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Symmetry and High Harmonic Spectroscopy in Solids

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SYMMETRY AND HIGH HARMONIC SPECTROSCOPY IN SOLIDS

by

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ABSTRACT

High harmonic generation (HHG) by intense femtosecond laser pulses has, over the last three decades, provided new coherent sources of extreme ultraviolet and soft x-ray light and enabled the field of attosecond science. Furthermore, as properties of the target are encoded in the harmonic emission, high harmonic spectroscopy has allowed extraction of molecular structure and dynamics from the spectra and polarization states of harmonics generated from gas-phase molecules. HHG from solids, discovered in 2011, now promises to offer similar benefits to condensed matter physics. In this dissertation, I describe progress on two fronts: extending attosecond techniques to generate new high harmonic sources based on solid-state targets, and applying high harmonic spectroscopy to probe symmetry properties of solids.

First, I demonstrate HHG from ZnO crystals using a high-power source of femtosecond mid-infrared pulses, and characterize the dependence of the harmonic spectrum on the orientation of the crystal with respect to the laser polarization. New features are observed in the orientation-dependent spectrum, which can be explained using symmetries associated with the transition dipoles. The same features are then investigated through polarization-resolved measurements of even and odd harmonic orders, which suggest a universal polarization behavior that is dictated largely by symmetry properties of the target. To test this conclusion, I investigate HHG from ferroelectric BaTiO$_3$ and LiNbO$_3$ crystals, for which the symmetry properties can be externally controlled.

Due to their unique temporal resolution, high harmonic pulses are capable of probing rapidly occurring phenomena such as carrier interactions and phase transition dynamics. For this reason, it is desirable to develop harmonic sources with few-femtosecond to attosecond pulse
durations. I take advantage of nonlinear compression in a bulk crystal to compress the mid-infrared laser pulse to $<3$ optical cycles. Employing these pulses for HHG may pave the way toward novel compact, high-power attosecond sources.
for Shadi
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# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... xi

LIST OF TABLES ............................................................................................................... xv

LIST OF ABBREVIATIONS ............................................................................................. xvi

CHAPTER 1: INTRODUCTION ......................................................................................... 1

CHAPTER 2: HIGH HARMONIC GENERATION AND SPECTROSCOPY ................. 9

  2.1 High Harmonic Generation .................................................................................. 9
    2.1.1 Ionization ....................................................................................................... 11
    2.1.2 Acceleration .................................................................................................. 13
    2.1.3 Recombination ............................................................................................... 15
  2.2 High Harmonic Spectroscopy ............................................................................... 17
  2.3 Solid State High Harmonic Spectroscopy ............................................................. 19

CHAPTER 3: HHG IN SOLIDS ..................................................................................... 23

  3.1 Frontiers in Solid State HHG ............................................................................... 23
  3.2 Three-step Model in Momentum Space ................................................................. 25
  3.3 Theoretical Framework for HHG in Solids ......................................................... 30
  3.4 Mid-IR Laser Technology for Solid State HHG ................................................... 32
  3.5 HHG from a-cut Bulk Zinc Oxide ......................................................................... 35
    3.5.1 Experimental Setup ...................................................................................... 35
3.5.2 HHG Spectrum ................................................................. 37
3.5.3 Wavelength Dependence of HHG Spectra ................................ 37
3.5.4 Non-perturbative Behavior of HHG ........................................ 38
3.5.5 Conversion Efficiency ........................................................ 39

CHAPTER 4: HHG AND SYMMETRY PROPERTIES IN CRYSTALS .......... 41

4.1 Solids and Structural Symmetry.................................................. 41
4.2 Role of Symmetry in HHG .......................................................... 43
  4.2.1 Symmetry and HHG Spectrum in Zinc Oxide .............................. 46
4.3 Symmetry and Polarization Properties of HHG .............................. 50
  4.3.1 Polarization Properties of HHG in Zinc Oxide ......................... 53
  4.3.2 Birefringence effect in Zinc Oxide ......................................... 61
  4.3.3 Jones Calculus Approach to Polarization ................................ 64
    4.3.3.1 Experiment and Results .................................................. 66
    4.3.3.2 Modified Orientation Dependent Spectrum from ZnO .................. 69

CHAPTER 5: FIELD-CONTROL OF HHG FROM FERROELECTRICS .......... 71

5.1 Ferroelectric Materials ................................................................ 71
5.2 Symmetry and Dipole Moment in Ferroelectrics ............................ 73
5.3 HHG in Bulk Ferroelectric Barium Titanate (BaTiO₃) ..................... 76
  5.3.1 Experimental Setup ............................................................. 76
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.3.2 Results and Discussion</td>
<td>77</td>
</tr>
<tr>
<td>5.4 HHG in Thin Film Ferroelectric Lithium Niobate (LiNbO$_3$)</td>
<td>85</td>
</tr>
<tr>
<td>5.5 Symmetry and Field-control of High Harmonics</td>
<td>90</td>
</tr>
<tr>
<td>5.5.1 Controlling HHG from LiNbO$_3$</td>
<td>91</td>
</tr>
<tr>
<td>5.5.2 Controlling HHG from BaTiO$_3$</td>
<td>94</td>
</tr>
<tr>
<td>CHAPTER 6: FEW-CYCLE COMPRESSED MID-IR PULSES</td>
<td>99</td>
</tr>
<tr>
<td>6.1 Few-cycle Pulses</td>
<td>99</td>
</tr>
<tr>
<td>6.2 Nonlinear Self-compression of Mid-IR Pulses</td>
<td>100</td>
</tr>
<tr>
<td>6.3 Self-compression of Mid-IR Femtosecond Pulses from 50 kHz OPA</td>
<td>105</td>
</tr>
<tr>
<td>6.3.1 Self-compression Setup</td>
<td>105</td>
</tr>
<tr>
<td>6.3.2 Few-cycle Driven HHG Setup</td>
<td>107</td>
</tr>
<tr>
<td>6.3.3 Theoretical Analysis</td>
<td>109</td>
</tr>
<tr>
<td>6.4 Anti-resonant Hollow-core Fiber</td>
<td>111</td>
</tr>
<tr>
<td>CHAPTER 7: SUMMARY AND OUTLOOK</td>
<td>115</td>
</tr>
<tr>
<td>APPENDIX: COPYRIGHT PERMISSION LETTER</td>
<td>117</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>120</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

Figure 2-1: HHG Process in Atoms ................................................................. 11
Figure 2-2: Multiphoton and Tunneling Ionization Regimes ................................ 13
Figure 2-3: Different Recollision Electron Trajectories ...................................... 14
Figure 2-4: Three-step Model ........................................................................ 16
Figure 2-5: Attosecond Pulse Generation ....................................................... 17
Figure 2-6: Schematic Diagram of Solid-state HHG Mechanisms ....................... 20
Figure 3-1: Representation of the Energy Levels in Solids Vs Atoms .................. 26
Figure 3-2: Long and Short Trajectories .......................................................... 29
Figure 3-3: Optical Parametric Amplification (OPA) ....................................... 34
Figure 3-4: Spectral Properties of OPA Idler Wavelength ............................... 35
Figure 3-5: Temporal Characterization of the Idler Pulses ............................... 36
Figure 3-6: Schematic Diagram of the Experimental Setup ............................. 36
Figure 3-7: HHG Spectrum of a-cut ZnO ....................................................... 37
Figure 3-8: HHG Spectrum for Various Idler Wavelengths from 3.4 μm to 4 μm .... 38
Figure 3-9: Harmonics Yield as a Function of the Fundamental Intensity ............. 39
Figure 3-10: Measured Conversion Efficiency and Average Power of Visible and UV Harmonics ...................................................................................... 40
Figure 4-1: Orientation Dependent Properties of Emitted Harmonics ................ 46
Figure 4-2: Orientation Dependent High Harmonics from a Tilted Plane .......... 47
Figure 4-3: Strong and Weak Symmetry Features of HHG ................................ 49
Figure 4-4: Theoretical and Experimental Orientation Dependence Harmonics ...... 50
Figure 4-5: Atomic Structure of a-plane ZnO in the Real Space

Figure 4-6: Polarization States of Below- and Above-gap Harmonics

Figure 4-7: Polarization-resolved Harmonics Spectrum

Figure 4-8: Polarization-resolved Orientation Dependence of Integrated Harmonics

Figure 4-9: Measured and Calculated Ellipticity of Harmonics

Figure 4-10: Orientation Dependent Ellipticity of Mid-IR Beam at the Crystal Exit Plane

