Photoelectron Spectroscopy using High Order Harmonic Generation

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ABSTRACT

The analysis of photochemical processes has been previously limited by the short time scale in which these processes occur. Modern advancement in ultra-fast lasing technology allows for the analysis of photochemical reaction dynamics in real time. In this paper, electron spectroscopy is com*bi*ned with high harmonic generation (HHG) to probe some photo ionization processes of Helium. Experimental parameters are tested for improvement of photoelectron spectra resolution. Increase in sample gas pressure and flight tube magnetic field enhance spectral peak intensities, with peaks at fast times resulting from HHG ionization of He by HHG. Additional peaks corresponding to low energy electrons appear with increase in sample gas pressure. These additional peaks may represent single photoionization of helium due to energy transfer by inter-atomic collisions. A large ratio between two magnetic fields of the spectrometer results in higher photoelectron spectra resolution and drastic changes to the spectral shape for peaks at slow time values. Approximations of peak assignment suggest that two differing photo ionization processes occur when analyzing He using a HHG laser.

INTRODUCTION

Interactions between light and matter are essential in many chemical processes that occur in nature. Photochemical reactions such as photosynthesis, production of color, production of atmospheric ozone etc. occur upon absorption of light by matter. Measuring the reaction dynamics of photochemical processes is important for understanding fundamental mechanisms that can provide information on the structure and reactivity of compounds. Previous studies have utilized various techniques of molecular spectroscopy using UV/VIS lasers to analyze the underlying mechanism of photochemical processes, however, scientists have recently turned to high intensity free electron lasers with electron spectroscopy to reach new frontiers of photochemical research. The use of ultra-fast high intensity lasers is a newly explored research area and has the potential to provide photochemical analysis's which were previously unreachable. Use of lasers under a certain intensity threshold exhi*bi*t light and matter interactions in which the electric dipole moment changes linearly with the electric field of light**.** In comparison, different physical phenomena are observed with the use of strong lasers, such as nonlinear processes. [1] Non-linear processes are seen only at high light intensities and alter certain properties of light waves; light waves may exchange energy and momentum. These altercations give way to newly observe physical processes and applications in laser technology development. High intensity lasers with electron spectroscopy can be used to not only analyze well known processes such as single photon ionization, fragmentation, and migration, but also newly observed non-linear processes such as multi-photon ionization and high harmonic generation(HHG). The advent of electron

spectroscopy with high intensity ultra fast lasers allows photochemical reactions to be measured in real time. [2] This method also has the a*bi*lity to directly measure the ionization potential energies of atoms.

In previous studies, production of strong laser fields in the soft x-ray/ UV region was inaccessible, however advances in lasing technology and recent discoveries of a nonlinear process known as high harmonic generation (HHG) has become a popular soft x-ray free electron source. The attractiveness of HHG is its practicality and simplicity as a potential source of high energy free electron lasers. Soft x-ray/UV lasers are conventionally generated in large facilities, while HHG uses an apparatus compact enough to be used in a small lab. HHG is a phenomenon explained by both a semi-classical and quantum mechanical model. The HHG is initiated by ionization of a target gas by means of optical tunneling using a strong laser. The laser's electric field influences the potential of the atom in such a way that it becomes favorable for the ejected electron to recom*bi*ne with the parent ion. Upon collision with the parent ion, a photon is ejected with extra kinetic energy gained during the electron's acceleration. As a result, new, higher frequency high harmonic wavelengths are produced.[3] However, it can be challenging to generate high harmonics due to the presence of free electrons, which induce a phase mismatch between the pump and the high harmonic waves. Phase mismatch can be avoided if the high harmonics interaction occurs before the ionization process, which may be achieved with extremely small pulse widths in com*bi*nation with high intensity lasers.[4]

EXPERIMENTAL

In the Yamanouchi lab, HHG is used with electron spectroscopy to probe the ionization potentials and or*bi*tal energy properties of certain gas molecules. This paper mainly focuses on adjustment of parameters for maximum resolution and collection efficiency of photoelectron spectra, and tentative peak assignments corresponding to different ionization processes. An 800nm Legend Duo on Coherent Inc. laser is focused, with a pulse width of 30-40 femtoseconds, into a vacuum chamber. An atomic gas, typically Neon or Argon, is introduced to the chamber to begin HHG. A micro channel plate (MCP) detector, at approximately 1351V, and phosphorus screen, at approximately 2972V, are used to measure the generation of the high order harmonics. The new frequencies generated

