\frac{1}{2}} - \frac{4}{3} \tan^{-1} \left[ \frac{I_o - (I + \Delta I)}{(I + \Delta I)} \right]^{\frac{1}{2}} \right\} - \\
\pi \omega_o^2 \left\{ \frac{4}{3} \left[ \frac{I_o - I}{I} \right]^{\frac{1}{2}} + \frac{2}{9} \left[ \frac{I_o - I}{I} \right]^{\frac{1}{2}} - \frac{4}{3} \tan^{-1} \left[ \frac{I_o - I}{I} \right]^{\frac{1}{2}} \right\}
\]

(2.42)

Similarly to RV experiments, the volume for the double ion has the same shape as the single ion except it is not hollowed out by the next ionic species, and thus has the shape of a "solid" peanut shell, or the second term of equation 2.42.

The peculiar turnover, or decrease, in the yields in figure 2.7 above \(3 \times 10^{15}\) W/cm\(^2\) is a result of the ADK model failing for this intensity range. In reality, the ADK model should not be applied for intensities in this range as the potential barrier no longer exists and all atomic states are completely unbound.
CHAPTER 3

EXPERIMENT

3.1 Laser System

The laser used in this investigation is a commercially available system purchased from Spectra Physics in 1996. The system is comprised of four separate components that collectively produce laser pulses of 120 fs in duration (FWHM), at a repetition rate of 1 kHz, with factory specified energy per pulse of 1 mJ. Typical day-to-day performance of the system yields maximum pulse energies of ≈ 0.8 mJ. The layout of the entire system is depicted in figure 3.1.

The initial component of the system is the Millennia. The core of this laser is a neodymium doped yttrium vanadate (Nd:YVO₄) rod that is pumped by two diode bars lasing at 809 nm. The Nd:YVO₄ rod lases at a wavelength of 1.064 microns. The light is then intra-cavity doubled by a lithium triborate (LBO) crystal to produce a cw 532 nm beam with an output of up to 5 W. The Millennia beam is used to pump the Tsunami. The gain medium of the Tsunami is a sapphire rod doped with Ti³⁺ ions.
Figure 3.1 The Spectra Physics laser system used is comprised of a Millennia Nd:YVO₄ cw pump laser, Tsunami Ti:Sapphire oscillator, Merlin Q-switched Nd:YLF pump laser, and a Spitfire Ti:Sapphire regenerative amplifier.

Ti:Sapphire rods are nearly exclusively used in high-intensity laser-matter interactions because of their very broad gain bandwidth. The gain region for Ti:Sapphire extends from around 650 nm to 1000 nm and is peaked around 800 nm, as illustrated in figure 3.2. Thus, a very large number of longitudinal modes can be supported in the laser cavity simultaneously. Each mode is some multiple of the fundamental frequency \( f = c / 2L \), where \( c \) is the speed of light and \( L \) is the length of the laser cavity. If a large number of sinusoidal waves are superimposed with random relationships between the relative phase of each mode, random noise will be produced. But, if at some point in space all the modes have the same phase, for example a maximum, then a field spike will be produced at that point. Now, if the optical path length of the laser cavity is the same
for all frequencies, then this field spike will oscillate back and forth within the cavity at the speed of light, and a short pulse is produced. The mechanism responsible for "locking" the phases of the numerous modes together is known as Kerr-lens mode-locking [17].

![Absorption and Emission Characteristics](image)

**Figure 3.2** Absorption and emission characteristics for Ti:Sapphire.

Only a small region, 8 to 12 nm, of the gain curve of Ti:Sapphire is used by the Tsunami to produce ~120 to 80 fs pulses at a repetition rate of 82 MHz. The average power output of the Tsunami ranges from 350 to 450 mW, corresponding to an average energy per pulse of 4 nJ. Although these pulses are short, they lack the energy to reach into the TW/cm² intensity regime when focused.
The Merlin and the Spitfire work cooperatively to amplify the pulses generated by the Tsunami. The Merlin uses a krypton flashlamp to pump a neodymium doped yttrium lithium fluoride (Nd:YLF) rod. Similar to the Millennia, the output of the laser rod is intra-cavity doubled to produce 527 nm light. Inside the laser cavity is an acusto-optic Q-switch that drives the output of the laser at a kilohertz producing ~250 ns pulses with an average energy of ~10 mJ. This energy is deposited in a Ti:Sapphire rod in the Spitfire which is the gain medium used to amplify the seed pulses from the Tsunami.

Amplifying short laser pulses can be rather tricky and dangerous for the amplifying medium or other optical components, as well. Because of the short duration of the pulses, it does not take much of an increase in the energy per pulse to exceed the damage threshold of Ti:Sapphire, which is on the order of 10 GW/cm². To circumvent the possibility of damaging the gain medium, the Spitfire uses a clever trick known as chirped pulse amplification (CPA) [18]. In CPA the pulse to be amplified is "stretched" such that the frequencies that comprise the pulse are temporally dispersed. The higher frequencies are made to travel a longer distance than the lower frequencies stretching the pulse by a factor of $10^3$ to $10^4$. The pulses can now be safely amplified by the Spitfire to an average energy per pulse of up to 1.5 mJ. After amplification the pulses are then "compressed" back to within 150% of their original pulse width, or around 120 fs.

3.2 Vacuum Chamber

The vacuum chamber built for and used in this work is affectionately known as "Peggy". The central piece of Peggy is a stainless steel cube with an internal volume of one cubic foot. The wall thickness of each side of the cube is 0.75". The top of the cube
and two of the sides has a 10" conflat flange. The other two sides each have one 8" conflat flange, and four 2 3/4" conflat flanges. The bottom of the cube has an extended 6" conflat flange. A large capacity (16.9 liter) liquid nitrogen trap is attached to the top of the cube to act as a cold plate to terminate the magnesium beam after it has passed through the interaction region. The magnesium beam is generated by the effusion cell (described in the following section), which hangs off of the bottom of the cube. The whole chamber sits upon a 1" thick aluminum shelf with a hole for the 6" bottom flange. The shelf extends off of the optics table allowing for the effusion cell to be attached to the bottom of the cube. This arrangement is necessary such that the crucible in the cell is upright, and the generated atomic beam is directed straight up through the chamber and terminates on the bottom of the liquid nitrogen trap.

The chamber is evacuated using a Balzers turbomolecular pump, model TPU 330, which pumps at a maximum rate of 330 liters per second. The pump is attached to the chamber via an electro-pneumatic gate valve. The gate valve and the pump are incorporated into an interlock circuit such that the valve will close and the pump will shut off in the situation where either a power outage/flicker occurs or the backing pressure of the pump climbs to high. The system will remain off with the gate-valve closed until it is manually reset. The general layout of the vacuum chamber is illustrated in figure 3.3.

After the chamber has been assembled or vented it is cleaned via the method of baking. Once the chamber has reached a "dirty" base pressure of around 100 nTorr, it is wrapped with heater tapes and aluminum foil (to reflect the radiated heat back in). Typically the entire chamber is heated to 100 to 140°C, for a period of time from 12
hours to up to 3 to 4 days. The base pressure of a clean chamber with the liquid nitrogen trap empty is around 250 to 300 pTorr, and 150 to 200 pTorr with the trap full.

![Diagram of vacuum chamber](image)

**Figure 3.3** "Peggy" the vacuum chamber.

### 3.3 Effusion Cell

Much of the focus of experimental and theoretical work in the field of high-intensity laser-atom interactions has been the response of noble gases and helium atoms. One of the main reasons why these target atoms have been so extensively studied is due to their experimental simplicity. At room temperature helium and the noble gases are collections of individual atoms. No additional steps are needed to observe the response of a single atom to the incident light. Each atom in the interaction region (and the entire vacuum chamber in most cases) is already free of molecular or any other type of bond to
another atom. The only preparation necessary for the interaction region between the laser and the target is to remove all undesirable atoms or molecules; accomplished by establishing a good base pressure in the vacuum chamber.

One primary difficulty in building an experimental setup for observing the atomic response of magnesium atoms is that magnesium is a solid at room temperature. In order to observe the response of a single atom (and not that of the properties of a solid), an atomic beam source is required. In the earlier stages of this investigation a home-built "oven" was used to generate an atomic beam. The oven was composed of a thin-walled stainless steel tube containing magnesium granules through which 50 to 75 amps passed, heating the magnesium. As the magnesium is heated the vapor pressure of the magnesium evaporating off of the granules increases nonlinearly with the temperature. (See reference [19] for a discussion of high-temperature vapors and tabulated values for any element.)

The original home-built beam source was not used in this study because of relatively large fluctuations in the atomic beam density. The beam density is dependent upon the cell temperature, which is dependent upon the voltage and current supplied to it, which is in turn dependent upon the temperature of the stainless steel tube. Due to the various nonlinear dependencies, small fluctuations in the current source and the temperature of the tube resulted in large variations in the atomic beam density and eventually signal counts.

To alleviate this problem, we opted to use a commercially available effusion cell from EPI MBE Products Group (now named Applied EPI). The Low Temp SUMO effusion cell has a factory specification stability of <1% temperature fluctuation over an 8
hour period. Use of this cell dramatically improved the stability of the atomic beam density such that counts from one data run to another, for repeated measurements using the same parameters, fail to within a few percent of normal counting statistics.

3.4 Setup for Full Volume or Restricted Volume

The interaction region of the flight tube used in these experiments is designed such that the laser can pass on either side of the pin-hole plate, illustrated in figure 3.4. If a RV experiment is desired, the laser beam will be steered such that it passes between the sweeping plate and the pin-hole plate. For a FV experiment, the laser beam passes on the flight tube side of the pinhole so that the width of the interaction region that is exposed to the detector is that of the width of the inside diameter of the flight tube, or 2.75".
Figure 3.4 Cartoon of the experimental setup. The laser can pass on either side of the pin-hole plate for either RV or FV experiments.
3.5 Time of Flight Spectroscopy

3.5.1 Introduction

Time of flight (TOF) spectroscopy is the use of the flight time of a particle over a known distance to extrapolate other information about that particle. How the raw time data is manipulated is dependent upon what other information about that particle is desired, and what is already known. In this work the TOF information is either manipulated to give a charge per mass ratio histogram for ionic measurements, or a histogram of the distribution of the raw kinetic energies of electrons ejected from the interaction region, for photoelectron measurements.

3.5.2 Mass Spectrometry

The laser intensities used in this work can ionize any element or molecule, at least once. Once they are ionized, the ions can be swept towards the detector where they will register as a count. The mass of each ionized atom or molecule can then be determined by their flight time. Mass spectrometry (MS) yields a plot of the number of ions detected versus their charge per mass ratio.

All ionic experiments conducted in this work utilize a RV interaction region as depicted in figure 3.4. The laser beam is focused between the sweeping plate and the pinhole plate. The plates are separated by 12.7 mm, and are held at a constant voltage (typically between 1000 and 1500 V). The pinhole plate is held at ground. For a given sweeping potential, the mass and charge of the ions produced can be determined by their respective flight times. The kinetic energy of each ion is
\[ KE = \frac{md^2}{2t^2} = qV, \]  \hspace{1cm} (3.1)

where \( m \) is the mass of the ion, \( d \) is the distance to the detector, \( t \) is the flight time, \( q \) is the charge of the ion and \( V \) is the potential of the location of the interaction region between the plates. From equation 3.1 the mass to charge ratio can be written as

\[ \frac{m}{q} = \frac{2Vt^2}{d^2}. \]  \hspace{1cm} (3.2)

MS is a useful tool for not only collecting data on the ionization of the target of interest, but for diagnostic purposes as well. Since everything in the interaction region will ionize, background gasses and contaminants can be identified. Figure 3.5 is a sample mass spectrum of a dirty vacuum chamber with the magnesium beam turned off. The x-axis of figure 3.5 is the mass to charge ratio for the ions. Thus, a doubly charged ion will show up at a value half of that of its singly charged counterpart, as is evident in figure 3.5 with carbon. Figure 3.6 is a mass spectrum of a clean chamber with an atomic beam of magnesium. The detected percentages of \(^{24}\text{Mg},^{25}\text{Mg},^{26}\text{Mg}\) isotopes are 79\%, 10\% and 11\%, as expected.

What is of interest to the experiments conducted in this work is how many, and what species of ions are produced for a given number of laser shots. Counting the number of ions that are created per laser shot or data run can give insight into the probability of ionization of an atom and the rate at which this probability changes as a function of various controllable laser parameters. Thus an MS data run consists of many individual mass spectrums, each for a predetermined set of laser pulse characteristics.
Once a data run is complete the number of ions detected for each spectrum is plotted versus either laser intensity or field ellipticity, as will be discussed in the next chapter.

Although MS is a very powerful tool for determining what is being ionized, how many times it ionizes, and how the ionization rate depends upon laser field intensity and ellipticity, it still only reveals that an atom or ion was ionized. MS only detects what ions are present after the pulse has already passed. It is very difficult to use MS to extract any information about what happened to the atom, or electron, as it was ionized.
3.5.3 Photoelectron Spectroscopy

A photoelectron spectrum (PES) is essentially a very finely spaced histogram of the kinetic energies of electrons that are ejected from the interaction region. Unlike MS, where only the number of ionization events is counted, photoelectron spectroscopy reveals the kinetic energy of each electron as it is released from the atom as well. Knowing the kinetic energies of the ejected electron reveals some information about what happened to the electron as it was ionized. But, more information of one type usually comes with a sacrifice of another type of information. A PES gives information about the kinetic energy of an electron, but it does not discriminate from which atom, molecule, or ion it came. Thus, a very clean chamber and target source is essential in conducting a
PES experiment. A clean chamber and target source (determined prior to a PES data run by MS) ensures that any atom that is ionized is that which is desired.