Figure 4-11: Ellipticity Dependent Yield of 11th Harmonic in a-cut and c-cut ZnO

Figure 4-12: Ellipticity of Mid-IR at the Exit Plane of ZnO for All Configurations of HWP and QWP

Figure 4-13: Experimental Setup for Simulating HHG from Thin film a-cut ZnO

Figure 4-14: Polarization State of Mid-IR at the Exit Plane of ZnO at Different Orientations

Figure 4-15: Polarization Characterization of Mid-IR Beam at the Crystal Exit

Figure 4-16: Corrected Polarization State of Mid-IR at the Exit Plane of ZnO at Different Orientations

Figure 4-17: Experimental HHG Spectra with/without Propagation Effect

Figure 5-1: Polarization-electric Field Hysteresis

Figure 5-2: Polarization Configurations under an Applied Electric Field

Figure 5-3: Phase Diagram for BaTiO$_3$

Figure 5-4: Structural Transition in BaTiO$_3$

Figure 5-5: The Experimental Setup and Spectrum of Emitted Harmonics from BaTiO$_3$
Figure 5-6: Wavelength Dependence of Generated Harmonics from BaTiO₃ .......... 78
Figure 5-7: Influence of Multiple Domains in HHG from BaTiO₃ ......................... 79
Figure 5-8: Orientation Dependence of Harmonics from BaTiO₃ .......................... 80
Figure 5-9: Measured and Calculated Orientation-Dependent Spectrum ................ 81
Figure 5-10: Measured and Calculated Orientation-Dependent Spectrum .............. 82
Figure 5-11: Polarization States of Emitted Harmonics for Particular Crystal Orientation .......................................................... 83
Figure 5-12: x-cut LiNbO₃ Crystal Structure at Room Temperature ...................... 85
Figure 5-13: Orientation-dependent Measurement HHG in LiNbO₃ ....................... 86
Figure 5-14: Polarization-resolved Orientation Dependent HHG Spectrum ............ 88
Figure 5-15: Polarization States of High Harmonics from LiNbO₃ ....................... 89
Figure 5-16: Nano-scale Gold Design for Electric Conductivity ....................... 91
Figure 5-17: Laser-induced Thermal Effects at the Focal Spot ......................... 93
Figure 5-18: Orientation-dependent Measurement for BaTiO₃ (100) Plane Designed for Control of HHG .......................................................... 95
Figure 5-19: HHG Hysteresis Loop Retrieved Through Applied DC Field .......... 96
Figure 5-20: HHG Hysteresis Loop Retrieved Through Applied DC Field .......... 97
Figure 6-1: Filamentation in an Optically Transparent Medium ....................... 102
Figure 6-2: GVD in Bulk Materials with Transparency to Mid-IR Range ............. 104
Figure 6-3: Self-compression and HHG Setup ............................................. 105
Figure 6-4: Mid-IR Pulse Characterization ............................................. 107
Figure 6-5: HHG Spectrum from Few- and Multi-cycle Driving Pulses ............... 108
Figure 6-6: Simulated Harmonic Spectra Driven by Uncompressed and Compressed Pulses
....................................................................................................................................................................................... 110
Figure 6-7: Design of Anti-resonant Fiber and High Pressure Durable Chamber........ 111
Figure 6-8: Simulation of Power Spectral Density and Spectral Evolution ................. 112
Figure 6-9: Simulation of Temporal Evolution and Maximum Pulse Compression ...... 112
Figure 6-10: Focal Spot Size Measurements Based on the Pixel Size of Image ............ 113
Figure 6-11: Measured and Fitted Data for Transverse Plane of the Beam............... 114
LIST OF TABLES

Table 4-1: Crystal Families and Their Bravais Lattice ......................................................... 44
Table 6-1: Nonlinear Refractive Index in Bulk Materials Transparent to Mid-IR Pulses
..................................................................................................................................................... 103
Table 6-2: Measurement of Focal Spot Size............................................................................... 113
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_0$</td>
<td>Laser Frequency</td>
</tr>
<tr>
<td>$\omega_{tu}$</td>
<td>Tunneling frequency</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Laser Field Strength</td>
</tr>
<tr>
<td>$m_e$</td>
<td>Electron’s mass</td>
</tr>
<tr>
<td>$I_p$</td>
<td>Ionization Potential</td>
</tr>
<tr>
<td>$U_p$</td>
<td>Ponderomotive Energy</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Kelydish Parameter</td>
</tr>
<tr>
<td>$t_{tu}$</td>
<td>Tunneling time</td>
</tr>
<tr>
<td>$T$</td>
<td>Laser field period</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Driving wavelength</td>
</tr>
<tr>
<td>$v_0$</td>
<td>Electron’s Initial velocity</td>
</tr>
<tr>
<td>$x_0$</td>
<td>Maximum displacement of the ionized electron</td>
</tr>
<tr>
<td>$\hbar$</td>
<td>Dirac’s constant</td>
</tr>
<tr>
<td>$p$</td>
<td>Continuum momentum</td>
</tr>
<tr>
<td>$A$</td>
<td>Vector potential</td>
</tr>
<tr>
<td>$k$</td>
<td>Crystal momentum</td>
</tr>
<tr>
<td>$J_{er}$</td>
<td>Interband current</td>
</tr>
<tr>
<td>$J_{ra}$</td>
<td>Intraband current</td>
</tr>
<tr>
<td>$v_m(k)$</td>
<td>Group velocity of the $m$-th band</td>
</tr>
<tr>
<td>$E_m(k)$</td>
<td>Energy dispersion relation</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<td>--------</td>
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</tr>
<tr>
<td>K</td>
<td>Quasi-canonical momentum</td>
</tr>
<tr>
<td>d(K)</td>
<td>Transition dipole matrix</td>
</tr>
<tr>
<td>BZ</td>
<td>Brillouin zone</td>
</tr>
<tr>
<td>n(K,t)</td>
<td>Band population</td>
</tr>
<tr>
<td>π(K,t)</td>
<td>Coherence of medium</td>
</tr>
<tr>
<td>w(K,t)</td>
<td>Ionization rate</td>
</tr>
<tr>
<td>T_2</td>
<td>Dephasing time</td>
</tr>
<tr>
<td>S(K,t)</td>
<td>Semiclassical action</td>
</tr>
<tr>
<td>E_g</td>
<td>Band energy</td>
</tr>
<tr>
<td>τ</td>
<td>Pulse duration</td>
</tr>
<tr>
<td>I_n</td>
<td>Intensity of n-th harmonic</td>
</tr>
<tr>
<td>P(E)</td>
<td>Nonlinear response of medium</td>
</tr>
<tr>
<td>χ</td>
<td>Susceptibility tensor</td>
</tr>
<tr>
<td>Δφ</td>
<td>Phase retardation</td>
</tr>
<tr>
<td>n</td>
<td>Refractive index</td>
</tr>
<tr>
<td>ε</td>
<td>Ellipticity</td>
</tr>
<tr>
<td>P_r</td>
<td>Remnant polarization</td>
</tr>
<tr>
<td>E_c</td>
<td>Coercive electric field</td>
</tr>
<tr>
<td>T_c</td>
<td>Curie temperature</td>
</tr>
<tr>
<td>P_{cr}</td>
<td>Critical power</td>
</tr>
<tr>
<td>n_2</td>
<td>Nonlinear refractive index</td>
</tr>
<tr>
<td>β(ω)</td>
<td>Spectral phase</td>
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</table>
CHAPTER 1: INTRODUCTION

For roughly a century, materials science research has benefitted from x-ray diffraction (XRD) as a means to characterize the atomic-scale structure of solid crystals. More recently, time-resolved XRD has allowed measurements of dynamics in solid-state reactions. However, such measurements have largely relied on synchrotron x-ray sources, and therefore have been confined to the picosecond timescale. X-ray crystallography using femtosecond pump-probe XRD [1] is only now becoming feasible through the use of x-ray free electron laser (XFEL) facilities [2]. Due to the challenges associated with such experiments, and especially the difficulty of obtaining beam time at currently-available XFEL facilities, it is desirable to bring some of the science and applications of large particle accelerators and XFELs down to the table-top scale [3,4]. To this end, ultrafast laser techniques have been proposed for x-ray [5-8] and electron imaging [9,10] of molecules and crystalline solids with femtosecond resolution.