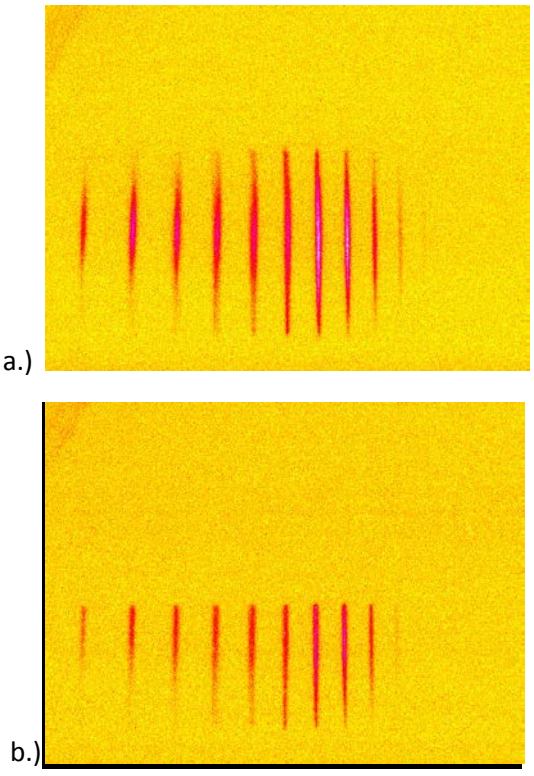


Figure1. High order Harmonic generation with Neon gas and 800nm light pulsed at 30-40 fs. a.) HHG spectrum without Aluminum filter b.) HHG spectrum with Aluminum filter of transmission >17.42nm

are dispersed by a grating onto the MCP

detector and result in multiple wavelength bands shown in figure 1.a, ranging from approximately 25-13nm (approx.72-54eV). Each wavelength represents a harmonic of order n; only odd numbered harmonics are observed due to symmetry properties. A corresponding HHG spectrum, figure 1.b, shows the broadband spectrum with the addition of an Aluminum filter with an absorbance range of <17.42nm. Comparison of Figure 1.a and Figure 1.b confirm the production of two HHG wavelengths below 17nm. The total range of harmonics generated and dispersed onto the detector is approximately 49^{th}-27^{th} high harmonic order. The band of HHG x-rays produced is then introduced into a magnetic bottle electron spectrometer and pulsed at approximately 1 kHz. The magnetic bottle electron spectrometer consists of an ionization region, a velocity-or energy dispersion region, and a micro channel plate detector. The laser is polarized so that the photoelectrons are ejected parallel to the flight tube towards the detector. However, two magnetic fields within the spectrometer are used to correct the trajectories of any electrons ejected at an angle to the flight tube. The ionization chamber is kept at 1T while the flight tube is at least 1e-3T. An accumulation of spectral data is done over 20minutes for each TOF spectrum. The resulting spectrum plots occurrences vs. time. This spectrum is then transformed by equation 1, to produce an intensity vs. energy plot. The analysis of the energy plots provides information about the ionization potentials of the atom.

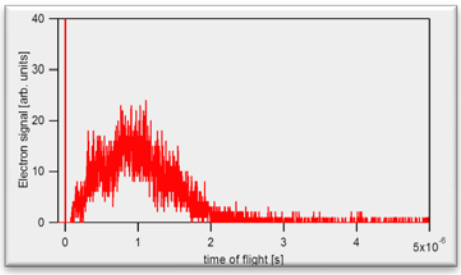
$$\text{Eq.1} \quad E = \frac{m_e l^2}{2et^2}$$