The increase in atomic information gained by a PES also comes with higher demands of the experimental setup. The greatest experimental challenge encountered in this work was the ability to detect low energy (less than 3 to 4 eV) electrons a distance of half of a meter away from the interaction region. Detection of ions using MS is a much easier task. The ions are much heavier than an electron and are much harder to steer away from the detector by a stray electric or magnetic field. For the ionic experiments conducted in this work, the kinetic energy of a magnesium ion is typically around 700 eV. Although a 2 eV electron travels 11 times faster than a 700 eV magnesium ion, it can be steered away from the detector much more easily by a perpendicular electric or magnetic field. If the same stray field is present for both, the radius of curvature of the electron will be 3900 times smaller than that of the magnesium ion. Experimental requirements for conducting a MS experiment are much more forgiving than those for obtaining a PES. Even a very large stray field, such as the earth's magnetic field, will not significantly steer an ion away from the detector over a distance of half of a meter. Whereas a 2 eV electron in the earth's magnetic field will have a radius of curvature of 4.8 cm. So, even the smallest of stray fields can steer a low energy electron away from the 2.54 cm diameter detector located half of a meter away.

To protect the flight path of the electrons from stray magnetic fields the flight tube is wrapped with multiple layers of magnetic shielding μ-metal. The μ-metal shielding extends from the detector to just over 10 cm past the interaction region. In order to allow the laser and atomic beams into the interaction region small apertures are
cut through the \( \mu \)-metal. The laser holes are each 0.25 " in diameter and the aperture for the atomic beam is a 2 mm square hole. Thus, the width of the atomic beam in the direction of laser propagation in the interaction region is just over 2 mm. The measured magnetic field in the interaction region is between 10 and 15 mG, and just a few mG farther down the flight tube.

3.6 Detection

3.6.1 Detector

The central piece of the detector is a pair of chevroned micro-channel plates (MCPs). A cartoon of a chevroned pair of MCPs is depicted in figure 3.7. A single MCP used in this experiment is disk shaped with a diameter of 2.54 cm and a thickness of 0.5 mm, and contains thousands of small channels that pass through the plate at an angle. Each channel of the MCP acts very much like a photomultiplier tube. A potential gradient is established from one side of the plate to the other. As an incident particle approaches the MCP it can enter one of the channels where it will collide with the channel wall, releasing numerous electrons. Each of these electrons will then impact the opposite side of the channel wall, releasing more electrons. Thus, each incident particle releases a cascade of electrons that are emitted from the opposite side of the MCP. A chevroned pair of MCPs is two MCPs sandwiched together such that the angle between the direction of their channels is maximum. The potential across the pair of channel plates is set to around 2000 V, and the total gain of the pair is on the order of \( 10^6 \).
Figure 3.7 Cartoon of a chevroned pair of MCPs with an expanded view of an incident particle entering a single channel and creating a cascade of electrons off of each channel wall.

The entire detector setup is illustrated in figure 3.8. Because a field-free flight path is desired the screen on the end of the flight tube, as well as the flight tube itself, is set to ground. The potential of the front and back surfaces of the MCPs can be varied depending upon what experimental setup is required. The back MCP surface is generally held at a high positive potential with the potential of the anode slightly higher (attracting all of the electrons generated by the MCPs). The output of the entire detection assembly is connected to a constant fraction discriminator (after further amplification of the signal by an EG&G Ortec 1-GHz amplifier). The constant fraction discriminator cleanly triggers the picosecond timing analyzer (PTA) to stop timing for that event. As illustrated in figure 3.4, the PTA is triggered to start timing for each laser pulse by a photodiode placed within the Spitfire. The conical anode is necessary in order to impedance match the signal from the anode to the 50-Ohm impedance of the constant

Gain is $\sim 10^6$
Figure 3.8  Entire detector assembly.
fraction discriminator. Because the anode is held at a very high potential and the output of
the conical anode is electronically connected to other sensitive electronics, it is necessary to capacitively couple the signal from the anode to the conical anode via the use of several layers of insulating mylar sheets. This ensures that the input signal to the amplifier is not at the same potential as that of the anode, which is on the order of 2000 V.

3.6.2 Detection Efficiency

If quantitative measurements and comparisons are to be made between ions of different charges and electrons of different kinetic energies, it is essential to know the quantum efficiency of the detector as a function of kinetic energy of the incident particles. The quantum efficiency of MCPs is certainly not constant for incident ions and electrons of different kinetic energies. Recent experiments in the literature have used the correction factor of

\[
\text{Correction factor} = \frac{Z}{\sqrt{M}},
\]

(3.3)

where \(Z\) is the charge of the ion and \(M\) is its mass, to quantitatively compare yields of ions possessing different charges and masses[20-22]. The quantum efficiency plots for MCPs provided by Burle Industries, Inc. (the manufacturer of our MCPs) for ions and electrons are shown in figures 3.9(a) and 3.9(b), respectively [23].

Figure 3.10 is a plot of data taken with Peggy for the detected signal for Mg\(^+\) and Mg\(^{2+}\) ions as a function of their kinetic energy. For this experiment, the sweeping potential is kept constant, and the potential difference between the screen and the front
Figure 3.9 Detection efficiency of MCPs for (a) ions and (b) electrons as a function of their kinetic energy.
surface of the MCPs is varied. Varying a "final" accelerating potential, instead of the sweeping potential, ensures that the flight time of the ions is constant from one data point to another. The screen and the front MCP are separated by only 0.025", and the difference in flight time of each ion from one final accelerating potential to another is negligible. For typical experiments conducted in this work Mg\(^+\) ions have a kinetic energy of 700 to 800 eV, and the Mg\(^{2+}\) ion has twice that of Mg\(^+\). Using the data of figure 3.10 we see that the difference in quantum efficiency between ions of 800 eV and 1600 eV is a relative factor of 2.0. The correction factor obtained from our data coincidentally is the same as that which is obtained from equation 3.3, but as observed from figure 3.10 the relationship is not exactly linear.

![Graph](image)

Figure 3.10 Detected signal of counts of ions versus the final kinetic energy of the ions. The doubly charged ion yields are shifted by a factor to correct for the difference in absolute number of ions created for each species.
As seen in Figure 3.9(b), the quantum efficiency of MCPs for electrons of different kinetic energies is also a rather complex function. Unfortunately, a constant, calibrated source of electrons of different kinetic energies is not readily available, nor easily incorporated into the experimental setup, for calibration of the MCPs quantum efficiency for electrons. Instead, we opted to increase the kinetic energy of all of the electrons, such that the difference between the final kinetic energy of an electron ionized with a low kinetic energy is negligibly different than that of an electron ionized with a high kinetic energy. After experimenting with various final acceleration potentials, between the screen and the front MCP, it was found that differences between low and high energy photoelectrons no longer were noticeable for a final accelerating potential of 900 V. Using a final accelerating potential of 900 V, the final kinetic energy of a 1 eV photoelectron differs from a 20 eV photoelectron by 2%. Once again the difference in flight time with and without the final accelerating potential is negligible.
CHAPTER 4

ENHANCED DOUBLE IONIZATION

4.1 Introduction

The identification of multi-electron processes, including those responsible for multielectron detachment, has been the focus of many investigations for over two decades. The first reported measurements of multiply charged ion production via multiphoton ionization (MPI) were made by Aleksakhin et al. [24, 25] in 1977 and 1979, with 1.06-μm, 30-ns laser pulses. As laser technology advanced and shorter pulse durations became possible (also enabling higher peak intensities), new physical phenomena became observable, including high-order harmonic generation [26], above threshold ionization (ATI) [27], short-pulsed soft-x-ray sources [28], etc. A few years later, L'Huillier et al. reported ion yield measurements for krypton and xenon using 1.064-μm 50-ps laser pulses [29, 30].

These later measurements revealed a much higher yield of multiply charged ions than expected according to a stepwise ionization process for the lower intensity range. A stepwise or sequential ionization process assumes that a singly charged ion is created by the ionization of a neutral atom; a doubly charged ion is created by the ionization of a
singly charged ion, and so on. When displayed on a log-log scale of counts versus peak intensity, L'Huillier's measurements of the first ionic species initially grew linearly, following a power law dependence for increasing ionization probability, as previously observed by Aleksakhin. As the intensity was increased the probability of ionization increased up to the saturation intensity. The saturation region starts when this probability approaches unity. In this intensity regime the number of neutral atoms in the ionization volume begins to be depleted and the singly charged ionic species is dominant. For full volume experiments (where the entire focal region along the axis of beam propagation is exposed to the detector) the ionization yield curve above the saturation limit is expected to grow as the Gaussian focal volume grows, by an $I^{3/2}$ rate. The enhancement of the double and triple ions observed by L'Huillier occurred for an intensity region below the saturation of the previous ionic species, contrary to what would be expected by sequential ionization models. A sequential model would not expect the second ionic species to be measurably detected until the ionic volume contains a significant number of singly charged ions. The observation of an unexplained "nonsequential" (NS) process sparked the interest of many investigations to come, both theoretical and experimental.

A decade after the first reported enhancement of doubly charged ionic species Fittinghoff et al. [31] observed a prominent enhancement of He$^{2+}$ ions using 614-nm 120-fs laser pulses. The enhancement occurred in an intensity region where there should have been virtually no double ions as compared to their sequential Ammosov-Delone-Krainov (ADK) tunneling ionization model [15]. Soon after, Walker et al. [32], utilizing 780-nm 160-fs pulses reported ion yield measurements for helium over a vast detection and intensity range. The double ionization curve of this investigation illustrated an
enhancement of the doubly charged ions several orders of magnitude above what would be expected for various sequential ionization models (ADK and SAE) below the saturation of the first ion. For peak laser intensities above this NS intensity region the number of ions detected started to increase again following the sequential models.

In this chapter we present results of strong-field ionization experiments with magnesium. Magnesium was chosen because it is a model two-electron atom with a moderately high first and second ionization potential, for an alkaline-earth element. The first three ionization potentials for magnesium are 7.646, 15.035, and 80.143 eV. A higher ionization potential is desired so that a larger number of photons is required to ionize the atom and results can be qualitatively compared to previous experiments of similar or higher MPI orders. There is also a lack of published experimental MPI or ATI studies of magnesium for Ti:Sapphire laser frequencies. We report ionization yield curves of singly and double charged ions as a function of laser intensity and field ellipticity.

4.2 Experimental Setup

The laser system used for these MS experiments is that which is described in chapter 3. The peak laser intensity in the interaction region was calibrated by collecting photoelectron spectra of argon for a variety of pulse energies. These spectra were then compared to spectra taken in a previous investigation [33] using the appearance of the eight-photon Freeman resonance of the 4f Rydberg level as a calibration point.

The laser is focused into the vacuum chamber via a 25-cm focal length lens with an initial 1/e beam diameter of 7.1 mm and propagates into the interaction region
mutually orthogonal to the atomic beam and the ion flight path. The ellipticity of the laser field is controlled via a quarter-wave plate. Polarization is oriented such that when the field is linear is it parallel to the flight path. To reduce the effects of spatial averaging over the laser focus volume we use a restricted volume technique [34] by placing a 1-mm pinhole in the flight path near the interaction region.

Each point is an integration of all of the counts detected for Mg$^+$ and Mg$^{2+}$, including the isotopes, and normalized to one million laser shots per data point. Up to 10 million shots were taken for lower yielding intensities for better statistics. The relative number of singly and doubly charged ions are corrected for the quantum efficiency of the MCPs, as discussed in section 3.6.2.

4.3 Results

The measured ion yield curves are displayed in Figure 4.1 for linear polarization, and in Figure 4.2 for circular polarization. For both figures 1 and 2 some gross structural characteristics are apparent. On the log-log scale the detected yield of Mg$^+$ increases nearly linearly at low peak laser intensity followed by a decrease in slope until the saturation intensity is approached. For a restricted volume experiment, an iso-intensity volume for an intensity less than that of the peak does not continue to grow as quickly as it does for an unrestricted volume detection region, forcing the ion yield curve to flatten out for higher intensities. For a more detailed discussion of volume effects on the detected ion yield see the appendix of Larochelle et al. [35].
Figure 4.1  Magnesium ion yields for linearly polarized light.
Figure 4.2 Magnesium ion yields for circularly polarized light.
The single ion yield for linear polarization (LP) has a power-law slope of about 11 for intensities up to about $1.5 \times 10^{13}$ W/cm$^2$ and then begins a gentle roll-off to saturation at about $4 \times 10^{13}$ W/cm$^2$. It is clear that a simple power-law expression cannot describe the ion yield over the range $(1.5$ to $4) \times 10^{13}$ W/cm$^2$. The continually changing slope of the ion yield from the lowest intensity up to saturation is indicative of the participation of excited states for the intermediate intensities. If ionization were to occur from the ground state for all intensities, one would expect a slope that resembles that of non-resonant MPI (as discussed in section 2.1) with a value of 5 or 6. An enhancement of the ionization rate of neutral magnesium in the intermediate intensity range from $(1$ to $4) \times 10^{13}$ W/cm$^2$ would push up the number of ions detected for this range. On an ion yield graph this would have the effect of a higher slope for lower intensities whose value would slowly decrease until saturation.