One possible route to realizing tabletop femtosecond time-resolved crystallography involves the application of high harmonic spectroscopy in solids. Due to advances in time-resolved spectroscopies using high harmonics over the last few decades, high harmonic spectroscopy has allowed tomographic imaging of electronic orbital structure[11] and time-resolved studies of dynamic wave packets [12]. The realization of high harmonics in solids in 2011 [13] has now opened the field of solid-state high harmonic spectroscopy. While solid state high harmonic sources are relatively new, high harmonic spectroscopy has already been used to reconstruct the electronic band structure [14], study orbital dynamics, and observe dynamic quantum phase transitions. As high harmonic generation supports the generation of attosecond pulses in solids [15], the time resolution exceeds that of femtosecond XRD using XFELs [3,4,16,17].
The high temporal resolution of the generated harmonics has now opened for probing the ultrafast phenomena in atoms and molecules [12,18,19]. The realization of high harmonics in solids has opened the field of solid-state high harmonic spectroscopy. Although the field is relatively new, solid-state HHG has been proposed as a tool to reconstruct the electronic band structure [14], study carrier interaction [20,21] and probe phase transition dynamics [22,23]. Compressing the pulse duration of the light source to the few-cycle regime has recently enabled the generation of isolated attosecond pulses [24,25] from solids, enabling measurements of electron dynamics in solids at the current extremes of time resolution.

In this dissertation, I introduce the fundamentals of high harmonic spectroscopy using solid materials [26] and demonstrate their potential to characterize structural symmetries in solids. Through polarization-resolved and orientation-dependent measurements of the high harmonic spectrum generated in ZnO crystals, I utilize harmonic radiation as a high resolution probe to investigate the electronic and symmetry properties of solids [27]. To further apply the symmetry induced effects to a correlated material, I study the generation and control of high harmonic generation from ferroelectric BaTiO$_3$ and LiNbO$_3$ crystals, as their symmetry features can be controlled by an applied external field. Lastly, to improve the temporal resolution for further investigation of the time-resolved structural measurements, I take advantage of nonlinear self-compression in bulk YAG crystals to compress the pulses, and further apply them to generate high harmonics [28]. The following paragraphs outline my dissertation framework:

- In chapter 2, I review the fundamentals of high harmonics spectroscopy technique, relying on high harmonic generation (HHG). I describe the generation of attosecond XUV pulses through the well-established three-step model, and explain how the emitted pulses can be applied as an
in-situ spectroscopy technique to study a variety of ultrafast phenomena in atomic and molecular targets. I describe that harmonics have essentially the same origin in solids as in gases, and that in general, electron and hole motion in solids can be described in a similar manner as in the gaseous media. I explain how high harmonics encode structural information of the generation medium. Particularly in solids, I introduce high harmonic spectroscopy as a method to investigate electronic and structural dynamics with the capacity to offer sub-cycle time resolution, which can complement ultrafast XRD measurements.

- In chapter 3, I discuss the experimental and theoretical basis for high harmonic generation in solid crystals, and demonstrate the generation of high harmonics using a high-power mid-infrared femtosecond laser source in bulk crystals of zinc oxide. I illustrate the characteristics of the emitted harmonics spectrum by shifting the driving field’s frequency and establish that harmonics are generated in the non-perturbative regime for both near- and above-gap harmonics through the intensity scaling of harmonics. Additionally, I measure the conversion efficiency of near- and above-gap harmonics for high harmonics generated using a high-power, high-repetition rate mid-IR light source.

- In chapter 4, I investigate the role of symmetry in the generation mechanism of harmonics from ZnO. I study the polarization properties of the emitted harmonics, and discuss the role of structural symmetry in determining their polarization states, with respect to the laser source polarization. I explain how the symmetry of the medium can be incorporated into the dipole amplitude and phase used to calculate harmonics emission in the theoretical model. I conclude that the polarization properties of solids are collective features which are mainly governed by
symmetry, enabling the polarization-resolved high harmonic spectroscopy as a technique for crystallography.

- In chapter 5, I introduce ferroelectric materials as a ‘tunable’ medium for exploring the role of symmetry properties in HHG and describe the structural phases in such targets. I demonstrate that harmonics generated from ferroelectric BaTiO$_3$ are sensitive to the magnitude and direction of the dipole moment and that the coherent control of emitted attosecond pulses may be possible by applying an external field. I describe the challenges that occur due to the light propagation in the bulk as well as the laser induced photorefractive effects in thin film ferroelectrics, and offer potential solutions, such as experimental methods based on Jones calculus for bulk ferroelectrics, and voltage measurements accompanied by low repetition rate mid-IR beam.

- In chapter 6, I compress the mid-infrared pulses down to the few-cycle regime using self-compression in bulk medium, and study the parameter space that allows such compression factors. I characterize the compressed pulses and utilize them to generate isolated attosecond pulses in ZnO with enhanced yield. The potential for further compression using microstructured fibers is explored.

This dissertation suggests the potential for using orientation-dependent and polarization-resolved measurements of high-order harmonics to probe structural properties in solids. With the addition of time resolution, such measurements could provide new perspectives on light-driven electronic population distributions and structural phase transition dynamics in novel heterostructures [29] and quantum materials [30,31].
The topics discussed in this dissertation were published in the following peer reviewed journal articles:

  * Equal contribution as Jiang, S., mentioned in the Authors’ contribution section.

and the following conference proceedings:

- Gholam-Mirzaei, S., Jiang, S., Crites, E., Beetar, J. E., Singh, M., Lin, C. D. & Chini, M. “Role of symmetry properties in polarization of high-order harmonics in ZnO” APS Division of Atomic, Molecular, and Optical Physics, Milwaukee, WI (May 2019).
- Gholam-Mirzaei, S., Crites, E., Beetar, J. E., Chen, A. & Chini, M. “Anisotropic polarization dependence of high harmonic generation in ferroelectric crystal BaTiO₃” APS Division of Atomic, Molecular and Optical Physics, Fort Lauderdale FL (June 2018).
• Gholam-Mirzaei, S., Crites, E., Beetar, J. E., Chen, A. & Chini, M. “Anisotropic polarization dependence of high harmonic generation in ferroelectric crystal BaTiO₃” Conference on Lasers and Electro-Optics (CLEO), San Jose CA (May 2018).


The topics related to the following articles and conference proceedings are not included:

Articles:


Conferences:


ultraviolet high harmonic generation in solids.” APS Division of Atomic, Molecular and Optical Physics, Sacramento CA (2017).
CHAPTER 2: HIGH HARMONIC GENERATION AND SPECTROSCOPY

2.1 High Harmonic Generation

When an intense light field is focused into a medium, integer multiples of the original light frequency, namely harmonics, are generated. The generated harmonics are the result of nonlinear light-matter interactions, which have historically been described using perturbation theory [32]. Second harmonic generation was first discovered in 1961 by Franken et. al. [33] using a commercially available ruby maser and with crystalline quartz as the nonlinear medium. In 1967 New et al. first observed third harmonic generation from inert gases [34]. Later, the advancement in laser technology allowed for exposure of materials to higher intensities and thus the generation of higher harmonic orders in gases. The discovery of higher order harmonics was first reported by Burnett et al. [35] at National Research Council of Canada where the interaction of intense CO$_2$ laser pulses with the plasma resulting from ablation of a quartz target lead to series of integer harmonic lines at reasonably high intensity extending from the third up to at least the eleventh harmonic. Following that, high harmonic generation (HHG) from gases were observed separately by McPherson et al. [36] and Ferray et al. [37] in the late 1980s.

The generation of low order harmonics can be understood in the weak field regime by considering an atom absorbing absorbing $n$ photons with frequency $\omega$, then emitting a single high-energy photon with frequency $n\omega$. Since the probability of absorbing $n$ photons decreases as $n$ grows, the spectrum of low-order (perturbative) harmonics is characterized by the sharp decrease in the harmonics intensity as the harmonic order grows. However, in the strong field regime [38],

---

1 4Trion Instruments, Inc., Model No. TO-3000
a slowly varying succession of high harmonics form a plateau-like region and a distinct cut-off frequency, above which no harmonics are generated, was observed in the experiments. The non-perturbative scaling of HHG suggested that the mechanism for the generation of high harmonics differed from that of perturbative harmonics driven at low intensities and began an effort to understand the underlying physics behind the generation of non-perturbative high harmonics. In 1993, in the separate studies, Corkum [39] and Kulander, Schafer, and Krause [40] developed a three-step model to describe the mechanism behind HHG process. The so called ‘recollision’ model, explains how the coherent generation of ultrashort XUV/x-ray pulses through a process involving (1) tunnel ionization of the electron wave packet, (2) propagation of the free electron in the field, and (3) electron-ion recombination can explain the observation of the high harmonic spectrum.