DATA

Focusing and HHG

A Helium gas sample is used in the magnetic bottle spectrometer for finding optimal peak intensity and resolution of the spectrometer. A primary experimental run using Neon HHG shows the need for improvement in both resolution and intensity in the time of flight (TOF) electron spectrum, Figure 2.a. A focusing mirror for the HHG laser beam is installed to decrease the interaction region of the laser and gas in order to sharpen the spectral peaks. Figure 2.b. shows improvement in resolution with four distinguishable peaks. The experiment was then done with Argon HHG, resulting in a lower HHG energy cut off due to the low ionization potential of Argon. Figure 3. Shows the comparison of a helium TOF photoelectron spectra using Neon HHG versus Argon HHG. Peaks in the Argon HHG spectrum shift to slower time values as expected, suggesting the peaks indeed arise from the HHG as opposed to noise. Resolution slightly improves by using Argon HHG.

a.)



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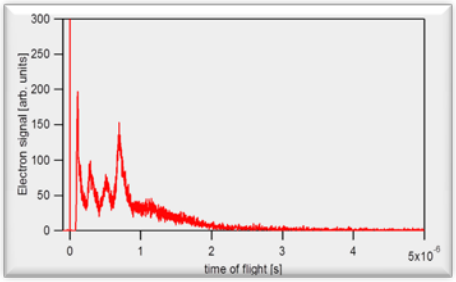

Figure 2. Photoelectron Spectrum of He gas using Neon HHG. a.) Spectrum before addition of focusing mirror. b.) Spectrum after addition and adjustment of focusing mirror.

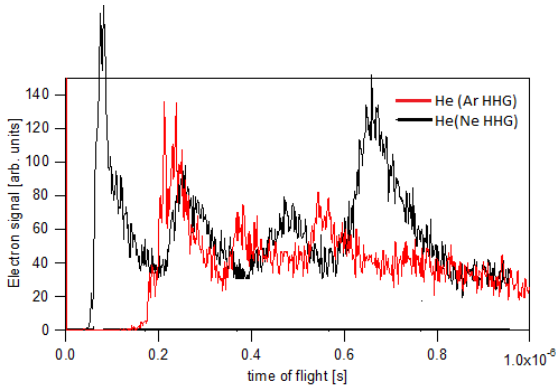

Figure 3. Photoelectron spectra of He using Ar HHG(red) and Neon HHG (black). Both spectra were taken at approximately $3x10^{-3}$Pa with magnetic fields at 900mT, and 3.8mT.

Sample Gas Pressure

Photoelectron spectra of He using Argon HHG were taken at three different gas pressures. Theoretically the sample gas pressure is proportionally related to the peak intensity, therefore high gas pressures are expected to result in high peak intensities. This is supported by Figure 4, however an increase in sample gas pressure results in the appearance of additional peaks at slower time values. The spectrum taken at $1.1x10^{-3}$ Pa shows three broad peaks at approximately $2.44x10^{-6}$s, $3.96\ x10^{-6}$s, and $5.98\ x10^{-6}$s. These peaks are shifted slightly to faster times when lowering the pressure to $3.4x10^{-4}$Pa, and disappear at $9.3x10^{-5}$Pa.

Magnetic Fields

A unique feature of the magnetic bottle spectrometer is the two magnetic fields used to correct the trajectories of electrons that are not parallel along the z-axis of the flight tube. In general, the magnetic field in the ionization region (B_i) should be significantly larger than the magnetic field in the flight tube (B_f). Electrons are captured in the high field region and follow a helical motion as they gradually transition to the lower field region. [5] Photoelectron spectra were measured over a range of magnetic field strengths, B_f, while B_i was held constant at approximately 900mT. Figure 5 shows the comparison of Helium gas using Argon HHG taken at four different B_f values. Peaks between $0.18\text{-}0.28x10^{-6}$ s show an increase in resolution and a decrease in peak intensity as B_f decreases. In contrast peaks ranging from $0.28\text{-}1.0x10^{-6}$ s are more sensitive the changes in B_f, as the peaks completely disappear when decreasing B_f of 1.8mT.