The Mg$^{2+}$ yield increases initially up to a peak intensity around $(2$ to $3) \times 10^{13}$ W/cm$^2$, then the rate decreases up to an intensity of $6 \times 10^{13}$ W/cm$^2$. Above this intensity a secondary, and higher, ionization rate begins to take over until saturation of the interaction region is reached around $1 \times 10^{14}$ W/cm$^2$. One interesting result of using the RV technique with a two-electron atom is that the number of doubly charged ions created can exceed that of the maximum number of singly charged ions. For a purely sequential ionization model, the disk-shaped ionization volume is dominated by singly charged ions at lower peak intensities. As the intensity is increased the total ionization volume grows in radius to the point where the central peak intensity is capable of double ionization. Further increases in the intensity will yield an annulus-shaped singly charged ionization
volume, which does not grow in total volume for further increases in intensity, circumscribing the disk-shaped doubly charged ionic volume. Since the doubly charged ion is the highest charge state of the model, its ionization volume will continue to grow beyond saturation as there is no higher charged state to deplete its central region. Any enhanced double ionization will blur the geometric borders between singly and doubly charged ionization volumes in favor of the double and hence increase the difference in their maxima as a function of intensity.

The use of circular polarization (CP) shows a clear power-law dependence for the single ion yield with a slope of 6 over the lower intensity range up to about $1.8 \times 10^{13}$ W/cm². Because the average pulse energy is the experimentally controlled variable, the intensity axis for the points of figure 4.2 is shifted towards higher intensities by a factor of 2 to account for the peak field difference between LP and CP for the same pulse energy. For LP, the peak field is twice that of the average, and for CP the field amplitude is constant, and thus always the average value. A straight power law dependence of 6 from the lowest intensity up to saturation for the first ionic species is indicative that ionization from the ground state of the neutral is the dominant mechanism, and excited states do not play a significant role. This is not at all surprising since $6\hbar$ would be the first accessible state for population with CP light.

Remarkably, the double ion yield persists below the saturation intensity for single ionization. An obvious "knee" structure is observed similar to that observed for linear polarization in a wide variety of noble gas atoms [32, 35-37].

The overall shapes of the Mg²⁺ ion yields for linear and circular polarization have similar characteristics. Overall, the largest difference in the double ionization yield
curves between linear and circular polarization is the pronounced suppression of double ionization for circular polarization. At the saturation intensity of Mg$^{2+}$, linear and circular yields only differ by a factor of 3. For lower intensities, in the region of the primary ionization rate, the yields differ by up to 3 orders of magnitude.

4.4 Discussion

It is important to stress here that we are in a regime where the traditional Keldysh parameter, $\gamma$, [16] would indicate that multiphoton ionization is the more dominant mechanism for the majority of peak laser intensities used. The minimum photon orders for each ionization process are shown in Table 4.1. If $\gamma < 1$, quasistatic tunneling ionization (as modeled by ADK) is accepted to be the dominant mechanism. If $\gamma > 1$, MPI is the dominant mechanism. The Keldysh parameters for single and double ionization of magnesium are shown in Table 4.2. For the majority of field strengths considered in this work all ionization should proceed above the Coulomb barrier and hence there exists no barrier for a tunneling mechanism. For an electric field of $1.3 \times 10^{13}$ W/cm$^2$ the field-free magnesium ground-state energy is equal to the saddle point of the combined Coulomb and laser potential, resulting in barrier suppression ionization (BSI). Scrinzi et al. later adapted the motion and response of the electron, along with BSI, and called it above the barrier ionization, or ABI [38].
<table>
<thead>
<tr>
<th>Multiphoton Ionization Process</th>
<th>Process Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mg}(3s^2) + 5\gamma \rightarrow \text{Mg}^+(3s) + e^-$</td>
<td>(1)</td>
</tr>
<tr>
<td>$\text{Mg}^+(3s) + 10\gamma \rightarrow \text{Mg}^{2+}[\text{Ne}]+ e^-$</td>
<td>(2)</td>
</tr>
<tr>
<td>$\text{Mg}(3s^2) + 15\gamma \rightarrow \text{Mg}^{2+}[\text{Ne}]+ 2e^-$</td>
<td>(3)</td>
</tr>
</tbody>
</table>

Table 4.1 Photon orders for three multiphoton ionization processes.

<table>
<thead>
<tr>
<th>Process Number</th>
<th>Intensity (W/cm²)</th>
<th>Keldysh Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$2 \times 10^{13}$</td>
<td>1.8</td>
</tr>
<tr>
<td>(1)</td>
<td>$1 \times 10^{14}$</td>
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<tr>
<td>(2)</td>
<td>$2 \times 10^{13}$</td>
<td>2.5</td>
</tr>
<tr>
<td>(2)</td>
<td>$1 \times 10^{14}$</td>
<td>1.1</td>
</tr>
<tr>
<td>(3)</td>
<td>$2 \times 10^{13}$</td>
<td>3.1</td>
</tr>
<tr>
<td>(3)</td>
<td>$1 \times 10^{14}$</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Table 4.2 Keldysh parameters for the MPI processes of table 4.1.

Thus, magnesium presents an interesting case where ionization cannot be clearly labeled by a single simple process. Upper limits of the ionization rate for ABI can be calculated using ADK rates [38] and are found to fall in the range of 370 to 1 fs⁻¹ for intensities from 1.3 to $6 \times 10^{13}$ W/cm². Although the coulomb barrier is greatly suppressed, the escape time for the electron is much longer than the optical period, and the quasi-static approximation fails. The dominant ionization mechanism should be multiphoton in nature for the lower intensities and possibly contain character of ABI at higher intensities.
The enhancement of doubly charged ions for intensities lower than the saturation intensity of the singly charged ion is generally referred to as nonsequential double ionization (NSDI) [31]. Ion yields are traditionally compared to calculated curves based upon ADK tunneling rates [20, 31, 32, 35, 39] that assume the atom is entirely without structure, and the electron tunnels through the suppressed coulomb barrier from the ground state of the neutral to the ground state of the ion. Sequential ADK ionization models do not predict any appreciable double ionization until the single ionization yield has reached its saturation intensity. Thus, any enhancement of the double ions above that predicted for a structureless atom has been referred to as "nonsequential" ionization.

A frequently used measure of nonsequential, or enhanced, double ionization is to plot the ratio of doubly charged ions to singly charged ions as a function of laser intensity [20, 32, 35, 36, 40]. Compared to the strong intensity dependence of observed ion yields the ratio of the double ion to the single ion in the enhanced, or nonsequential, region exhibits a low order dependence on peak laser intensity. The dramatic difference of their intensity dependence shows that the number of singly and doubly charged ions is relatively independent of each other and the precursor to the double ion is not the single ion. Figure 4.3 displays the ionic ratios for magnesium for both linear and circular polarization of the laser field.

Although the exact ionization mechanism may not be clear, it is possible to address the enhanced double ionization of magnesium using four possible mechanisms: first and second generation rescattering models, the population of intermediate states via multiphoton absorption, and shake-off/shake-up.
Rescattering has become an accepted mechanism responsible for observed enhanced double ion yields for helium [36, 41-43] and a contributing mechanism in the other noble gasses [35]. The theory is based on the dynamics of an electron driven by the laser field after being born into the continuum [44]. As the motion of the electron is governed mostly by the oscillating laser electric field it can reencounter its parent ion where an elastic or inelastic collision can take place. Elastic collisions are responsible for the production of high energy or "plateau" electrons, while inelastic collisions produce ionic excitations or possibly ionization, resulting in the observed enhanced double ionization. Theoretical calculations using the rescattering model predict a plateau, or extension of photoelectron spectra (PES) beyond the 2.5 $U_p$ cut-off predicted for
tunneling ionization in the absence of rescattering [45], where \( U_p \) is the ponderomotive energy. With rescattering, this plateau extends out to a cut-off energy of 10 \( U_p \) [45]. The model used by Lohr et al. [45] also predicts a MPI cut-off energy of 4.5 \( U_p \). Extensions of PES energies are frequently observed for He [32, 36, 40] and the noble gasses [33, 40, 46].

No significant extension of photoelectron energies is observed for magnesium, as illustrated in Figure 4.4 showing spectra of both magnesium and argon, measured using the same experimental system, laser intensity and pulse width. The ponderomotive energy for an intensity of \( 6.3 \times 10^{13} \) W/cm\(^2\) is 4 eV, giving a MPI cut-off at 18 eV and a rescattering cut-off at 40 eV, which agrees well with Mg and Ar PES, respectively. The plateau for argon is both calculated and observed [33] to be anomalously high compared to helium [32, 40] and neon [40] where they occur between 3 and 6 orders of magnitude below the signal of the first few ATI orders. It is possible that magnesium PES may have a plateau occurring at a level not detectable at this point. Furthermore, if the majority of rescattering events produced inelastic collisions, no high-energy signature would persist. Thus, while the data are suggestive of no rescattering, it cannot be ruled out completely.

In addition to hot-electron production, the rescattering model predicts a strong ellipticity dependence for double ionization. Generation of high-order harmonics, for example, is a phenomenon based on rescattering that relies upon the freed electron reencountering its parent ion. In 1993, Budil et al. observed that emission of harmonics is highly dependent upon the driving field ellipticity [47]. As laser ellipticity approached only 0.2, emission of harmonics dropped by two to three orders of magnitude. Only the slightest degree of ellipticity is required for the electron wave packet to be steered away
Figure 4.4 Observed PES for Ar and Mg using the same experimental system and intensity of $6.3 \times 10^{13}$ W/cm$^2$, with a pulse width of 120 fs.
from a direct collision with the ion [43]. Lohr et al. reported measurements of photoelectrons near the 10 $U_p$ cut-off for neon drop by 2 orders of magnitude for ellipticities between 0.3 and 0.4 [45]. Figure 4.5 shows a plot of ion yield measurements for magnesium as a function of the ellipticity of the laser field for LP intensities of 1.5, 2.9 and $5.0 \times 10^{13}$ W/cm$^2$. For these plots the total field energy is kept constant while the ellipticity of the field is adjusted. A strong dependence on the field ellipticity is observed for the double ion, but not comparable to that observed for helium and neon. In order for the double ion yield to drop by two orders of magnitude for a laser intensity on the lower end of the enhanced region an ellipticity of roughly 0.7, or greater, is required.

The fact that we measure a clear double ionization enhancement for CP raises interesting questions. The only other measurement showing this effect for CP is the recent work of Guo using the diatomic molecule NO [48]. Semi-classical trajectory calculations for the noble gases and CP show that the electron excursion is quite large [49]. We estimate a return impact parameter on the order of 6-7 atomic units with a wave packet spreading of about 6 a.u. A reasonable estimate of the size of the magnesium ion ground state is approximately 1-2 a.u. which could produce enough "soft" collisions with the returning electron to excite the ion to the $3p$ state. Ionization of the $3p$ ion proceeds with nearly the same rate as the neutral and thus gives an enhancement of the double ionization below the saturation of the single ionization process for CP.
Figure 4.5 Ellipticity dependence of singly and doubly charged Mg ions for LP intensities of (a) $5.0 \times 10^{13}$, (b) $2.9 \times 10^{13}$, and (c) $1.5 \times 10^{13}$ W/cm$^2$. The total field energy is held constant as the ellipticity is changed.
One shortfall of the first generation rescattering model to explain enhanced, or nonsequential, ionization is the assumption that the atom is completely without structure. The cut-off intensity for the laser field to provide enough energy to the freed electron in order to ionize the ion from the ground state is typically higher than the observed region of nonsequential ionization. Walker et al. reported this in the benchmark nonsequential experiment [32]. The cut-off intensity for magnesium and 800-nm photons would be $7 \times 10^{13}$ W/cm$^2$, which is also higher than the observed enhanced double ionization region.

Second generation rescattering theory models have not only incorporated collisional excitations of the ion into higher states allowing subsequent ionization via a lower order process [42], but also include Coulomb focusing, or trapping, of the oscillating free electron by the Coulomb potential well of the ion [36]. The former model improved the agreement between experiment and calculation for Kr, Xe [37], and Ar [35], but still falls up to a couple orders of magnitude lower than measured ratios of the single to double ion. The latter model allowed for excellent agreement for He [36]. Although, at this time the ellipticity dependence for these models is unknown, their collision-based principles exclude them as dominant enhanced ionization mechanisms for circular and near-circular fields.

Population of intermediate states via multiphoton absorption must be considered as a probable dominant mechanism for magnesium with 800-nm light. Magnesium has a very rich electronic structure as illustrated in Figure 4.6. For linearly polarized light the number of parity allowed transitions, and subsequent ionization paths through intermediate states is considerably large. Table 4.3 indicates some of the stronger
Figure 4.6 Energy level diagram for Mg and Mg$^+$ including some known doubly-excited auto-ionizing states.
<table>
<thead>
<tr>
<th>Transition</th>
<th>Photon Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(3s^2) → 3s3p</td>
<td>3</td>
</tr>
<tr>
<td>Mg3s3p → 3s3d</td>
<td>1</td>
</tr>
<tr>
<td>Mg^+3s → 3p</td>
<td>3</td>
</tr>
<tr>
<td>Mg^+3p → 4s or 3d</td>
<td>3</td>
</tr>
<tr>
<td>Mg^+4s → 4p</td>
<td>1</td>
</tr>
<tr>
<td>Mg^+4p → 5s or 4d</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4.3 List of some transitions near integer photon energies apart.

possible transitions that are near integer photon energies apart. If any of the lower ionic excited states are significantly populated then the new effective ionization limit, and photon orders necessary to ionize them, becomes comparable to that of the neutral. Ionization from the 3p ionic state requires 10.6 eV, from the 4s 6.4 eV, and from the 3d state 6.2 eV. Ionization rates of excited ions would then be similar to that of neutral magnesium atoms. Subsequently, the observed ionization yields for singly and doubly charged ions would have similar slopes forcing a plot of their ratio to flatten out.