The three-step model can be explained in the following way for an isolated atom under the single active electron approximation. Initially, the ground state electron is bound to the nucleus by Coulomb force. When the strong laser beam is incident on the atom, it perturbs the Coulomb potential. At the peak of the laser field, the electron tunnels through the distorted potential barrier, and once set free, accelerates in the continuum. After approximately one quarter of the light wave's oscillation period, the sign of the field changes and the electron is forced back towards its parent ion, allowing for the electron-ion recombination. While atomic ionization and collision process both obey quantum mechanics, the acceleration of the electron can be treated classically. Hence, the model can be mathematically described as a semiclassical model.
2.1.1 Ionization

In the presence of an intense laser field, ionization can occur via either multiphoton absorption or field-induced tunneling. At moderate intensity, the atom can simultaneously absorb several photons, while at higher intensity the Coulomb potential is distorted to form the tunnel barrier during a single cycle of the laser field, allowing for tunnel ionization to occur on the timescale shorter than the inverse frequency of the light field. As a result, high intensity and low frequency driving beams are suited for tunnel ionization. This means that the ionization process can be quantitatively predicted for different frequency and intensity regimes of driving pulses. A quantitative description of multiphoton and tunnel ionization in an intense laser field was first realized by Keldysh [41], who theorized that the ionization regimes can be differentiated by the ratio of the laser frequency ($\omega_0$) to the tunneling frequency ($\omega_{tu}$) known as Keldysh parameter,
\( \gamma = \frac{\omega_0}{\omega_{tu}} \). Considering the cycle averaged kinetic energy that the electron gains in the laser field \( U_p \) as \( U_p = \frac{(E_0)^2}{4m_e\omega_0^2} \) (known as pondermotive energy, with \( E_0 \) as laser field strength), and the ionization potential \( I_p \) as \( I_p = \frac{(E_0)^2}{2m_e\omega_{tu}^2} \) the Kelydish parameter can be defined as \( \gamma = \sqrt{\frac{I_p}{2U_p}} = \omega_0 \frac{\sqrt{2I_p}}{E_0} \). When \( \gamma << 1 \), the cycle-averaged energy provided by the field is much larger than the ionization potential, meaning that the electron is able to overcome the Coulomb potential and be released to the continuum. Hence, for \( \gamma << 1 \), tunnel ionization dominates the generation of harmonics. In contrast, when \( \gamma >> 1 \), \( U_p \) is much smaller than \( I_p \) and the excitation of the electron from the ground state requires several photons to be absorbed, referring to the multiphoton ionization regime.

Intuitively, for the ease of understanding, the ionization regimes can be specified based the ratio between the equivalent classical time it takes for the electron to tunnel out the potential barrier while the potential is bent down. since the potential is bent down during half a cycle of the field oscillation and the ratio can be expressed as \( \gamma = \frac{t_{tu}}{T} \). Let us consider that the electron has zero velocity once released from the distorted Coulomb potential. The kinetic energy attained by the electron is \( I_p \), defining the electron velocity at the time of tunneling as \( v_0^2 = -2I_p^2 \). Therefore, \( v_0 = i\sqrt{2I_p} \). On the other hand, the work done by the laser field changes the kinetic energy of the electron while traveling the width of the potential barrier (\( x \)). Hence, \( I_p = E_0x = \frac{1}{2} E_0 v_0 t_{tu} \), resulting in \( t_{tu} = \frac{\sqrt{2I_p}}{E_0} \). From these calculations, we find \( \gamma = \frac{\sqrt{2I_p}}{TE_0} \), which is equivalent to the definition given in the previous paragraph.
In this approach, for $\gamma << 1$, the tunneling occurs in an extremely short time ($t_{tu}$), relative to the period of the laser ($T$), elaborating on the attosecond temporal duration of the emitted photon as a result. If $\gamma << 1$, the temporal duration for an emitted pulse will exceed the laser period, hence there is no chance for the emission of attosecond pulses. Over five decades, the Keldysh theory of photoionization has provided a universal framework for the qualitative analysis of ionization process and has been fundamental to the research in light-matter interaction.

### 2.1.2 Acceleration

The classical motion of the accelerated electron in the vicinity of the parent ion can be described by the equation of motion:

![Figure 2-2: Multiphoton and Tunneling Ionization Regimes](image)

*Panels present (a), multiphoton ionization, occurring when the frequency of the laser field is much larger than the tunneling frequency, and (b) tunneling ionization for which the tunneling frequency greatly exceeds that frequency of the intense light field responsible for the distortion of the Coulomb barrier.*
\[
\frac{d^2x}{dt^2} = \frac{e}{m_e} E_L(t) = -\frac{e}{m_e} E_0 \cos(\omega_0 t)
\]  
(2-1)

with \( m_e \) and \( e \) being the mass and the charge of the electron respectively, and the field is given by \( E_L(t) = E_0 \cos(\omega_0 t) \), where \( E_0 \) and \( \omega_0 \) are the driving laser amplitude and frequency respectively.

At the particular time \( t' \), namely the electron’s ‘birth time’, the electron escapes from the Coulomb potential, and equation (1-1) can be solved as

\[
x(t) = \frac{e E_0}{m_e \omega_0^2} \cos(\omega_0 t) - \cos(\omega_0 t') + \omega_0 \sin(\omega_0 t')(t - t')
\]  
(2-2)

Substituting \( x_0 = \frac{2e E_0}{m_e \omega_0^2} \) in equation (1-2) turns it into

\[
\frac{x(t)}{x_0} = \frac{1}{2} \left[ \cos(\omega_0 t) - \cos(\omega_0 t') + \omega_0 \sin(\omega_0 t')(t - t') \right]
\]  
(2-3)

Equation (2-3) is the normalized trajectory for an electron released at \( t'=0 \) and \( x_0 \) is the maximum displacement for the ionized electron.

**Figure 2-3: Different Recollision Electron Trajectories**

Panel represent the electron trajectories for different ionization/recombination events, differentiating between the emitted photons of different frequencies.
The resultant attosecond pulses from a recollision process can cover a broad range of photon energies (about hundreds of electron volts) and the energy of each emitted photon corresponds to a distinct excursion time which scales linearly with the driving wavelength. Different excursion times for the trajectories are presented in Figure 2-3.

2.1.3 Recombination

The electron-ion recollision at \( x_0(t) = 0 \) results in the emission of a photon with total energy of

\[
\hbar \omega \chi(t) = I_p + \frac{1}{2} m v^2(t) = I_p + 2 U_p \{\sin(\omega_d t) - \sin(\omega_d t')\}^2, \tag{2-4}
\]

with \( U_p = \frac{(eE_0)^2}{4m_e \omega_0^2} \). At the recollision time, the electron displacement can be written as

\[
x(t) \propto \left[ \cos(\omega_d t) - \cos(\omega_d t') + \omega_0 \sin(\omega_d t')(t - t') \right] = 0 \tag{2-5}
\]

The numerical solution for equation (1-5) can be written as

\[
\omega_d t = \frac{\pi}{2} - 3 \sin^{-1} \left( \frac{2 \omega_d t'}{\pi} - 1 \right) \tag{2-6}
\]

By combining equations (1-6) and (1-4) the energy of the emitted photon can be calculated as

\[
\hbar \omega \chi(t) = I_p + 2 U_p \{\cos[3 \sin^{-1}(\frac{2 \omega_d t'}{\pi} - 1)] - \sin(\omega_d t')\}^2 \tag{2-7}
\]

Now it is possible to numerically calculate the maximum kinetic energy of the electron, which is approximately \( 3.17 U_p \).

Finally, the cut-off energy of a photon can be obtained as

\[
E_{\text{cut-off}} = \hbar \omega = I_p + 3.17 U_p \tag{2-8}
\]
Figure 2-4: Three-step Model.

Panel shows the three-step process of strong field interaction with the medium during the course of a cycle. The time of ionization, acceleration and recombination of an electron is labeled.

From the classical approach to the electron propagation, some key features can be extracted from the HHG mechanism: First, tunnel ionization occurs at a distinct time. Second, the returning electron wave packet is a plane wave, and the recollision is dictated by the overlap with the ground state wave function. Third, the electron excursion time is incorporated into the emitted harmonic frequency. This means that the recollision harmonics can encode the information about the sub-optical dynamics of the electron and the parent ion. Lastly, the harmonic spectrum cut-off scales linearly with the driving beam’s intensity and quadratically with wavelength. Therefore, obtaining higher cut-off energy is viable by using longer wavelength or higher intensities in the experiment.
Figure 2-5: Attosecond Pulse Generation

Figure illustrates the recombination process, resulting in an attosecond pulse, and the creation of pulse train in the time domain during several cycles, and the emission of odd harmonics in the frequency domain. Even harmonics are suppressed due to symmetry of the medium.