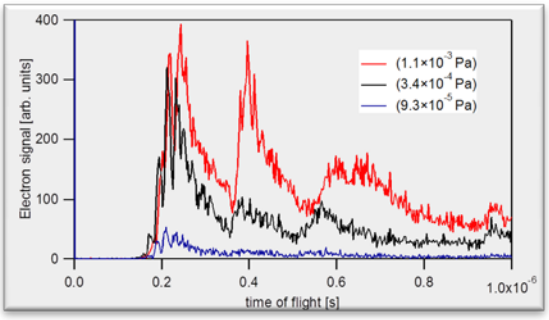

Figure 4. Photoelectron spectrum of Helium using Ar HHG at varying Helium gas pressures. Magnetic fields were kept constant at 950mT and 2.1mT.

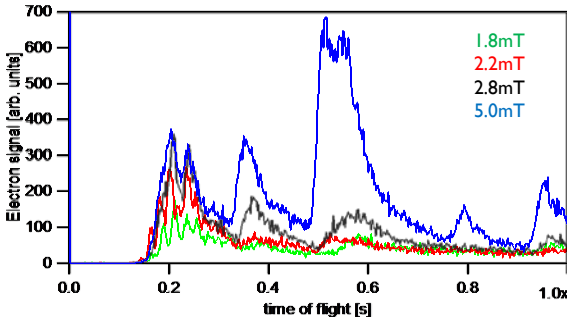

Figure5. Photoelectron spectra of He using Ar HHG at varying flight tube magnetic fields, B_f while B_i is held at approximately 960mT. Sample gas pressure for all spectra was $1.7x10^{-3}$Pa

DISCUSSION

Focusing and HHG

Comparison of the He TOF photoelectron spectra using Argon HHG versus Neon

HHG, Figure 3, shows no significant improvement in resolution. . Figure 6 compares corresponding energy plots of He using Neon HHG, 6.a, and Argon HHG, Figure 6.b. Figure 6.b. While there is resolution improvement in Figure 6.b, it is still insufficient for accurate assignment of peaks. However it can be approximated that the peaks found at 25-20eV are a result of single photoionization of He from the 33rd,31st, and 29th harmonics. The absence of peaks above 40eV agrees with the observation of the low energy HHG cut off of Argon. In Figure 3.a, the most significant feature is the presence of peaks around 70eV, which may arise from the single photoionization from the 61st harmonic. This suggests that high order harmonics as high as 100eV were successfully generated and used in the ionization of Helium.

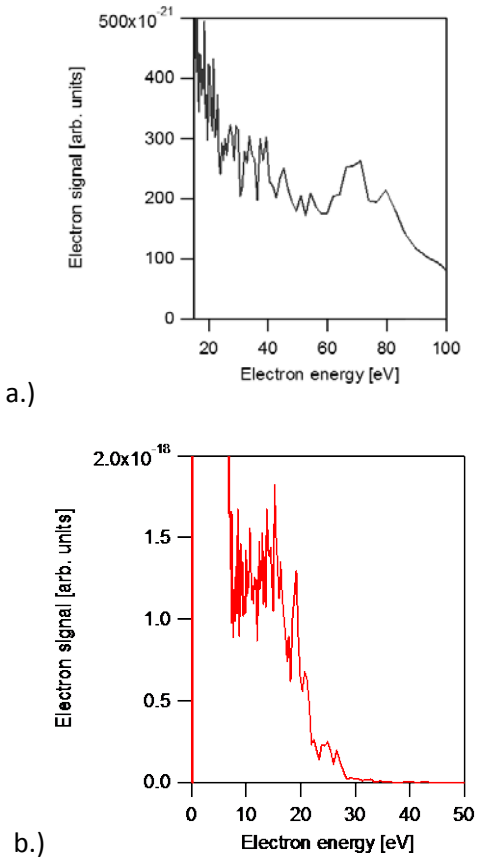

Figure 6. Photoelectron energy spectra of He corresponding to Figure 3. A.) Using Neon HHG. b.) Using Argon HHG