The importance of including the rich atomic structure of magnesium when considering enhanced double ionization was made evident by the investigation of Trainham et al. [50] for a "direct" channel for NSDI of magnesium. Their investigation led them to believe that isolated core excitation (ICE) and non-resonant multiphoton
transitions would lead to low-lying excited states of the ion and doubly excited autoionizing states and not a direct channel. As mentioned above, excited ions would have similar ionization rates and intensity dependences to that of neutrals. Xenakis et al. [51] observed a less pronounced enhancement of double ionization of magnesium for LP light using 400-nm photons and attributed the enhancement to atomic structure, or resonances and channel closings.

Magnesium atoms exposed to 800-nm circularly polarized light essentially look like structureless atoms. For ionization of the neutral, there are virtually no accessible excited states due to angular momentum selection rules. The only available states are $6h$ and higher angular momentum states. Such states would be Rydberg states ponderomotively shifted into resonance with five or six photons. For ionization of the ion, the states would have to have an angular momentum of 10 or higher. All of these states of the neutral and the ion reside very close to their respective ionization limits. Thus, all of the probable ionization paths through intermediate states available for LP are essentially closed for CP. As the polarization changes from linear to circular, the number of accessible intermediate states falls off slowly at first. Thus, an ellipticity dependence for multiphoton transitions is expected to be less severe than for the rescattering case.

Finally, it is possible for the rapid departure of the first electron to create a change in the potential for the remaining electron that is sufficient to shake it into excited ionic states. As pointed out earlier, any ionic excitation reduces the effective ionization order for the ion to that of the neutral. Shakeup is a well-known phenomenon in the alkaline earth atoms [52] and in single photon x-ray excitation of atoms [53]. Shakeup exhibits no
strong ellipticity dependence and hence does not preclude the production of enhanced double ionization for circular polarization.

4.5 Conclusion

We have measured single and double ionization yields for magnesium using 800-nm intense laser light and both linear and circular polarization. Enhanced double ionization is observed for both linear and circular polarization. It is not clear that conventional rescattering theory can explain the ellipticity dependence of the data and quantitative calculations must be performed. The persistence of enhanced double ionization for circular polarization contradicts simple rescattering theories and opens the possibility for studying other ionization mechanisms.
CHAPTER 5

INTENSITY DEPENDENCE OF MAGNESIUM PHOTOELECTRON SPECTRA

5.1 Introduction

Photoelectron spectra (PES) have been used quite extensively over the past 20 years as a tool to investigate what actually happens when matter is irradiated with high-intensity light. In the earlier days the pulse widths of lasers were long with respect to the time it takes the ionized electron to leave the interaction region. PES for this long pulse regime yielded structureless peaks separated by a photon order revealing little information about the ionization dynamics other than the number of photons the electron absorbed and the relative probabilities for each order [11]. In 1986, Freeman et al. reported that as the laser pulse width is decreased, the peak of each ATI order shifted slightly to lower energies and broke apart into sets of structured peaks [11]. The peaks in the PES correspond to population of specific atomic states during the ionization process and became known as Freeman resonances. The ability of shorter laser pulses to observe atomic transitions during the ionization process opened up the door for a whole new field of study in high-intensity laser-atom interactions.
Historically, the majority of high-intensity PES have been taken with a noble gas as the target atom [11, 33, 46, 54-59], and have yielded similar overall results. The overall characteristics of a noble gas PES fall into four different categories. (1) The kinetic energies of the ejected electrons have a smooth, continuous background distribution. (2) On top of the continuous background are groups of ATI peaks separated by the photon energy, and each having some sort of sub-structure. (3) The signal of (1) and (2) first decreases logarithmically for higher and higher kinetic energies, and finally, (4), the distribution of kinetic energies has a "plateau" or extension beyond that of (3), where the detected photoelectron signal levels off, or decreases much more slowly as a function of higher kinetic energies. An illustration of these four characteristics is displayed in Figure 5.1, a PES for argon collected for 800-nm, 120-fs pulses with a peak intensity of $10^{14}$ W/cm$^2$. All of these characteristics have been explained and theoretically modeled using single active electron, and rescattering theories. Comparisons of experimental results and theoretical data [33, 58] indicate that for atoms with a closed outer shell only one electron interacts with the laser field at a time, and no evidence is seen for non-ponderomotively shifted states, or doubly excited states in the PES.

In this chapter we present high-resolution photoelectron spectra for magnesium atoms exposed to 800-nm, 120-fs laser pulses, with peak intensities of $10^{12}$ to $10^{13}$ W/cm$^2$. To the best of our knowledge, these are the first reported results of high-resolution photoelectron data for magnesium atoms irradiated by laser light of these characteristics. The data reveal some of the expected behaviors of ATI PES for lower intensities, as well as some interesting peculiarities for higher intensities that are not
easily explained by traditional ATI theories. These variations of PES from previous ATI experiments will be presented and discussed.

![Illustration of the four features of PES for argon atoms exposed to a laser intensity of $10^{14}$ W/cm$^2$. (1) Continuous background of photoelectrons, (2) repeating sets of structured peaks separated by the photon energy, (3) monotonic decrease for higher orders, and (4) plateau or extension of high-energy photoelectrons.]

**Figure 5.1** Illustration of the four features of PES for argon atoms exposed to a laser intensity of $10^{14}$ W/cm$^2$. (1) Continuous background of photoelectrons, (2) repeating sets of structured peaks separated by the photon energy, (3) monotonic decrease for higher orders, and (4) plateau or extension of high-energy photoelectrons.

### 5.2 Experiment

The laser system and general experimental setup used in this investigation is the same as that described previously [21]. The laser is focused into the vacuum chamber via a 250 mm focal length lens with an initial beam diameter of roughly 7 mm. The laser beam propagation, atomic beam path, and flight tube path are all mutually orthogonal. The interaction region used to collect the photoelectron data is located between a pinhole
plate and the open end of the flight tube. Due to collimating apertures the width of the atomic beam in this region is 2 mm. Using this focal geometry, and 800-nm light the Rayleigh range is about 1.5 cm. Even though the width of the interaction region exposed to the detector is larger than previous experiments [21, 33, 34, 46, 54], the condition that the interaction region exposed to the detector is much smaller than the Rayleigh range is still satisfied in order to be considered a restricted volume experiment. The flight path between the interaction region and the micro-channel plates (MCPs) is 49.5 cm, and the flight tube is grounded and wrapped with multiple layers of high magnetic susceptibility μ-metal to ensure that the flight path of the electrons is free of any residual electrical or magnetic fields, enabling the detection of low kinetic energy electrons. Just prior to impacting the MCPs the electrons are accelerated through an additional 900 V over a distance of 2 mm. The final accelerating potential reduces the difference in kinetic energy between a 1 eV electron and a 20 eV electron to only 2%, ensuring that the quantum efficiency of the MCPs is relatively constant over the kinetic energy range of photoelectrons detected in this work.

The photoelectron spectra were collected by measuring the time difference between the laser pulse exiting the laser and the detection of each count by the MCPs. The time data are then converted to kinetic energy and the signal is normalized to 10^6 laser shots per spectrum. Up to 15 x 10^6 laser shots were taken per spectrum.

5.3 Results and Discussion

A sample PES for magnesium atoms exposed to a laser intensity of 33 TW/cm² is displayed in figure 5.2. Upon inspection of figure 5.2 and comparison to figure 5.1, only
three of the four characteristics, discussed in the previous section for PES for argon and other noble gasses, are present in the PES for magnesium. (1) The foundation of a smooth and continuous distribution of kinetic energies for the photoelectrons is evident from very low energies out to around 15 eV, where the signal begins to degrade into the noise level. (2) Structured sets of peaks are arranged throughout the PES and separated by the energy of a single photon, 1.55 eV, and (3) there is a monotonic decrease in the signal of detected photoelectrons as a function of higher and higher kinetic energy. In this section we will first discuss the general characteristics of photoelectron spectra of magnesium: the monotonic decrease in signal characteristic, and the apparent lack of a photoelectron plateau extension. Then we will conclude with a discussion of the structured peaks within the first few orders.

5.3.1 General PES Characteristics

Results from both observed and calculated PES reveal that, for any element, the number of counts or kinetic energy probability for characteristic (3) should decrease monotonically from one order to the next higher order. The exact rate and cut-off kinetic energy can depend upon a large number of different parameters and variables, including the target element, laser frequency, peak intensity, dominant ionization mechanism, signal to noise ratio, etc. The effects of the first three noted physical parameters on the ionization process are all somewhat intertwined. If the energy per photon is small
Figure 5.2 Photoelectron spectrum for magnesium atoms exposed to a laser intensity of 33 TW/cm².
compared to the binding energy of the ground state of the element, and the distortion of
the coulomb potential due to the peak field intensity is small with respect to the depth of
the ground state then multiphoton ionization is considered to be the dominant ionization
mechanism. As the distortion of the coulomb potential becomes non-negligible with
respect to the depth of the ground state, and the tunneling time becomes comparable to
the optical cycle time then tunneling ionization takes over and becomes the dominant
mechanism. For experiments in the multiphoton and tunneling regimes it is more
convenient to discuss the combined effects of the laser frequency and the peak field
intensity by using the ponderomotive energy, $U_p$, where $U_p = I/4\omega^2$ in atomic units.

As discussed in section 2.7, the tunneling model is a semi-classical ionization
model. First, the coulomb barrier observed by the electron is distorted such that the
energy level of the ground state is both bound, near the core, and unbound some distance
away. Thus, a quantum mechanical barrier exists through which the wave function of the
electron can tunnel. The wave function that escapes is then treated as a classically free
charged particle in an oscillating electric field. Depending upon the phase of the laser
field at the time of ionization, the electron can escape from the core with a kinetic energy
up to 2.5 $U_p$ [60]. Lohr et al. also predicted the maximum kinetic energy for an electron
ionized via multiphoton absorption, which appears in the continuum at the position of the
core with some initial kinetic energy, to be 4.5 $U_p$ [60]. Experimental observation of a
predicted PES cut-off is not as straightforward as it might first appear. If the signal to
noise ratio is not high enough, the higher kinetic energy electrons can physically be
present but lie beneath the floor of the noise and not be detected. If the signal to noise
ratio is high enough, or the decreasing rate of probability between the lowest and highest
kinetic energy is low enough, electrons with kinetic energies up to and beyond the predicted cut-off can be detected. Due to the quantum mechanical nature of atomic ionization, a sharp classically predicted cut-off does not exist, but rather a more gradual and broad cut-off in the probability or signal exists. Thus, identifying a precise cut-off on a PES can be slightly subjective.

The location and rate of the photoelectron plateau region, characteristic (4), is discussed in section 4.3. Generally, if rescattering is the dominant ionization mechanism a cut-off of 10 U_p is expected for the plateau region of the photoelectron spectrum. Thus, after the monotonic decrease in counts per ATI order a much "flatter" region of the kinetic energy of the photoelectrons with a significantly lower fall-off rate from one order to the next is expected. After a kinetic energy of 10 U_p, the number of counts per ATI order will once again decrease more quickly. The degree of the gentler fall-off rate in the plateau region can vary dramatically from one element to another. For some elements, such as argon [33], the number of counts per order can actually increase by almost an order of magnitude for higher kinetic energies within the plateau. Other elements such as helium [32, 61], neon [61], and xenon [54] tend to have generally flatter plateau regions.

No extension of photoelectron energies is observed for magnesium, as can be seen in figure 5.2. Although at first glance it appears that PES for magnesium completely lacks a plateau region, it may be possible that magnesium PES actually does have a plateau region for two separate cases. First, the fall-off rate from order to order in the plateau may be much closer to the initial fall-off region, and consequently indistinguishable from, characteristic (3). Second, the plateau photoelectrons may physically be there, but reside below the noise floor. Between the two possible cases, the latter is less likely as longer
data runs of up to 20 million laser shots have been conducted, where the signal to noise ratio is on the order of $10^5$ to $10^6$, for intensities below 60 TW/cm$^2$, and no significant plateau region has been observed. It has also been discussed in chapter 4 and shown [21], based on ionization rate ellipticity studies, that rescattering does not appear to be as dominant an ionization mechanism for magnesium as it is for the noble gasses; for which case a much smaller, if any, plateau region would be expected due to electron rescattering.

For the PES in figure 5.2 the ponderomotive potential is 2 eV, and the PES begins to fade into the noise around 13 to 16 eV. Thus, a soft cut-off threshold can be said to occur around 6 to 7 $U_p$. A cut-off value of this value illustrates that high-intensity photoionization of magnesium is not easily categorized as either multiphoton or tunneling/rescattering.