The emission of an attosecond pulse occurs once per half laser cycle. Thus, for a multi-cycle pulse, a train of attosecond pulses is generated with a periodicity of half an optical cycle that corresponds to discrete harmonic peaks in the frequency domain, shown by Figure 2-5. In other words, HHG is a manifestation of attosecond pulse train [42].

2.2 High Harmonic Spectroscopy

In most time-resolved spectroscopy techniques, changes in the observable are measured as a function of the time delay between pump and probe, and can then be used to monitor the dynamic of excited molecules. In high harmonic spectroscopy, the intense driving laser field triggers the dynamics through ionization, while the emitted high harmonics serve as the probe. It uses the
three-step model to excite and capture the carrier dynamic [4,12,18]. The amplitude, phase, and polarization of the emitted photons encodes the information about the structural and electronic features of the parent ions as well [11,43,44]. Unlike traditional pump-probe measurements for which the obtained information from observables ties to the pulse envelope, high harmonic spectroscopy enables the access to the tunneling regime in the strong field, and offers the intrinsic sub-cycle temporal resolution in capturing the both the excitation and relaxation process. The coherent nature of the emitted harmonics enables coherent control of the light driven phenomena.

High harmonic spectroscopy is well suited to study the structure and dynamics of systems with broken inversion symmetry at specific spatial orientations, giving rise to the appearance of even harmonics. The relative intensities of the even harmonics encode information about both the orientation and the electronic asymmetry of the system. An instance of such application is to probe the evolution of electronic structure following a photochemical reaction on the sub-femtosecond time [45]. First, the molecules are excited as they are exposed to the laser field. The excited molecules follow the chemical process to the more stable state. Next, interferometric measurement of high harmonics emission from the excited and unexcited molecules is carried out, with excited molecules serving as the reference. In order for the measurements to be sensitive enough, phase locking of excited and unexcited molecules is required. The method has a high sensitivity to the transient electronic structure of the molecules arising from the photo-recombination step. This property can be further applied to capture the molecular vibrational dynamics[12], and coupling of electronic and nuclear motion[46].

High harmonic spectroscopy can be developed further to study strong-field electron dynamics in condensed matter and can provide insight into fundamental structural and dynamic
properties of solids. It can be applied to solids to study coupling of electronic and lattice dynamics, paving the way to probing the time-dependent carrier dynamics [47], or coherent phonon diffraction during phase transition [6,48] complementing existing techniques based on synchrotron-radiation, optical spectroscopies and time resolved x-ray diffraction. Yet, this requires thorough understanding of the generation mechanism of high harmonics from solids and developing techniques to control such systems. Here, the observation of high harmonics from solids and their application for spectroscopy of condensed matter systems is discussed.

2.3 Solid State High Harmonic Spectroscopy

In 2011, HHG from solids was discovered when emitted harmonics of up to 25th order resulted from focusing the intense mid-IR beam (\( \lambda = 3.25 \, \mu m \)) onto the exit plane of a zinc oxide crystal. The observed harmonics well exceeded beyond the band gap energy of the generation medium. Measurements of the intensity-dependent harmonic yield revealed that these harmonics did not follow the perturbative scaling laws of traditional nonlinear optics, and instead showed a non-perturbative scaling similar to that of gas-phase high harmonics. Surprisingly, contrary to the gas-phase harmonic generation, the cut-off energy from the harmonics spectrum of solids scaled linearly with the driving field strength. This different scaling behavior suggested that the generation mechanism of above-gap harmonics exhibits some differences from that of gas-phase harmonics. To understand the HHG picture in a solid material, it is worthwhile to draw an analogy between the energy levels in solids, or energy bands, and the energy orbitals in an atom. The valence band plays the role of highest occupied orbitals in the atom, and the conduction band can be linked to the lowest occupied orbitals. Analogous to the ionization potential, a band gap can be
defined for a solid target. For the electron to be ejected from the valence to the conduction band, it must tunnel through the band-gap. Considering the band-gap energy of the target, proper wavelength regime can be chosen to maintain the requirement for the tunnel ionization.

![Figure 2-6: Schematic Diagram of Solid-state HHG Mechanisms](image)

Panels a) and b) show the interband, and intra-band contributions respectively. Panel c) shows the contributions of multiple conduction bands, leading to a multiple plateau in the spectrum of harmonics.

By studying a two-band model of a wide bandgap semiconductors it has been demonstrated that harmonics can have essentially the same origin in solids as in gases. Hence, it is possible to generalize the picture of electrons and holes motions in solids to that of electrons and ions in gases, but with electrons and holes that move with band corrected masses within their respective bands in a semiconductor. More detailed research demonstrated that high harmonic radiations originate from two main competing mechanism, which govern the emission of ultrashort pulses in different frequency regimes. On one hand, the interband mechanism occurs when electron is pushed from the valence band to the conduction band at the peak of the laser cycle, and accelerate along the band until it has the chance to recombine with the hole that is left in the valence band. This recombination results in the emission of the XUV pulses known as interband, or recollison.
harmonics. On the other hand, intraband harmonics are emitted as the result of electron’s acceleration and Brillouin scattering. The intraband harmonics are considered the equivalents of Brunel’s harmonics in gas-phase harmonic generation. Recent study in ZnO and silicon shows that both inter- and intra-band harmonics contribute to high harmonic spectrum [49,50]. The details of solid-state two-band analysis will be discussed further in chapter 2.

High harmonics from solids have been demonstrated in variety of solid-state systems, including bulk insulators [51-54] and semiconductors [55-58], as well as thin film semiconductors down to a single mono-layer structures [59-61] and now is viewed as the universal feature of strong laser-solid interaction [62]. This has provided the platform for high harmonic spectroscopy to be utilized in a broad extent, and under extreme conditions where techniques such as angle resolved photoemission spectroscopy (ARPES) might not be feasible, or straightforward [14] (e.g. in the presence of high magnetic field or extreme pressure, materials with large band-gap). High harmonic spectroscopy is well suited to study the structure and excitation dynamics in crystalline solids [52,61] as the relative intensities and orientation of the harmonics encode information about both the structural and the electronic properties of the system. In centrosymmetric crystals, high harmonic spectroscopy sheds light on the real-space trajectory picture [52], and coupled inter- and intra-band mechanisms [49]. In spectroscopy of noncentrosymmetric crystals, appearance of even harmonics has been reported for laser polarization along high symmetry axes [27,58,59]. Similar to the case of atomic and molecular gases, the reliance of high harmonic generation on the polarization properties of the driving beam [27,63,64] suggests the polarization-resolved high harmonic spectroscopy as the route to study solids’ structural and symmetry properties in a more detailed and inclusive manner. Now perceived as the universal feature [27], the polarization-
resolved high harmonic spectroscopy enables the crystallography of condensed matter systems as a complementary technique to XRD measurements. This highlights the potential applicability of high harmonic spectroscopy to a broad range of ultrafast phenomena, such as coupling of electronic and lattice dynamics [65], charge migration in two dimensional heterojunctions [29], and transient structural changes during the phase transition [31,66], paving the way to probing the time-dependent electron density distribution, or band structure during a phase transition. Yet, this requires the generation and manipulation of high harmonics from such systems.
CHAPTER 3: HHG IN SOLIDS

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In this chapter, I describe the theoretical analysis for high harmonic generation in solid crystals, analogous to high harmonics emitted from atomic and molecular targets. By reviewing the advancement in the mid-IR laser technology, I discuss the potential for high harmonic emission from solid and experimentally demonstrate high harmonic generation by means of a high-power mid-infrared femtosecond laser source in an a-cut zinc oxide bulk crystal. By shifting the driving field’s frequency high harmonics are differentiated from the band fluorescence emission and the non-perturbative regime for both near- and above-gap harmonics is found through the intensity scaling of harmonics. Finally, I measure the conversion efficiency of near- and above-gap harmonics and show that the efficiency of such harmonic range is comparable to a gas-phase harmonics generated by a standard Ti:Sapphire laser, paving the way to the solid-state table top attosecond source.