Sample Gas Pressure

Higher sample gas pressures increase peak intensity as expected; higher numbers of atoms available for ionization results in an increase in electron collection. Increase pressure also resulted in additional peaks at slower times. This may be due to a shortened mean free electron path at higher pressures resulting in more atomic collisions. An excited electron may transfer its energy upon collision with a neutral atom and induce photoionization. However, energy transferred from excited atoms is significantly smaller than HHG energies, resulting in spectral peaks at slower times. Table 1 shows the calculated energies of electrons ionized by HHG and by collision. In the spectrum at 1.1×10^{-3}Pa, the peak centered at 3.96×10^{-6}s corresponds to 5.7eV, which approximately matches the energy resulting from collisional ionization originally induced by the 35th harmonic. The following peak centered at 5.98×10^{-6}s corresponds to 2.39eV, which approximately

n^{th} Harmonic Order	n^{th} HHG Energy (eV)	Single Ionization by HHG(eV)	Single Ionization by Collision (eV)
39	60.45	35.85	11.45
37	57.35	32.75	8.35
35	54.25	29.65	5.25
33	51.15	26.55	2.05
31	48.05	23.45	N/A
29	44.95	20.35	N/A
27	41.85	17.25	N/A
25	**38.75**	**14.15**	**N/A**

Table 1: High Harmonic Order and corresponding HHG wavelength energy, energy difference of HHG and I_p of He, and energy difference resulting from inter-atomic collision

matches the energy resulting collisional ionization originally induced by the 33rd harmonic. In comparison, the first range of peaks in Figure 4 at approximately .18-.28x10^{-6} s corresponds to electron energies of 25-15eV, and therefore represent peaks produced from single photoionization of He with HHG. The spectra suggests that the occurrence of two different photoionization processes is dependent on the sample gas pressure.

Magnetic Fields

Change in the magnetic field of the flight tube, B_f, has an intriguing effect on the shape of the photoelectron spectra. Resolution changes the most for peaks 0.18-3x10^{-6}s, with optimal resolution at the lowest B_f measured at 1.8mT. In contrast, maximum peak intensity is observed at the highest B_f measured at 5.0mT. Analysis using a B_f of 1.8mT also results in the disappearance of peaks at approximately 0.38x10^{-6}s,.55 x10^{-6}s, 0.8 x10^{-6}s, and 0.96 x10^{-6}s. The peaks are significantly affected by the change in B_f and disappear at low B_f values. It is expected that as the ratio of B_f/B_i increases, the acceptance angle of the spectrometer and electron collection efficiency is also increased, resulting in higher peak intensities. However the opposite is observed, as a larger B_f/B_i results in a decrease in peak intensity. Therefore the B_f/B_i may not be the reason the spectral patterns observed. However, if B_i is initially too strong, it is possible for electrons to never transition to a parallel trajectory induced by B_f, and instead crash into the walls of the spectrometer. When B_f becomes stronger, the electrons have the chance to be influenced by B_f and reach the detector. Low energy electrons are heavily influenced by magnetic fields and would more strictly follow the trajectory of B_i than high energy electrons would. This is shown by the appearance of slower time electrons only when B_i is high enough to change the trajectory of the electrons. There is less impact on peaks at 0.18-3x10^{-6}s because high energy electrons may resist B_i just long enough to transition to B_f and reach the detector. Future experiments in which B_i is the variable are necessary to confirm this hypothesis.

CONCLUSION

Resolution of the photoelectron spectra of He using HHG was improved with the adjustment of a focusing mirror, the sample gas pressure, and the magnetic field. Position of the focusing mirror plays an important role in decreasing the size of the ionization region and sharpening spectral peaks. A high sample gas pressure is useful for increasing peak intensity and inducing phenomena other than single photoionization by HHG. Despite inadequate resolution, spectral analysis suggests that additional peaks observed at high pressures are caused by energy transfer between two atoms upon inter-atomic collision. At high pressures, the magnetic field of the flight tube, B_f, was adjusted, showing an increase in peak intensity as B_f increased. This pattern was attributed to the strength of B_i; B_i may be too strong for electrons to properly transition to B_f and reach the detector. Optimal resolution is observed when B_f/B_i is large, and so analysis at high gas pressures and large B_f/B_i provides a much improved photoelectron spectrum of He. This improvement will help to identify peaks to specific energy levels within He and in future, be applied to compounds to determine unknown potentials and electronic structure.

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