It should be noted here that as the intensity is continually increased, a plateau region is observed for magnesium for very high intensities as illustrated in figure 5.3. As discussed in section 4.3, results of ion yield investigations show that for intensities above $1 \times 10^{14}$ W/cm$^2$ the relative population of the second ionic species of magnesium is larger after the laser pulse has passed by than that of the first ionic species, and photoionization in the interaction region becomes dominated by the photoionization of Mg$^+$. The ionization limit of Mg$^+$ is 15.035 eV, comparable to that of argon, 15.759 eV, and the core which the Mg$^+$ electron interacts with is that of neon. Since the ionization dynamics of Mg$^+$ are qualitatively similar to photoionization of argon and neon we would then expect to see a plateau extension for photoionization of Mg$^+$, as observed in figure 5.3.
Figure 5.3 PES for magnesium for much higher intensities, units are in W/cm². Above an intensity of $1 \times 10^{14}$ W/cm², the interaction region is dominated by Mg⁺.

Some recent theoretical investigations have been able to explain the plateau extension using zero or short-range potentials and attribute the enhancement to the presence of channel closures for specific intensities [62, 63], instead of rescattering. According to these investigations, the high-energy enhancement of the plateau region of photoelectron kinetic energies is attributed to a dramatic increase in the probability of ionization through higher order channels when a lower order channel closing occurs. As the intensity of the laser is increased in Bogdan et al.'s calculation and a channel closing is crossed, the ionization probabilities through numerous higher order ionization channels approach the same value [62]. If we were to apply the results and principles of these models to the photoionization of magnesium we would still not expect to see any significant enhancement of higher-energy photoelectrons. For the intensities used
throughout most of this investigation only one channel closing occurs, the 5-photon transition from the ground state to the continuum. Although a channel closing does occur, the intensity threshold for the n=5 channel closing is 1.7 TW/cm² which is below our signal sensitivity threshold, and consequently undetectable. There is also a fundamental reason why the results of these theoretical investigations are not entirely applicable to the photoionization of an alkaline earth element. The zero and short-range potentials used for these experiments support either no bound states [62] or only a single bound state [63]. As will be discussed in the next section, population of excited states in magnesium plays a significant role in the ionization process.

5.3.2 Resonance Structure Within the First and Second ATI Order

For intensities in the $10^{12}$ to $10^{13}$ W/cm² range, ionization from excited states is clearly evident as a significant, if not a dominant, mechanism. Photoelectron data obtained in these investigations illustrates that population of excited states via Freeman resonances and subsequent ionization is a very strong mechanism in the response of magnesium atoms to high-intensity laser light. Figure 5.4 is a graph of numerous low kinetic energy intensity scans of PES collected for magnesium from 3 to 33 TW/cm². Note that even on a logarithmic scale, the height and width of the resonance peaks indicates that a significant number of the photoionized electrons are originating from atomic states other than the ground state. For the lower intensities, the ATI peaks are
structureless and appear to shift slightly to lower energies as the intensity is increased up to where the maximum signal of the MPI order is about 2,000. Below this intensity, each ATI peak is composed of unresolved high-lying Rydberg states, which are ponderomotively shifted into resonance with a 5-photon transition from the ground state. The apparent shifting of the structureless peak to lower kinetic energies is actually more and more unresolved Rydberg states coming into resonance as the 5-photon maximal ponderomotive probing depth (MPPD) probes deeper and deeper into the tightly spaced high-lying Rydberg states. These states appear on the lower kinetic energy side of the ATI peak and continue to grow in size and number as the intensity is increased, resulting in the illusion of a shifting, structureless ATI peak.

The MPPD is illustrated in figure 5.5, a theoretical calculation of the time-dependent levels of the $f$ states of magnesium and the ionization potential. This model assumes that all of the $f$ states shift ponderomotively with the laser intensity. The calculation for figure 5.5 assumes a peak intensity of 15 TW/cm$^2$, and that the temporal profile of the laser pulse is Gaussian with a FWHM of 120 fs. The 5-Photon MPPD is the maximum depth to which the 5-photon energy, with respect to the ground state, drops into the bound energies of the atom, or

$$5\gamma, \quad MPPD = \left[ U_p - (5\hbar\omega - IP_o) \right], \quad (5.1)$$

where $IP_o$ is the field-free ionization potential.

If all of the $f$ series states shift ponderomotively then for a peak intensity of 15 TW/cm$^2$ we would expect that all of the $f$ states will be populated except for the lowest, $4f$, because the MPPD does not probe deeply enough into the atoms to bring the $4f$ state into resonance with a 5-photon transition, as observed in figure 5.5.
Figure 5.5 Illustration of the 5-photon maximum ponderomotive probing depth (MPPD) for a peak intensity of 15 TW/cm$^2$.

Further qualitative inspection of figure 5.4 reveals that as the intensity is increased, and the MPPD probes deeper and deeper into the bound states, more and more resolvable excited atomic states are becoming populated and subsequently ionizing in the laser field leaving their signatures on the PES in the form of resolved peaks with different kinetic energies. In order to be a little more quantitative, the PES of figure 5.4 are separated and displayed in groups of 3 to 4 different intensities in figures 5.6 and 5.7.

Figures 5.6 and 5.7 are expanded views of the first and second ATI orders. The thick solid black vertical lines located at 3.1 and 4.65 eV correspond to the energies of
two and three photons above the ionization threshold barrier, respectively. In addition, figures 5.6 and 5.7 have the MPPDs for each intensity displayed on the same graph as vertical lines with the same shade of gray as their corresponding PES. Any bound states that are populated and subsequently ionized by one photon more than necessary will show up as peaks to the lower kinetic energy side of the vertical black line located at 3.1 eV. If a populated state is ionized by absorbing two photons more than necessary it will show up to the lower kinetic energy side of the line located at 4.65 eV. For the graphs in figures 5.6 and 5.7 we can see that as the intensity and the ponderomotive potential increases, the MPPD probes and populates more deeply bound atomic states. If a state is ponderomotively shifted, its signature in the PES will turn on just as, or just after, the MPPD passes that kinetic energy value. Thus, for ponderomotively shifted states we would expect to observe ionization signatures in the PES only to the right of the MPPD vertical line, and left of the energy limit for that order.

All of the graphs of figures 5.6 and 5.7 are displayed with a linear vertical scale except for figure 5.6 (a). The signal rate as a function of decreasing intensity drops off very rapidly for these lower intensities. For intensities below 6.6 TW/cm² the ATI PES are composed of unresolved high-lying Rydberg states. Once a peak intensity of 7 to 8 TW/cm² is reached the MPPD begins to probe bound states that are far enough apart in energy to be resolved in the PES. In figure 5.7 it can be observed that after an intensity of about 20 TW/cm² no additional peaks appear in the ATI PES as the intensity is increased, but some do continue to grow.
Figure 5.6 Mg PES for intensities for (a) 4.6, 5.3, 5.9 (b) 6.6, 7.3, 7.9, (c) 8.6, 9.2, 9.9, (d) 10.6, 11.2, and 11.9 TW/cm², and each of the corresponding 5-photon MPPDs. The thick dark lines at 3.1 and 4.65 eV are the energies of IP plus 2 and 3 photons, respectively.
Figure 5.7 Mg PES for intensities for (a) 12.5, 13.2, 14.5 (b) 15.8, 17.2, 18.5, 19.8, (c) 21.1, 22.4, 23.8, (d) 25.1, 26.4 and 28 TW/cm$^2$, and each of the corresponding 5-photon MPPDs. The thick dark lines at 3.1 and 4.65 eV are the energies of IP plus 2 and 3 photons, respectively.
After observing the population and subsequent ionization of bound atomic states, the next course of action is to attempt to identify *which* states are being populated. The first step taken in this investigation is to identify the parity of the states that we would expect to be populated, given angular momentum selection rules. Since these Freeman resonances are occurring for a 5-photon transition from the ground state, we generally would expect that the states being populated have an odd parity, limiting the possibilities to \( p, f \), or \( h \) states. Using equation 2.17 we can calculate where in the PES we would expect to see a peak for electrons that are photoionized from a particular ponderomotively shifted state, or

\[
KE = m\hbar \omega - E_b ,
\]

where \( E_b \) is the binding energy of the chosen state, and \( m \) is the number of photons absorbed.

The series whose expected kinetic energies best match with the observed states are those of the \( p/f \) series. Within the energy resolution width of 0.015 eV, due to the bandwidth of the laser, the \( p \) and \( f \) series energies are indistinguishable from each other. The fits of the \( f \) series and the obtained PES for the first two ATI orders are illustrated in figure 5.8.

For intensities below 10 TW/cm\(^2\), both ATI orders have similar peaks originating from \( 6f \) and higher resonantly populated states, exhibiting threshold and growth characteristics expected from weakly bound, ponderomotively shifted states. For intensities above 10 TW/cm\(^2\), some unexpected peculiarities arise in the photoelectron
Figure 5.8 First and second ATI orders with the expected kinetic energies for $f$-series states populated by Freeman resonances and subsequent ionization.
spectra that are not easily explainable using basic ATI theory. For the first ATI order, all of the peaks that do appear have turn-on intensities as would be expected for ponderomotively-shifted states. Even so, there are a couple of unexpected characteristics. First, a peak appears with an energy of 2.64 eV that does not correspond to a \( p/f \) state. A corresponding state appears in the second ATI order with an energy of 4.18 eV. For the first ATI order the peak remains there for all higher intensities. For the second ATI order, the shoulder of another peak for intensities above 19 TW/cm\(^2\) overruns the peak at 4.18 eV. This anomalous peak has the same energy that would be expected of a ponderomotively-shifted d-state as illustrated in figure 5.9. But, the fact remains that there should be no even number photon resonance that could possibly populate a 6\( d \) state.

The very broad peak with an energy of 2.1 to 2.4 eV in the first ATI order, and 3.65 to 3.9 eV in the second ATI order appears to possibly be composed of 2 closely spaced, broad peaks. The higher-energy side of this structure appears to turn on around 14 to 15 TW/cm\(^2\), with kinetic energies of 2.34 and 3.84 eV, while the lower-energy side appears to turn on around 17 TW/cm\(^2\). In the first ATI order these two peaks are resolvable in the intensity range of 17 to 20 eV. The lower-energy side of this structure overlaps with the expected kinetic energies of photoelectrons originating from a 4 \( p/f \) state, while the higher kinetic energy side does not correspond to any ponderomotively shifted state.
Figure 5.9  First and second ATI orders with the expected kinetic energies for $d$ series states populated by Freeman resonances and subsequent ionization.
In addition to the peculiar PES results mentioned above, the second order ATI spectrum has some additional unexpected results. A peak appears with a kinetic energy of 3.98 eV, and does not have a counterpart in the first ATI order. This peak is seen in figures 5.8 and 5.9 and coincidentally overlapped with the 5d energy line. A counterpart in the first ATI order would have an energy of 2.43 eV, where there is actually a minimum in the PES. The appearance of a feature in one ATI order and not in another is not explained by basic ATI theory. Basic ATI theory cannot explain why a bound state populated by a resonant transition would subsequently ionize by absorbing only three more photons, and not ionize by absorbing two more photons. Thus the possibility that this energy peak originates from a resonantly populated bound state that subsequently ionizes via a higher order process, but not a lower order process, is very unlikely.

Two methods will be presented and discussed in the next section, which will aid in the identification of the particular states that are being populated and subsequently ionized, and their threshold intensities. A partial yield (PY) graph is an ionization yield graph for a particular range of electron kinetic energies, a technique which helps identify the threshold intensity for a particular ionization process. Angular distributions (ADs) are an analysis of the ejection angles of the electrons from the interaction region, and lend insight into the shape of the atomic state from which the electron was ionized. All of the peaks discussed so far are further analyzed in section 5.3.3 using partial yields and angular distributions.

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5.3.3 Partial Yields and Angular Distributions

In section 5.3.2 we observed that numerous excited states are populated and subsequently ionized by the applied laser field. As the laser intensity is increased the MPPD increases as well and more and more deeply bound states are tuned into resonance. A first-pass analysis of the data, based upon angular momentum selection rules, indicates that the states being populated are of an odd-parity and most likely \( p \) or \( f \) states. By simply matching up the expected kinetic energies observed with those expected for either a \( p \) or \( f \), it could not be determined whether the electrons originated from a Freeman resonance to a \( p \) or an \( f \) state due to the overlap of the energies of these two atomic series. In this section we will present two methods for (1) better identification the threshold necessary to initiate the Freeman resonance, and (2) better identification of the parity and angular momentum of the state from which the electron ionized.

A partial yield (PY) is a data analysis method where only a small range of the photoelectron kinetic energies is integrated within a single PES. The integration is then repeated for a variety of peak laser intensities, and the resulting PY is displayed as the number of integrated counts per PES as a function of the peak laser intensity. By observing the change in counts as a function of peak laser intensity the threshold intensity for a given resonant process can be more quantitatively identified than by simple inspection of multiple PES displayed on the same graph. An expected PY curve for a single ionization channel, using a restricted laser-atom interaction volume, has similar characteristics as those discussed for a tunneling ionization process in section 2.9, using a restricted volume. The yield does not appreciably grow until the threshold intensity is
reached. Once the threshold intensity is reached, the rate of ionization through that channel increases rapidly until saturation where the rate of increase of signal levels out, as the Gaussian volume does not continue to grow for increasing peak intensities. The Gaussian ionization volume, for a particular process, adopts the shape of an annulus whose inner and outer radii increase with increasing intensity such that the total volume remains constant.