3.1 Frontiers in Solid State HHG

Following the discovery of HHG in solids, new avenues in ultrafast condensed matter research emerged. The developed techniques for attosecond science in gases can be reformed and implemented to the solid phase. Solid targets offer a much denser medium from which attosecond pulses of UV/XUV can be generated with only a few TW/cm², which is nearly about 100 times less than the required intensity for gas-phase harmonics generation. Additionally, the optical damage threshold of the target medium scales favorably with decreasing pulse duration, allowing
for compact isolated attosecond light sources from solid-targets. Another benefit of solids as a medium for HHG is the chance to modify and tailor the target using principles from semiconductor processing to localize or boost the high harmonic generation process. Towards that end, a variety of condensed matter media such as bulk and thin film semiconductors, dielectrics, monolayers, and rare gas solids have been examined for high harmonics emission, and there has been growing interest in modifying the properties of semiconductors to enhance their capabilities as a route towards new HHG devices. Such techniques include controlling the material composition through ion implantation and doping (in which morphology and local composition of the target is altered), controlling the carrier density through pre-excitation, and fabrication of conically shaped nanostructures that has been investigated both in theory and in experiment.

However, solid-phase HHG light sources can be developed only if reasonable conversion efficiency for harmonics is achieved from solids. Aside from that, advancing HHG-based spectroscopies requires dependable sources and models of HHG, and therefore the generation of high harmonics still needs to be studied in a wide range of solid systems. Lately, numerous studies have examined the emission of harmonics for different spectral ranges in the visible to XUV regime. Such studies reveal multiple distinctions between gas-phase and solid-phase harmonics. Rapid dephasing of harmonics which is absent in gases, the linear dependence of the cut-off energy, the presence of second plateau region in the spectrum of emitted harmonics, and unusual polarization dependence of emitted harmonics still show the need to understand the material-specific electron dynamics underlying solid-state HHG.
3.2 Three-step Model in Momentum Space

To discuss the high harmonics generation mechanism in solids, the representation of the atomic three-step model in the momentum space can shed light on understanding of the electron-hole dynamics. As mentioned in Chapter 1, in an atom, the electron is bound to the ground state. At the peak of the laser field, the electron is freed from the Coulomb potential and occupies the lowest energy state in the continuum with energy of $E = \frac{p^2}{2m_e}$, describing a parabolic band shape. The acceleration of electron, described by equation (1-1), can result in the gained momentum, defined as $P(t) = A(t) - A'(t)$. In solids, however, the valence electron originally resides in the continuum of occupied states, represented by the valence band, and is separated from the lowest unoccupied band (conduction band) by a minimum energy, referred to as the band gap energy. Since the valence bands are also represented by the continua of states, the electrons are considered delocalized in the quantum mechanical framework. The bands are defined by more complex non-parabolic functions due to the interactions with the ion lattice. In the following section, the motion
of the electron in momentum space is described in detail, to describe the recollision picture of HHG in both gases and solids.

**Figure 3-1: Representation of the Energy Levels in Solids Vs Atoms**

*Panel a) shows the atomic energy levels. The electron is initially localized in the ground state, and release to the continuum. panel b) refers to the solid energy levels. Both valence and conduction bands are defined by continua of states.*

Let us follow the motion of the electron in the valence band due to the intense light field: close to the peak of the laser field, the electron tunnels through the band gap to conduction band. The tunneling can occur at $k \neq 0$ (depending on the bands function) and with a different rate from the atomic case. Here crystal momentum is defined as $k$, to distinguish it from the real space momentum. For the ease of understanding, the comparison between tunneling in the atoms and solids is shown in Figure 3-1. Let us consider that the ionization happens at $k \neq 0$, where the electron tunnels through the minimum bandgap. The laser field accelerates the electron-hole pair along their corresponding bands. Unlike the atomic case, the hole in solids also move with the same momentum as the electron. In the real space, the hole accelerates in opposite direction with respect to the electron’s motion. However, in the momentum space, the electron-hole pairs move
in the same direction, and the momentum has the same sign for both. As the electron accelerates along the band, it may undergo periodic oscillations in the conduction band, scatter from the edge of the Brillouin zone, continues oscillation in the conduction band, and ultimately re-encounter the corresponding hole, at which point recombination or recollision of the electron/hole pair is possible. In the atomic model, the electron in the continuum has a momentum of \( \mathbf{p}(t) = m\mathbf{v}(t) \) whereas in solids, the form of the band is more complex and cannot be treated as parabolic shape. Hence, the velocity is given by the gradient of the momentum-dependent field:

\[
v_m(k) = \nabla_k E_m(k)
\]

(3-1)

Hence, the motion of electron and hole is calculated according to:

\[
x_e(t) = \int \nabla_k E_e(k(t))dt, x_h(t) = \int \nabla_k E_h(k(t))d\tau
\]

(3-2)

Where \( c \) represents conduction band and \( v \) stands for valence band. Solving equation (3-2) by substituting \( k(t) = A(t) - A'(t) \), results in the trajectory of the electron and hole. From equation (3-2), we can see that the trajectory of an electron in a solid depends not only on the band structure, but also on what part of the band the carrier explores. Furthermore, the energy of the recollision electron in the two-band model is limited to the maximum band gap energy, unlike in atoms. Including the higher conduction energy bands can give rise to the formation of multiple plateaus which can extension of the cut-off in the spectrum of emitted harmonics to XUV regime [51,53,67].

The main features in the atomic, and solid three-step models are summarized below:
• In atomic HHG, the electron is initially localized within the ground state and only the final state lies within the continuum. In solids, besides the conduction band(s), valence band(s) also lies within the continuum, and the electrons are delocalized.

• In solids, contrary to the atomic three-step model, the bands are nonparabolic, and the lowest band gap can be found at \( k \neq 0 \). For most of the semiconductors, the maximum of the valence band is located at \( k = 0 \). However, some like silicon, have indirect band gap due to the minimum of the conduction band at \( k \neq 0 \) [68]. In such cases, the momentum conservation would be met by absorption/emission of phonons.

• In the atomic three-step model the continuum states can be described in momentum space as parabolic. However, for solid-HHG, the bands functions are non-parabolic.

• In solid-HHG, the hole is not stationary. Like the electron, it is driven by the laser field. The hole moves in the opposite direction as the electron in real space, and in the same direction as the electron does in momentum space.

• Considering only two bands, the maximum band gap energy presents a maximum value for the harmonic cut-off, which is not the case for atomic recollision model. However, if higher conduction energy bands are involved, multiple plateaus with extended cut-off energies are obtained [51,53,67].

Similar to the case of an atomic system, short and long trajectories can be defined based on different excursions of the electrons. As Figure 3-2 suggests, in the picture provided by the recollision model, high harmonics can be similarly emitted from the recombination of electron-hole pair that are created after the peak of the laser field, with short trajectories recolliding earlier, and long trajectories recolliding later, thus having higher excursion than the trajectories
responsible for the cut-off. The contribution of long trajectories in the atomic HHG is hard to probe due to the small recombination cross section and that the large dipole phase causes such trajectories to be highly divergent [69]. In solids, long trajectories have not been experimentally observed.

![Diagram](image)

**Figure 3-2: Long and Short Trajectories**

*Long and short trajectories correspond to electron-hole pair with different ionization/recollision times.*

*Unlike the atomic high harmonic generation, long trajectories from solids are not detected.*

Finally, in order to realistically describe HHG in solids, the existence of carrier interactions, namely the electron-electron, electron-hole, and electron-phonon interactions, ultimately results in the relatively shortened effective lifetimes for intraband carriers [70-72], which is known as dephasing. This, in turn, affects the coherence in the interband harmonics. Dephasing times in semiconductors have been measured using four-wave mixing spectroscopy to be on the order of ~10 fs [73]. However, in solid-state HHG, phenomenological dephasing times on the order of ~2 fs are required to reproduce experimental results [28,74]. The reason for this discrepancy is still not known. However, due to the rapid dephasing, detection of the long
trajectories is challenging. Short dephasing time also suppresses occurrence of recombination, as it greatly reduces the chance for the electrons to explore the higher energy portion of the band. In the theoretical studies, tuning the value of dephasing time indicates that for long enough dephasing time, the effect of long trajectories is pronounced and intensity modulation of the odd harmonics occurs as the result of interference between the quantum paths of short and long trajectories [75]. variation of the intensity in the pulse envelope can add to the effect of interference, and ultimately causes the harmonic to lose their distinct spectral peaks [74,75].

3.3 Theoretical Framework for HHG in Solids

The theoretical models to derive high harmonics from solid materials mainly rely on time-dependent Schrödinger equation (TDSE) [76], semiconductor Bloch equations (SBEs) [77,78], and time dependent density functional theory (TDDFT) [79,80]. For a standard semiconductor material such as ZnO, considering that only two (the highest valence and the lowest conduction) bands effectively reproduce the experimental HHG spectrum [81], using one-dimensional SBEs offers a simple and convenient framework for a qualitative description of HHG, including the effects of dephasing of the electron trajectories through the inclusion of one or more phenomenological dephasing times [82], to take into account the effect of electron-phonon scattering and impurities [77]. To study the strong carrier correlations in the materials, the calculations based on TDDFT is ongoing.