Angular distribution (AD) plots have been used for nearly 10 years to aid in the interpretation of PES collected for strong field ionization of atoms. Much of the interpretation of the results have been to identify high probability scattering angles, or "jets", as the ionized electron scatters off of the core during its motion in the laser field [54, 64, 65]. It was observed that as the laser field drives the electron it has the highest propensity to scatter off of the core at angles of 30° and 45°. The observation of the scattering angles for select regions of the kinetic energies of ejected electrons was yet another supporting argument that the plateau extension observed in the photoelectron spectra for the noble gasses is a result of a rescattering mechanism. The scattering jets for xenon are most pronounced for electrons with energies of 8 to 10 $U_p$ [54, 65]. The earlier investigations were unable to resolve the structure within each ATI order, which results in an AD that is averaged over an entire ATI order, while a later investigation by Nandor et al. [54] illustrated that within each order the appearance of the ADs can vary quite remarkably.

Although AD plots have been used to identify rescattering mechanisms, they have also been used to help identify the angular momenta carried away by the electron as it is ionized and the parity of its last state, for lower ATI orders [54, 66, 67].
The fact that the observed angular distributions can both be a measure of the angular momentum of the last state of the electron, and the angular scattering probability of a free electron scattering off of its parent ion, reduces the absolute validity of claiming either one. Nevertheless, considering which ionization processes are dominant, and what region of kinetic energies is being studied the uncertainty of interpreting ADs can be reduced. If the dominant ionization process is multiphoton in nature, then the angular momentum carried away by the electron will also be multiphoton in nature. For this case, the ADs will more likely be a reflection of the angular momentum of the last state of the electron. Since higher energy electrons are produced predominantly by a rescattering mechanism, the angular distributions for higher kinetic energies will reflect the angular scattering probability. This assumption holds especially true for photoelectrons whose kinetic energies fall with the plateau region [54, 64, 65].

For low kinetic energy electrons and multiphoton processes, ADs can reveal properties of the last state of the electron. The last state of an ionized electron is a virtual state located somewhere in the continuum. As an example let us consider an electron that is excited through a $5f$ state of the atom. For the MPI order the electron will absorb one more photon, exciting it into an unbound $d$ or $g$ state carrying away with it an angular momentum of $l = 2$ or 4. Thus, for this simplistic case, we would expect the AD to reflect a superposition of $d$ and $g$ angular probability distributions.

Figures 5.10, 5.11, and 5.12 are a collection of PES, PYs, and ADs for the high-lying Rydberg states with kinetic energies above 2.7 eV and 4.2 eV in the first and second ATI orders, respectively. These figures are organized into two columns, with the left column displaying data for the first ATI order and the right column displaying data
for the corresponding energy range in the second ATI order. In each column the energy range of interest is displayed in the top PES graph. A select few intensities are displayed in each PES to illustrate the general trends of the photoelectron spectral dependence upon the peak laser intensity. The middle graph of each column is a PY plot of the integration of that energy range as a function of peak laser intensity. The two vertical lines in the PY represent the threshold intensities for the MPPD to populate states whose binding energies would result in ionized photoelectrons with kinetic energies that correspond to the maximum and minimum energies of the energy range of interest. The bottom graph for each column is the AD data for the chosen energy range. The angular distributions are collected for a peak field intensity of 23 TW/cm². Each point on the AD is an integration of the chosen range of kinetic energies, for a particular orientation of the laser field with respect to the flight path. Since the parity of the final state of the electron is expected to be either even or odd, the AD data are normally fit with a sum of either even or odd Legendre polynomials. The fits of the Legendre polynomials serve a dual purpose. First, the fits allow for a nice smooth representation of the AD data, and second the coefficients of the fits can aid in the identification of the angular momentum of the possible final states.
Figure 5.10 PES showing the integration used in the PYs and ADs, for 2.88 and 4.42 eV. The MPPD threshold intensities for the maximum and minimum energy values are displayed on the PY plots.
Figure 5.11 PES showing the integration used in the PYs and ADs, for 2.82 and 4.36 eV. The MPPD threshold intensities for the maximum and minimum energy values are displayed on the PY plots.
Figure 5.12  PES showing the integration used in the PYs and ADs, for 2.74 and 4.28 eV. The MPPD threshold intensities for the maximum and minimum energy values are displayed on the PY plots.
For all three of these figures, an inspection of the PYs reveal that the increase in the integrated number of counts as a function of peak intensity correlates well with the expected turn on threshold for ponderomotively shifted states. The recorded number of counts for the chosen energy ranges does not significantly increase until the threshold intensity is reached in order to ponderomotively shift the state into a 5-photon Freeman resonance. The ADs for the first order illustrate three distinct lobes per quadrant. The highest count rate is observed for the orientation of 0°, or parallel to the flight path, and two more maxima located at 36° and 70°. At an angle of 90°, a minimum is observed as would be expected for a superposition of various odd states. Although a minimum is observed for a 90° orientation between the laser field and the flight path, the count rate still does not go to zero. The best fit of the data (mainly to correct for a non-zero count rate for ±90°) was found to be one that included a sum of even Legendre polynomials with a weighting factor of 1 to 0.1 between the odd and even coefficients, respectively.

The PYs and ADs for the other two observed f states, the 4f and the 5f, are displayed in figures 5.13, and 5.14. The observed threshold intensities for ionization through the 4f and 5f states do not exhibit as sharp a turn on as that observed for the higher f states, but still agree with the calculated threshold for ponderomotively shifting states. Table 5.1 summarizes the resonant state, threshold intensity and kinetic energy for above threshold ionization from that state, for all of the states studied in figures 5.10 through 5.14.

Ion yield measurements discussed in chapter 4 indicate that for the peak field intensity used to collect the ADs, 23 TW/cm², roughly 10 to 20% of the ions detected are doubly charged ions. If a singly charged ion is present in the interaction region it will be
Figure 5.13  PES showing the integration used in the PYs and ADs, for 2.54 and 4.08 eV. The MPPD threshold intensities for the maximum and minimum energy values are displayed on the PY plots.
Figure 5.14  PES showing the integration used in the PYs and ADs, for 2.26 and 3.78 eV. The MPPD threshold intensities for the maximum and minimum energy values are displayed on the PY plots.
ponderomotively shifted through an even parity state and subsequently ionize. If the ion is originally in its ground state and encounters a 10-photon Freeman resonance it will ionize from an even parity state. A calculation performed by Xenakis et al. [51] for magnesium atoms exposed to similar laser pulses using 400 nm predicted that photoionization from Mg(3s)$^2$ to Mg$^+$$3p$ is a non-negligible process. Even if a significant percent of the Mg$^+$ ions are created in the first excited state, they will encounter a 7-photon Freeman resonance from an odd-parity state to an even-parity state and subsequently ionize. Thus, a mixture of 1 to 0.1 of odd and even coefficients of Legendre polynomial coefficients for the fits to the AD data is justifiable, and an accurate representation of the different ionic species produced. Figure 5.15 is an illustration of the two ionization channels for the singly charged ion discussed. The ground state of the ion will encounter a 10-photon Freeman resonance to an even parity state and then subsequently ionize, and the Mg$^+$$3p$ state will encounter a 7-photon resonance to an even parity state and subsequently ionize, as well.

For all of the numerical fits to the observed data, the largest coefficients indicate that the most significant angular momentum contributions have values of $l = 1$, 3, and 5 for the first ATI order, and $l = 0$, 2, 4, and 6 for the second ATI order. Table 5.2 is a summary of the odd Legendre polynomial coefficients used for the fits of the angular distributions for the first ATI order peaks analyzed in figures 5.10 through 5.14. The observed number of AD lobes, and the results of fits using Legendre polynomials both indicate that the dominant initial states populated via a Freeman resonance must be those of an $f$ states.
Figure 5.15 Illustration of two ionization paths for the singly charged ion: through a 10-photon resonant transition from the ground state, or a 7-photon transition from the 3p state, to ponderomotively shifted even parity states, and subsequent ionization.
<table>
<thead>
<tr>
<th>State</th>
<th>Threshold Intensity (TW/cm²)</th>
<th>Kinetic Energy First ATI (eV)</th>
<th>Kinetic Energy Second ATI (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8f$</td>
<td>5.4</td>
<td>2.88</td>
<td>4.42</td>
</tr>
<tr>
<td>$7f$</td>
<td>6.5</td>
<td>2.82</td>
<td>4.36</td>
</tr>
<tr>
<td>$6f$</td>
<td>8.1</td>
<td>2.73</td>
<td>4.27</td>
</tr>
<tr>
<td>$5f$</td>
<td>11.0</td>
<td>2.54</td>
<td>4.09</td>
</tr>
<tr>
<td>$4f$</td>
<td>16.3</td>
<td>2.24</td>
<td>3.78</td>
</tr>
</tbody>
</table>

Table 5.1 Summary of the states populated via a 5-photon Freeman resonance from the ground state, the resonant threshold intensity, and observed kinetic energies for the first and second ATI orders.

<table>
<thead>
<tr>
<th>State</th>
<th>$l = 1$ Coeff.</th>
<th>$l = 3$ Coeff.</th>
<th>$l = 5$ Coeff.</th>
<th>$l = 7$ Coeff.</th>
<th>$l = 9$ Coeff.</th>
<th>$l = 11$ Coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8f$</td>
<td>0.63</td>
<td>0.38</td>
<td>0.56</td>
<td>0.18</td>
<td>0.27</td>
<td>0.19</td>
</tr>
<tr>
<td>$7f$</td>
<td>0.61</td>
<td>0.11</td>
<td>0.77</td>
<td>0.01</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>$6f$</td>
<td>0.56</td>
<td>0.10</td>
<td>0.78</td>
<td>0.18</td>
<td>0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>$5f$</td>
<td>0.27</td>
<td>0.13</td>
<td>0.89</td>
<td>0.29</td>
<td>0.14</td>
<td>0.08</td>
</tr>
<tr>
<td>$4f$</td>
<td>0.26</td>
<td>0.64</td>
<td>0.42</td>
<td>0.57</td>
<td>0.09</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Table 5.2 Summary of the odd Legendre polynomial coefficients used in the fits for the first ATI order peaks discussed in figures 5.10 through 5.14. For easier comparison, all coefficients for each fit are normalized such that the sum of their squares is one.

As discussed in section 5.3.2, in addition to the expected Freeman resonant transitions from the ground state to odd parity states, the PES reveal some unexpected results. These results include: (1) the broad distribution of photoelectron energies around the $4f$ peak which appears to be composed of a separate, resolvable state to the
higher kinetic energy side, and (2) each ATI order possesses a peak that does not appear to have a counterpart in the other ATI order.

Figure 5.16 contains PYs and ADs for a selected energy range that includes the peak that is resolvable from the $4f$ state for intensities from 17 to 20 TW/cm$^2$, as observed in 5.7(b). The PYs between figure 5.14 and 5.16 do not differ significantly, but there is an observable difference between their angular distributions. The fit of Legendre polynomials for figure 5.16 requires a relatively much smaller contribution from the higher order polynomials than those necessary to fit the data of the $4f$ peak in figure 5.14. The differences in the angular distributions would indicate that the origin of the peaks at 2.36 and 3.84 eV are different than the $4f$ peak, but the kinetic energy does not match up with any known ponderomotively shifting bound state.

Both the first and second ATI orders have features or peaks in the PES that appear not to be present in the other order. The PYs and ADs for the energy ranges of some of these features and peaks are displayed in figure 5.17. The first ATI order contains a peak with a kinetic energy of 2.64 eV with distinct minima on either side of it located at 2.60 and 2.68 eV. A counterpart in the second ATI order would have a kinetic energy of 4.19 eV. For lower intensities, there is a peak present in the second ATI order with a kinetic energy of around 4.2 eV, as observed in figures 5.6(d) and 5.7(a). There is a slight peak at this energy, but the PES is much more uniform between 4.05 and 4.2. The minima on either side of the peak at 4.19 eV, especially on the lower kinetic energy side, are much less pronounced, than they are for the corresponding peak in the first ATI order. The angular distributions for these energies do not significantly differ from those for the rest of the peaks with nearby kinetic energies. Overall, the PES for each ATI order have
Figure 5.16 PES showing the integration used in the PYs and ADs, for 2.36 and 3.84 eV. The MPPD threshold intensities for the maximum and minimum energy values are displayed on the PY plots.
Figure 5.17 PES showing the integration used in the PYs and ADs, for 2.64 and 3.98 eV. The MPPD threshold intensities for the maximum and minimum energy values are displayed on the PY plots.
different characteristics for these corresponding energy ranges. In addition, a peak is present in each order, with a more dominant presence in the first ATI order that the second, that does not correspond to any expected ponderomotively shifted states.

The appearances of peaks with kinetic energy values that do not correspond to any expected states can be explained if they originate from non-ponderomotively shifted states. As discussed in section 2.5, the observed binding energy in a photoelectron spectrum will be offset from its field free binding energy by a factor of \((1-\alpha)U_p\). Since the non-ponderomotive factor, \(\alpha\), is unknown the location of the peak on a PES is also unpredictable. The difficulty in verifying the observation of a non-ponderomotively shifted state lies in the fact that any unidentifiable peak can be classified as a "non-ponderomotively" shifted state. Without additional knowledge of the original state, or a verifiable prediction of its AC Stark shift claiming a particular peak as originating from a non-ponderomotive source cannot be made with any degree of certainty. Therefore the origin of the unidentifiable peaks discussed is still largely unknown at this point.

The peak that appears in the second ATI order with a kinetic energy of 3.98 eV is altogether unique. As discussed in section 5.3.2, this peak appears in only the second ATI order and a corresponding energy in the first ATI, 2.44 eV, is actually the position of a minimum in the PES. Similar to the other peaks discussed, the location of the peak in the PES does not correspond to a ponderomotively shifted bound state. But, unlike the other anomalous peaks discussed, the angular distribution of ejected electrons measured for this peak do differ significantly from the rest of the peaks observed in that kinetic energy range and within the second ATI order. In addition to a noticeable visual appearance with the near absence of minor lobes or "jets", the coefficients required to fit
this angular distribution are generally different than those used for the rest of the peaks within the second ATI order. A more even mixture of even and odd Legendre polynomials was required to simulate the single uniform lobe appearance.

It should be noted here that the second ATI order has one property that is present for no other ATI order. One possible reason why a photoelectron can have a kinetic energy in the range of 3 to 4 eV, and no other value for integer photon energies above or below this range, is that it originated from a doubly excited autoionizing state. The energy limit for any $3pnl$ doubly excited state is the Mg$^+$ (3p) level, or 4.422 eV above Mg$^+$ (3s). Historically, the $3pNs$ and the $3pNd$ doubly excited states are well known due to the experimental availability of these states [68-71]. First, a laser is tuned to the $3s^2 \rightarrow 3s3p$ transition. Then the $3p$ electron is excited to an $Ns$ or $Nd$ state, followed by a transition of the $3s$ electron to the $3p$ state. The expected energies of these states are illustrated in figure 5.18. Although the energies of these known states do not overlap well with the anomalous peaks of 3.98, 4.08, and 4.18 eV, the possibility that these order-specific peaks originate from unmapped autoionizing states cannot be ruled out completely.
5.4 Results and Discussion for Circularly Polarized Light

As discussed in sections 2.6 and 4.3, magnesium atoms appear to be nearly structureless atoms when exposed to circularly polarized light. Because of angular momentum selection rules for circularly polarized light, the first available state for a Freeman resonant transition is that of the $6h$ state, which has a binding energy of only 0.38 eV. The next available state would be the $7h$ state, with a binding energy of 0.28 eV. Thus, magnesium is a nearly structureless atom, except for a relatively small collection of high angular momentum states close to the ionization limit, for circularly polarized light. The PES collected for circularly polarized light fields are displayed in figure 5.19.
Figure 5.19(a) is a semi-log plot of all of the kinetic energies detected for a variety of peak laser intensities from 7.9 to 42.9 TW/cm². Similar to the PES for LP light, no noticeable plateau or PES extension is observed, as expected for CP light. As discussed in section 4.4, the rescattering mechanism is eliminated for CP light, which would eliminate any photoelectrons with kinetic energies beyond the 4.5 $U_p$ MP cut off. For the highest intensity of figure 5.19, the MP cut off energy is about 11.5 eV, which agrees well with the observed spectrum. Figure 5.19(b) is the same data as that of 5.19(a), but with only a few of the intermediate spectra, and over the lower kinetic energy range for better observation of the general trends as the peak intensity is increased.

The expected photoelectron spectrum for magnesium atoms exposed to circularly polarized (CP) light is very different than that for linearly polarized (LP) light. Since the atom appears to be structureless for CP light, the dominant state from which ionization will occur is that of the ground state. The pronounced structure within each ATI order observed for LP light (see section 5.3) is now absent from the spectra for CP light as illustrated in figure 5.19. Instead, a much smoother, structureless distribution is present.
Figure 5.19  Magnesium PES for circularly polarized light for (a) a variety of peak intensities from 7.9 to 42.9 TW/cm² for all detected kinetic energies, and (b) 7.9, 10.6, 13.2, 18.5, 28.0 and 42.9 TW/cm². Figure 5.19(b) also includes a vertical black line for the kinetic energy limit for each order.
for each order in the PES. Equation 2.21 gives the intensity dependent kinetic energy of an electron ionized by \( m \) photons from a particular state as

\[
KE(I) = m\hbar\omega - E_b(I),
\]  

(5.3)

where \( E_b(I) \) is the binding energy of that state for intensity \( I \). For ionization from the ground state, the binding energy is \( IP_o + U_p(I) \), which makes the kinetic energy of an electron ionized at intensity \( I \),

\[
KE(I) = m\hbar\omega - (IP_o + U_p(I)).
\]  

(5.4)

From equation 5.4 we see that for a distribution of ponderomotive potentials (which is unavoidable given the temporal and spatial distributions of a laser pulse) we will observe a distribution of kinetic energies within each ATI order. As the intensity, and the ponderomotive potential, increases the electron kinetic energy within each order will decrease until the kinetic energy has swept all the way across the energy range of that order. At that point, the next photon order will become the ionization mechanism for that ATI order and the kinetic energy will start sweeping towards the lower kinetic energies from the highest kinetic energy possible for that ATI order. Thus, it will never appear that the width of the kinetic energy distribution, per order, will be wider than the energy of one photon. But, the resulting PES will be a smooth distribution of kinetic energies, within each ATI order, with a width dependent upon the range of ponderomotive shifting with a maximum width of the energy of a photon.
5.5 Conclusions

We have collected photoelectron spectra for magnesium atoms exposed to 800-nm, 120-fs laser pulses with peak intensities from $3.3 \times 10^{12}$ to $1.0 \times 10^{15}$ W/cm$^2$. Throughout the entire intensity range of $10^{12}$ to $10^{13}$ W/cm$^2$, the magnesium PES do not reveal a significant production of hot electrons, or a rescattering plateau region, which is not at odds with the results of ion yield measurements where it is demonstrated that enhanced double ionization is multiphoton in nature and not rescattering. The absence of this characteristic demonstrates that the ionization process(es) for magnesium differ from the ionization processes calculated and observed for the noble gasses. Although a significant plateau extension out to 10 $U_p$ is not detected for magnesium, observed cut off kinetic energies are in the 6 to 7 $U_p$ range for LP light, and 4 to 5 $U_p$ range for CP light. Thus, rescattering cannot be ruled out completely as a contributing ionization mechanism for the higher range of observed photoelectron kinetic energies. The plateau observed for intensities higher than $2 \times 10^{14}$ W/cm$^2$ is attributed to the photoionization of the Mg$^+$ ion.

For intensities up to 10 TW/cm$^2$ the PES consists of expected high-lying, odd parity. Rydberg states ponderomotively shifted into a 5-photon Freeman resonance. Kinetic energy studies indicate that the excited states populated are $p/f$ states. Further analysis using angular distributions indicate that the intermediate excited states are most likely $f$ states. PES collected for intensities in the region of 10 to 40 TW/cm$^2$ exhibit some unexpected structures in the PES. Photoelectron peaks appear in both the first and second ATI orders with energies that correspond to forbidden transitions to even parity states. The exact explanation of peaks appearing in both the first and second ATI orders
that do not correspond to 5-photon transitions to odd parity states is not known at this point.

We have also observed fundamentally different structure from one ATI order to another. Fundamental ATI theory does not have a widely accepted explanation of how order-to-order variations can occur. Order-specific structures of the second ATI occur in an energy range that contains numerous doubly-excited autoionizing states, both well-known and un-mapped. In addition, the angular distribution data for the kinetic energy peak of 3.98 eV is fundamentally different from the angular distributions observed for most of the other peaks within the second ATI order. The fact that these anomalies are observed, and not easily explained, indicate that photoionization of magnesium is unique from previous experiments with helium and the noble gasses, opening the door for possible future investigations of the strong-field photoionization of magnesium.
CHAPTER 6

PHOTOELECTRON SPECTRAL DEPENDENCE UPON THE CARRIER FREQUENCY OF THE LASER

6.1 Introduction

Historically, experiments investigating the structure of atomic states, and observing transitions from one state to another have been carried out under strictly controlled conditions while fine tuning a single individual aspect of the probing mechanism. In particular, many experiments control the population of excited states by scanning and varying the frequency of the incident radiation through very fine steps. The line-width of the incident radiation is incredibly narrow in order to observe population transfers between specific states with a high degree of precision. Using these methods, scientists can control and prepare atomic systems with a great deal of finesse.

The complexity of the response of atoms to incident high-intensity short-pulsed laser light, beyond that of traditional spectroscopy, is overwhelming. First, the absolute energy of atomic states, and the differences between them, is no longer constant. During the laser pulse, the energy level of a particular bound state can shift through many values of other un-perturbed atomic states. Energy levels of bound states are now no longer just
a function of frequency, but functions of time, and in a Gaussian focal volume, functions of position as well. In fact the laser light can also induce new bound states while original atomic states can disappear [14]. As discussed in chapter 5, population of excited states is a dominant process in the response of magnesium atoms to incident high-intensity laser light, but identification of which states are populated is a very difficult task. We may be populating a large number of excited states, but at a cost of a complete lack of control. Using high-intensity lasers to populate bound states is much the same as fly-fishing with a stick of dynamite. You may get the fish that you want but have created a huge mess in the process.

In this chapter we investigate the possibility of using the traditional spectroscopic method of varying the frequency of the laser in conjunction with the effects of high-intensity light on bound atomic states to try and gain a little bit of control over which states are populated.

6.2 Experiment

The laser system used in this investigation is the same as described in previous chapters. The experimental setup is nearly identical to that of chapter 5 except for the flight tube. The flight tube is that of an older design and has a flight path of 63.5 cm. The detection system on the end of the flight tube, amplifier, electronics, and counting/timing method is all the same. The carrier wavelength, and bandwidth of the pulses is tuned by adjusting the position and width of a slit inside the laser cavity of the Tsunami oscillator. The slit is located in the middle of two pairs of prisms that are arranged to function as a frequency dispersion compensator, to help correct for group

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velocity dispersion of the pulse as it travels through all of the laser cavity components. The location of the slit is in a position where the spectral frequencies of the pulse are spatially distributed, enabling us to physically select the bandwidth and center frequency of the pulse. The tuned pulse is then used to seed the Spitfire amplifier as it normally is operated. The angular orientation of the stretcher and compressor grating stage is adjusted to compensate for the change in wavelength of the pulse. The whole system is optimized such that the average output power and final pulse width is always 200 mW, and 120 fs.

An average power of 200 mW was chosen for a number of reasons. A lower average power is desired, as the PES is better understood for lower intensities. The use of lower intensities ensures that only neutral atoms dominate the interaction region and the resulting PES is specifically that for single ionization of magnesium. But, most importantly this particular average power was chosen because the calculated ponderomotive energies for the chosen wavelengths predict that only 5-photon resonances will occur.

6.3 Results and Discussion

The ponderomotive shifting of atomic states plays a crucial role in the observed effects of atomic reactions to high-intensity laser light. The results of chapter 5 illustrate that the laser field shifts numerous states such that a Freeman resonance can occur. The ponderomotive potential, described in section 2.3, is

\[ U_p = \frac{I}{4\omega^2}, \]  

(6.1)
where \( I \) and \( \omega \) are the intensity and frequency of the laser field in atomic units. From equation 6.1 we see that the value of the ponderomotive potential depends linearly with the intensity of the laser and inversely with the square of the frequency. In order for a 5-photon Freeman resonance to occur the energy of the bound state must be the same as that for five photons, or

\[
E_o + U_p = 5\omega ,
\]

(6.2)

where \( E_o \) is the natural bound state energy above the ground state. Now, substituting in equation 6.1 and solving for the intensity we find

\[
I = 20\omega^3 - 4E_o\omega^2 .
\]

(6.3)

According to equation 6.3, if the frequency is held constant, the intensity threshold for a Freeman resonance is only a function of the energy of the state with respect to the ground state, but if the carrier frequency is altered the intensity of the resonance can change quite a bit. As an example, let us consider the resonant population of a 7\( p \) or 6\( f \) state, whose energy above the ground state is 7.26 eV, or 0.267 a.u. For 800-nm light the 5–photon resonance occurs for an intensity of 8.1 TW/cm\(^2\). By tuning the carrier wavelength up to 830 nm, the intensity for the Freeman resonance decreases down to 3.2 TW/cm\(^2\), a reduction factor of about 2.5. Thus, a change in carrier frequency of less than 4% results in a factor of 2.5 change for the Freeman resonance intensity threshold. The change in the intensity threshold is less severe for more deeply bound states. Now if we calculate the Freeman resonance for the 4\( f \) state, we find that the resonance occurs at 16.3 TW/cm\(^2\) for 800-nm light, and 10.8 TW/cm\(^2\) for 830-nm light, a reduction factor of only 1.5. The
Figure 6.1 Calculated ponderomotively shifted f series states for laser parameters of 2.3 TW/cm$^2$, 120 fs, (a) 780 nm, (b) 800 nm, and (c) 830 nm.
differences in the ponderomotive shifting of the $f$ states of magnesium as a function of wavelength are illustrated in figure 6.1.

If a Freeman resonance occurs for a given state, and the laser frequency is decreased while the peak intensity is held constant the time at which the Freeman resonance occurs, within the laser pulse, is pushed farther out towards the wings of the pulse, lowering the relative intensity for that resonance process. Due to the nonlinearity of the process, only slight changes in the intensity threshold can have large effects on the observed signal. The observed signal for processes that occur below 10 TW/cm$^2$, drops off very rapidly as the intensity is further decreased. As an example, if we use the data obtained in chapter 5, the overall count rate for electrons of any kinetic energy for a peak intensity of 4.6 TW/cm$^2$ is 0.0044 counts per laser shot. If the peak intensity is increased to 8.6 TW/cm$^2$, the count rate increases to an average of 0.117 counts per laser shot. Thus, for an intensity decrease of less than a factor of 2, the total count rate decreases by a factor of 27. Therefore, if the threshold intensities for populating the high-lying Rydberg states drops, we would generally expect to see a substantial decrease in the detected signal of that process, due to the lower intensity.