In a semiconductor driven by a mid-infrared laser pulse the harmonic emission is given by the Fourier transform of the coherent sum of the intraband \( J_{ra} \), and interband, \( J_{er} \) current oscillations, \( J(t) = J_{ra}(t) + J_{er}(t) \) [13,83]. These components are defined according to:
Here, $m$ is an index which denotes the band ($m = v$ or $c$) for valence and conduction band, respectively. $v_m(k) = \nabla_k E_m(k)$ is the group velocity corresponding to the $m$-th band, $E_m(k)$ is the energy dispersion relation. $K = k - \mathbf{A}(t)$ is the quasi-canonical momentum defined in terms of the electron crystal momentum $k$ and the vector potential $\mathbf{A}(t)$ of the laser electric field through $E(t) = -\partial_t \mathbf{A}(t)$. This can be understood as that the crystal momentum $k$ has been transformed into a reference frame moving with the vector potential. The transition dipole matrix element between the conduction and valence band is defined by $d(K) = i \int u_v^*(x) \nabla_k u_c(x) d^3x$, with $u_{m,k}(x)$ the periodic part of the Bloch functions. The integral is performed on the first Brillouin zone shifted by the vector potential, $\overline{BZ} = BZ - \mathbf{A}(t)$. $n_m(K, t)$ and $\pi(K, t)$ are the population at each band and the coherence of the medium as function of the momentum and time. Our main task is to compute these last two quantities, known as semiconductor Bloch equations (SBEs) describe the response of solid material when interacting with the laser.

The coupled differential equations for population and coherence need to be solved in order to calculate the inter- and intra-band contributions to the total momentum. The moving reference
frame \(BZ\) allows us to remove the gradient term with respect to the crystal momentum \(\nabla_k\), resulting in the modified versions:

\[
\hat{\pi}(\mathbf{K}, t) = -i \left[ \varepsilon_s(\mathbf{k} + \mathbf{A}(t)) - i \frac{1}{T_2} \right] \pi(\mathbf{K}, t) - i \mathbf{E}(t) \cdot \mathbf{d}(\mathbf{K} + \mathbf{A}(t)) \omega(\mathbf{K}, t) \quad (3-5)
\]

\[
\hat{n}(\mathbf{K}, t) = i s_m \mathbf{E}(t) \cdot \mathbf{d}^* (\mathbf{K} + \mathbf{A}(t)) \pi(\mathbf{K}, t) + c.c. \quad (3-6)
\]

Here, \(s_m\) has the value +1 or -1 for \((m = v \text{ or } c)\) and is the energy gap between the conduction and valence bands. \(T_2\) is the parameter that includes the dephasing time. The difference in the population of valence and conduction band is defined by \(\omega = n_v - n_c\). Based on the Keldysh approximation, \(\omega(\mathbf{K}, t) \approx 1\) assumes that the population in the valence band remains the same throughout the time-dependent laser-crystal interaction, which is a valid assumption for mid-infrared lasers with intensity below \(~10^{13}\) W/cm\(^2\).

The advantages of SBEs is that they do not explicitly depend on the semiclassical action, \(S(\mathbf{K}, t) = \int_{-\infty}^{t} \varepsilon_g(\mathbf{K} + \mathbf{A}(t')) dt'\). As the result, simulations are less complex as one does not need to calculate the fast oscillating term \(S(\mathbf{K}, t)\) at each time step.

### 3.4 Mid-IR Laser Technology for Solid State HHG

Current advancement in the ultrafast laser systems has led the way towards accessing attosecond temporal resolution from gases and solids [25,84,85]. In solids, the few-cycle pulses in the mid-infrared regime has been utilized to study several ultrafast (femtosecond) phenomena resulting from the interaction of the intense light field with solids. The ponderomotive energy provided by the laser field scales quadratically with the driving wavelength. Thus, it is greater for the interaction of the mid-IR laser with solids relative to the visible, and NIR driving beams. This
means that for band semiconductors and dielectrics, the Keldysh parameter is less than one, corresponding to tunnel excitation regime, even with intensities as low as a few TW/cm². In particular, for band-gap solids, the photon energy of mid-IR pulses is much smaller than the band gap energy of the target, and the strong-field regime is accessible with moderate intensities, and the damage to the target due to few-photon excitation can be avoided. Another merit of using femtosecond mid-IR pulses to generate high harmonics is that the emitted harmonics normally cover the visible to ultraviolet spectral range are easier to detect and do not require ultrahigh vacuum conditions.

The technological progress in ultrashort pulse generation from solid-state laser systems has led power scalable sources of femtosecond pulses, based on two gain media; Ti:sapphire or Yb:doped fiber and solid state amplifiers. One of the main limitations associated with applying such sources for applications to time-resolved spectroscopy and strong-field physics is the fixed wavelengths at which they operate (800 nm for Ti:sapphire and 1030 nm for Yb), as such applications require ultrashort pulses with broad or tunable spectral range. In particular, for high harmonic generation process, the wavelength tunability of the driver pulses is plays a crucial role as different driving wavelengths can affect the harmonics spectrum cutoff and the ionization event.

As of now, no active laser media can support broadly wavelength tunable sources in the mid-infrared. However, there is the potential to utilize high peak powers of ultrafast sources to generate intense, tunable, femtosecond mid-IR pulses using the second order nonlinear optical effect known as optical parametric amplification (OPA). Based on OPA technique, the high frequency and high intensity pump beam ($\omega_{pump}$) transfers its energy to an amplified signal beam
(\(\omega_{\text{signal}}\)) in an appropriate nonlinear medium, and a long-wavelength idler beam (\(\omega_{\text{idler}}\)) is generated through difference-frequency generation. Conservation of energy requires that:

\[
\omega_{\text{idler}} = \omega_{\text{pump}} - \omega_{\text{signal}}
\]

with \(0 < \omega_{\text{idler}} < \omega_{\text{signal}} < \omega_{\text{pump}}\). The efficiency of the process relies on the phase-matching condition \(\mathbf{k}_{\text{pump}} - \mathbf{k}_{\text{signal}} - \mathbf{k}_{\text{idler}} = 0\) where \(\mathbf{k}\) is the wave vectors of the corresponding beams.

Figure 3-3: Optical Parametric Amplification (OPA)

Panel a) represents the Interaction geometry for difference frequency generation while panel b) corresponds to the energy-level diagram of difference frequency generation. In panel c), the OPA process is visualized as the power flow from an intense pump beam to a weak signal beam.

For the experiments described in this dissertation, femtosecond pulses in the mid-IR regime from a commercial OPA system (Light Conversion ORPHEUS) pumped by a high power solid state Yb:KGW regenerative amplifier (Light Conversion PHAROS) are utilized to generate high harmonics in solids. The laser provides up to 20 W of average power, with central wavelength of 1030 nm and tunable repetition rate (50-200 kHz). The OPA is pumped by 400 µJ, 280 fs pulses at repetition rate of 50 kHz, and after two amplification stages, the resultant idler wavelength pulses are tunable in wavelength from 2.5 to 4 µm. The idler pulse energy is greater than 10 µJ in the 3-4 µm spectral range. The tunable spectrum of the mid-IR output is shown in Figure 3-4. The
wavelength scan of the idler shows that for 3.8 μm, the spectral bandwidth exceeds 0.5 eV. For longer wavelengths, the absorption feature due to CO₂ in air is observed.

![Figure 3-4: Spectral Properties of OPA Idler Wavelength](image)

*Panel (a) shows the power and pulse energy for different signal and idler wavelengths. Panel (b) shows the normalized intensity of different idler wavelengths. Pulses with central wavelength of 3.8 μm have maximum energy bandwidth compared to other wavelength and amount of CO₂ absorption is negligible.*

**3.5 HHG from a-cut Bulk Zinc Oxide**

**3.5.1 Experimental Setup**

Since the pulses emitted from the OPA are negatively chirped, bulk silicon was used as a dispersive medium to compensate for the chirp. After dispersion compensation, the pulse duration was measured using Frequency-Resolved Optical Gating (FROG), with surface third-harmonic generation (THG) as the nonlinear process. For 3.8 μm central wavelength, a pulse duration of ~90 fs was obtained. The pulse characterization step is explained in chapter 5 in more details.
Panels (a,b) show the measured, and retrieved FROG traces of the idler beam, respectively, corresponding to 90 fs pulse duration from the OPA idler. Panel (c) presents the temporal profile of the pulse for a 3.8 μm idler wavelength.