Figure 6.2 is a collection of photoelectron spectra for carrier wavelengths of 780, 800, 810, 820, and 830 nm. The first noticeable difference between the PES of figure 6.2 and the PES of chapter 5 is the suppression of low-energy electrons. The lack of our ability to detect electrons with kinetic energies below 3 eV was a problem that plagued us for the first couple of years in setting up these experiments. It was found that the system worked quite well for detecting ions. So, this setup was used extensively for the investigation of ion yields as functions of various laser field parameters, resulting in the
Figure 6.2  PES for magnesium atoms exposed to 2.3 TW/cm$^2$, 120-fs laser pulses with carrier wavelengths of 780 nm, 800 nm, 810 nm, 820 nm, and 830 nm.
data presented in chapter 4 and in reference [21]. After we felt that we had done all that we could do with detecting ions, it was eventually discovered that the source of our problems with the detection of low energy electrons was a quarter inch long steel 8-32 set screw located in a support of the flight tube. The small steel set screw had a residual magnetic field large enough to penetrate through multiple layers of μ-metal shielding wrapped around the flight tube and would steer the slow moving electrons out of the 2.2° collection angle.

In order to help aid the eye in identifying the depth of the bound states that are resonantly populated and subsequently ionized, the energy value of the ionization limit of the second ATI order is illustrated by the black arrows. As the carrier wavelength of the laser is increased the location and separation energy between each ATI order decreases. From figure 6.2 it is clearly evident that as the carrier frequency is decreased, the rate of population of the high-lying Rydberg states significantly decreases, as discussed previously.

6.4 Conclusions

Increasing the carrier wavelength of the laser has a two-fold effect on the resonant population of weakly bound states. First, the ponderomotive potential increases as the inverse square of the change in frequency. Second, the energy of the 5-photon Freeman resonance decreases, eventually dropping down into the bound levels of the atom, closing that channel for ionization. By exploiting the interplay between a rising ponderomotive potential and a dropping 5-photon energy level, the time at which Freeman resonances occur within the pulse, and consequently the resonant intensity, can be experimentally controlled. We have shown that we can reduce the population and subsequent ionization
of the high-lying Rydberg states by selectively varying the carrier wavelength of the laser, effectively adding one more degree of control over strong-field ionization of atoms.
CHAPTER 7

CONCLUSIONS

Ion yield measurements and high-resolution photoelectron spectra have been collected in observation of the response of magnesium atoms to high-intensity laser pulses as a function of the laser field's peak intensity, ellipticity and carrier frequency. The results of both ion yield measurements and photoelectron spectra demonstrate the important role of population and subsequent ionization of excited states for the ionization process of magnesium atoms exposed to linearly polarized light. Ion yield measurements as a function of the field's peak intensity for linearly polarized light have a constantly changing slope for ionization of the neutral which cannot be fit with a simple power law dependence, which is observed with circularly polarized light. A constantly changing slope indicates that the ionization mechanism is not constant as more ionization channels open up for higher intensities. A strong enhancement of yields of doubly charged ions and similar ionization rates to those of ionization of the neutral show that ionization from excited ion states is a significant process in the production of Mg$^{2+}$. 

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Photoelectron spectra reveal that the majority of electrons that are ionized with linearly polarized light do so through resonant population of various excited states. Analysis of the photoelectron data using partial yields and angular distributions indicate that the dominant series populated by Freeman resonant transitions from the ground state is the $f$ series.

It has been demonstrated that the resonant population of bound excited states can be experimentally controlled by manipulation of the ellipticity and the frequency of the laser field. Both ion yield measurements and photoelectron spectra reveal that ionization of magnesium through excited states can be eliminated for circularly polarized light, and the dominant ionization process becomes multiphoton, non-resonant transitions from the ground state of the neutral. In chapter 6 we demonstrated that the resonant population of high-lying Rydberg states, with respect to lower energy excited states, can be controlled and reduced for a particular choice of peak laser intensity and carrier frequency.

The results of this work answer many questions about the response of magnesium atoms to intense laser light, and also reveal phenomena that are not fully understood. The appearance of unexpected peaks and order-to-order variations in the above threshold ionization raises new questions concerning the finer details of the photoionization of magnesium. Evidence has been unveiled that population of doubly-excited autoionizing states cannot be ruled out, and is one possibility focus of future investigations. Other possible future investigations are: two-pulse pump-probe experiments investigating long-lived states populated by the laser field, two-pulse, two-frequency experiments investigating the transitions from a resonantly populated excited state to a doubly-excited,
autoionizing state, and further investigation of the dependence of the photoelectron spectra on the ellipticity of the laser field.
APPENDIX

PHOTOELECTRON SPECTRAL DEPENDENCE UPON THE ELLIPTICITY OF THE LASER FIELD

1 Introduction

As discussed in chapters 4 and 5 there are significant differences in the ionization processes for magnesium atoms between linearly polarized light (LP) and circularly polarized light (CP) as the dominant ionization mechanism changes and numerous ionization channels close for elliptical and circularly polarized light fields. For LP light the dominant mechanism of ionization for lower intensities is multiphoton ionization through various excited states populated via Freeman resonances. As discussed in section 5.4, the dominant ionization mechanism for CP light is non-resonant multiphoton ionization from the ground state. The angular momentum selection rules for LP light are \( l = \pm 1 \), and for CP light \( l = +1 \). The original focus of this investigation was to observe how the photoelectron spectrum changes as a function of the ellipticity, and observe how the closure of various Freeman resonances depends upon the ellipticity of the field. In this appendix we will present and discuss the surprising and unexplainable results that we observed in the photoelectron spectra.
2 Experiment

The experimental setup for these investigations is identical to that used for chapter 5, except a quarter-wave plate (QWP) is inserted into the beam path instead of a half-wave plate. All of the photoelectron spectra are accumulated for 1 million laser shots. The QWP used for this investigation was obtained from CVI Laser Corporation, product number QWP0-800-10-4. The axes of the crystal, with respect to the axes of the rotatable mount, were determined by passing the horizontally polarized beam through a thin film polarizer (TFP) oriented such that horizontal polarization is transmitted, through the crystal, then reflected back along the same path by a dielectric mirror. If the input polarization is parallel to one of the crystal's axes, then the crystal does nothing to the beam and the beam is reflected back through the crystal and TFP. If the orientation of the crystal is such that the angle between its axes and the input polarization is $\pi/4$ then the polarization becomes circular. As the beam passes back through the QWP it is converted back to linear, but is now oriented vertically and reflects off of the TFP. The axes of the crystal were determined by measuring the maximum and minimum of the beam reflected by the TFP.

3 Results

The first step taken in this investigation was simply to observe the PES as a function of laser field ellipticity. The resulting data are displayed in figure A.1. An intensity of 23 TW/cm$^2$ was chosen because the MPPD is deep enough to populate the 4f
Figure A.1  Magesium PES as a function of ellipticity, for a peak intensity of 23 TW/cm^2.

(continued)
(Figure A.1 continued)
(Figure A.1 continued)
state. Thus, all of the Freeman resonances that occur are for the 5-photon order and the 6-photon energy level is still above the ionization threshold.

For ellipticities from 0 to 0.11, the behavior of the PES is as expected with a slow decrease in the signal of the high-lying Rydberg series between 1.14 and 1.44 eV in the MPI order, and 2.70 and 3.0 eV in the first ATI order. But, starting with an ellipticity of 0.16 and 0.21 three different peaks start to come in with energies of 0.72, 0.96, 1.16 eV, and 2.32, 2.58, and 2.74 eV, respectively. These three peaks continue to grow and remain in the PES for a large range of ellipticities. For an ellipticity of around 0.5 another peak on the low energy side of the middle peak turns on as the central peak starts to diminish. At an ellipticity of 1, CP, nearly all of the structure in the PES has disappeared and the pulse is as near to perfect circular as we can measure using the orientation calibration setup described in the previous section. Once past this point in the rotation of the QWP, the ellipticity will once again be elliptical with the major axis aligned parallel to the flight path.

As is discussed in section A.4, there should be no physical difference in the pulse on one side of circular and the other within the same quadrant of the QWP. Nevertheless, on the other side of circular polarization, which will be referred to as "side b", an altogether different pair of peaks, located at the exact minima between the set of three dominant peaks on "side a" of circular, turn on. This pair of peaks remains in the PES throughout a large range of ellipticities from 0.90 (b) until around 0.25 (b) where they disappear and the PES returns to what is normally observed for LP light.

The data recorded for the photoelectron spectral dependence upon the peak intensity of the light for an ellipticity of 0.38 (side a) is presented in figure A.2. For
this ellipticity, the high-lying Rydberg states observed for LP are absent. The dominant peaks present are those for an elliptically polarized laser field for an input orientation of the polarization to the QWP on "side a" of circular. For intensities above 25 TW/cm², another interesting peak turns on in the PES on the low energy side of the MPI and first ATI order, at energies of 0.6 and 2.2 eV. The relative amplitude of this peak, with respect to the other peaks within each order, decreases from order to order and does not seem to be present within any order higher than the first ATI order.

The PES collected as a function of intensity for an ellipticity of 0.38 on "side b" of circular are displayed in figure A.3. For this particular ellipticity two different sets of photoelectron peaks are present: the prominent pair of peaks present in figure A.1 for ellipticities of 0.90 (b) to 0.27 (b), and the set of high-lying f Rydberg states for LP light. For intensities below 13 TW/cm² the PES consists of only the f states. As the intensity is increased the two dominant peaks turn on as well as an unexpectedly broad low kinetic energy hump for each order. The PES displayed in figure A.4 are for parameters that are similar to that of figure A.3, except that for this slightly higher ellipticity of the field, the f Rydberg states are absent.
Figure A.2 Magnesium PES for an ellipticity of 0.38 (side a) as a function of intensity, units are in TW/cm².

(continued)
Figure A.3  Magnesium PES for an ellipticity of 0.38 (side b) as a function of intensity, units are in TW/cm$^2$. 

(continued)
(Figure A.3 continued)
Figure A.4  Magnesium PES for an ellipticity of 0.58 (side b) as a function of intensity, units are in TW/cm².
(Figure A.4 continued)
4 Discussion and Conclusions

As the QWP is rotated through an angle of 90°, the orientation of the linear input polarization, with respect to the crystal axes, rotates from originally being oriented parallel to one axis of the crystal through a combination of the two, and then to an orientation along the other axis of the crystal. As long as you stay within the same quadrant of the crystal, the helicity will remain the same and the only physical parameters of the beam that change are the relative amplitudes of the electric field along the fast or slow axes of the crystal. If the input orientation of the laser field is horizontal, then the output field changes from horizontal LP, to elliptical with the major axis oriented horizontally, to CP, back to elliptical with the major axis horizontal, and finally back to horizontal LP. The difference in the output field between an orientation along the fast axis and the slow axis is a quarter of a wave delay for one of them. In between the two, the location of the maximum field amplitude slowly gets shifted back. With respect to an un-altered reference beam, having the same optical path length as that through the fast axis, the delay of the field maximum shifts from 0 to \( \lambda/4 \). For our experiment and detection techniques this is a negligible amount of time delay, 0.68 fs. Whether the original orientation of the polarization is along the fast or slow axis of the quarter wave plate is not measurable or noticeable with our detection system and thus is not of importance to us.

Similarly, the only physical difference of the input orientation of the laser with respect to the QWP is whether or not it is more aligned with one of the axes than the other. Thus, neglecting the slight, negligible time delay, there should be no physical
difference between two equal ellipticities on either side of a circular laser field orientation, within the same quadrant of the crystal.

At this point, the exact source of the strange asymmetric behavior of the PES on either side of circular for fields of equal ellipticity and helicity is unknown. If the QWP is functioning properly, there should be no difference in the laser field itself, which leads us to believe that the difference in the PES is due to some strange effect the QWP itself has on the pulse. Some possible explanations for the asymmetry are: orientation of the QWP with respect to the incident direction of the laser beam, or a manufacturing defect in the QWP. The former is most likely not the reason because all of these experiments were conducted over a period of nearly a month and the QWP had been removed from the beam path and replaced in the beam path numerous times over that period of time. If the effect on the output beam characteristics were sensitively dependent upon small differences in the orientation of the QWP with respect to the input angle of the laser beam then variations in the asymmetry would be expected from one data run to another. No such variations were observed and the asymmetries of the PES were reproducible from one placement of the QWP to another. We are more likely to believe that the asymmetry is due to some manufacturing defect in the QWP that alters the pulse phase, shape, chirp, etc. in some consistent way depending upon which axis we are more aligned with. Because the exact effect the QWP has on the characteristics of the laser pulse is not known, identification of the source of the different sets of peaks that turn on and off as a function of ellipticity is not possible at this time.

The reason why these experiments were included with this dissertation, even though there are no explanations or physical reasons for the asymmetry, is because the
wild variations that we observed in the PES are interesting in themselves; that some seemingly slight, unnoticeable change in the characteristics of the pulse can have such a dramatic effect on the resonant signatures observed in the PES.

There are two main reasons why these experiments are reported in the form of an appendix and not as a separate chapter. First, we do not believe that the asymmetries are a function of the ellipticity, and thus not "real" for our intended purposes of this investigation. The second reason is that the exact source of the asymmetries is unknown, and the time and equipment necessary to investigating what precise changes occur to the laser pulse as a function of which axis the original field orientation is more aligned with is beyond our interest.
LIST OF REFERENCES