The unchirped pulses are subsequently magnified and focused close to the exit plane of a bulk a-cut zinc oxide, and the emitted harmonics in transmission geometry are detected with the help of a UV-enhanced high resolution grating spectrometer (Ocean HR 2000+ES). The schematic of the HHG setup is shown in Figure 3-5. The focal spot size of 60 μm on the crystal was measured using knife edge technique.

The idler pulses are focused to the exit plane of ZnO bulk crystal and the emitted harmonics are detected. CM stands for ‘Aluminum enhanced curved mirror’. All other mirrors are flat.
3.5.2 HHG Spectrum

To optimize the generated harmonics, the crystal was scanned along the beam propagation direction, and the corresponding harmonics spectrum was recorded using two different integration time to allow for spectral characterization of both below- and above-gap harmonics (1ms for below-gap harmonics, 500 ms for above-gap harmonics). Figure 3-6 shows the spectrum consisting of the plateau harmonics and the extension of the cut of in the UV regime. Due to the limited spectral range of the spectrometer, harmonics higher than 17th order are not detectable.

![Figure 3-7: HHG Spectrum of a-cut ZnO](image)

The detected harmonic spectrum stretches to 17th order, close to the spectrometer detection limit. Below- and above-gap harmonics are separated by the dashed line and measured using 1 ms, and 500 ms integration time, respectively.

3.5.3 Wavelength Dependence of HHG Spectra

To be able to differentiate the generated harmonics from other potential emissions, the wavelength scan of the driving beam is performed, and the corresponding harmonics intensity is plotted in figure 3-7. As expected, the frequency of the harmonics radiation shifts as the result of the driving wavelength scan whereas the band florescence remains stationary at around 800 THz ($E_{\text{gap}}=3.3\text{ eV}$) [86]. The change in the harmonic flux is possibly caused by the differences in the
intensity of different idler wavelengths. The pulse energy and duration are both optimized for \( \lambda = 3.8 \, \mu m \).

![Figure 3-8: HHG Spectrum for Various Idler Wavelengths from 3.4 \mu m to 4 \mu m](image)

*The panel shows the shift in the harmonics frequency as the result of change in the idler wavelength. The band fluorescence shown by red dashed line is stationary unlike the emitted harmonics. The silicon thickness to compensate for the dispersion is optimized for 3.8 \mu m driving beam.*

### 3.5.4 Non-perturbative Behavior of HHG

Next, the intensity dependence of below- and above-gap harmonics has been studied by increasing the intensity of the driving source. The purpose of this measurement is to explore the nature of the generated harmonics. Harmonics that are generated in the perturbative regime follow the intensity scaling, meaning that their intensity following \( I_n = I_0^n \). Here, \( I_0 \) is the intensity of the driving beam, \( n \) is the harmonics order, and \( I_n \) is the corresponding harmonics intensity. As figure 3-8 demonstrates, below-gap harmonics are generated in the perturbative regime, and they conform with the intensity scaling, while near- and above-gap harmonics deviate from the intensity scaling as the driving beam intensities goes beyond 1 TW/cm². These harmonics are
nonperturbative in nature since, contrary to the predictions of non-linear optics, their scaling is almost irrespective of the harmonic order [87].

Figure 3-9: Harmonics Yield as a Function of the Fundamental Intensity

The non-perturbative scaling for below-gap harmonics appears for driving beam intensity larger than \(~1.72\ \text{TW/cm}^2\). Above gap harmonics deviate from the perturbative scaling for laser intensity larger than \(1\ \text{TW/cm}^2\).

3.5.5 Conversion Efficiency

As mentioned earlier, one important aspect of solid-phase HHG is the potential to generate high flux table-top isolated attosecond sources. The high average power of the OPA allows for direct measurement of the conversion efficiency and average power of visible and UV harmonics. By using a calibrated Si photodetector, the conversion efficiency for 11\textsuperscript{th} to 17\textsuperscript{th} harmonics has been measured. The plot in figure 3-9 confirms the conversion efficiency of 11\textsuperscript{th} to 17\textsuperscript{th} harmonics change from \(10^{-7}\) up to \(10^{-6}\) with average power of \(~0.1\) to \(1\) microwatt per harmonic. These results suggest that conversion efficiencies of solid-phase harmonics are comparable to the measured conversion efficiency of HHG produced in noble gases by 0.8 µm driving laser beam [88].
The conversion efficiency of above-gap harmonics results in the average power of ~0.1 to 1 microwatt per harmonic, allowing for efficient solid-phase harmonics source similar to [88].
CHAPTER 4: HHG AND SYMMETRY PROPERTIES IN CRYSTALS

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In the following chapter, I explain the connection between symmetry of the medium and the generation of high harmonics and elaborate on how inversion symmetry governs the generation of high harmonics from crystalline solids. I study the polarization properties of the emitted harmonics, and discuss the role of structural symmetry in determining their polarization states, with respect to the laser source polarization. From the theoretical point of view, I describe how the dipole amplitude and phase is associated with the symmetry of the medium. Thereby, I establish the polarization properties of solid-state harmonics as the universal features of solids which are largely ruled by symmetry. With this, I conclude that the polarization-resolved high harmonic spectroscopy can be employed as a sensitive probe for investigating structural symmetry of crystalline solids.

4.1 Solids and Structural Symmetry

The study of the structural dynamics in different states of matter helps towards understanding their properties and the nature of the existing forces that forms the materials. Particularly in the case of solids, study of the structure and the arrangements of atoms in space allows for categorizing them into two distinct groups: crystalline and amorphous solids. As mentioned in [89]: “a crystalline solid is defined by units in which atoms hold a systematic arrangement in a certain geometric pattern.” The crystalline solid is able to maintain the same arrangement of atoms for relatively large distances compared to the interatomic distances. Unlike
crystals, in amorphous solids atoms do not follow a repetitive arrangement in a definite order over long distances. They might consist of microcrystalline structures, but the recurrence of such arrangements are limited to distances as short as the interatomic distances. In other words: “an amorphous solid is one in which three dimensional periodicities are absent.” [90]. This chapter focuses on the symmetry and the structural properties of crystalline solids.

In Physics, symmetry is defined as a transformation that doesn't change the physics of the system. In crystalline solids, the atomic orientation usually maintains specific symmetry. When symmetry exists in the crystal, it maintains the same atomic orientation after undergoing the relevant transformation about the defined symmetry axes. There are several types of symmetries that are observed in the crystals, examples of that is translation, rotation, and inversion.

Translational symmetry deals with situating atoms with their identical neighbors in a manner that preserves the same atomic orientation. The displacement that each atoms undergoes is described by the distance and the direction. Rotational symmetry defined as the invariance of the crystal structure when turned around an axis that passes through a fixed point in the arrangement; Inversion symmetry reallocates the atom to their mirror image without the change in the final structure when compared to the initial structure. That means that it is possible to define a mirror symmetry axis for which the structure on both sides of the axis look alike.

Crystals are also categorized to seven different systems based on the assembly and the shape of their unit cells. Within each category, there can be plenty of variations for the atom, or the group of atoms to be placed at the center or each faces besides the ones at the corners of the lattice. These variations are known as Bravais Lattice, and defines 32 subdivisions of crystal classes.
4.2 Role of Symmetry in HHG

In nonlinear optics, the emission of optical harmonics and the resultant selection rules in the generation process is connected to the symmetry of the medium [32,91]. In the perturbative regime, symmetry is contained in the structure of the susceptibility tensor [92]. Based on the perturbative analysis, the material’s nonlinear response to moderately strong field is described by:

\[ P(E) = \varepsilon_0 (\chi^{(1)} E + \chi^{(2)} E_0 E + ...) \]  \hspace{1cm} (4-1)

Similarly, in the non-perturbative regime, emission of high order harmonics has been associated with the symmetries of the generation medium. The first experimental realization of high harmonics generation in rare-gas atoms, [37] demonstrated the absence of even harmonics which corresponds to the structural symmetry in the target. One may explain this with the help of the superposition rules: In a linearly polarized laser field, the generation of harmonics is due to the interference between emissions from adjacent half-cycles. As the recombination occurs per half-cycle, with each flip in the driving field direction, the phase of the emitted harmonic acquires an added \( \pi \) shift relative to the adjacent emission. The interference becomes constructive for odd harmonics and destructive for even harmonics.

Below is the mathematical description for the superposition of only two harmonic waves of frequency \( n\omega_0 \), with the relative delay equal to half an optical cycle, suggesting the constraint for generation of even harmonics:

\[ e^{in\omega_0 t} - e^{i(n\omega_0 t + \pi)} = e^{in\omega_0 t} (1 - e^{in\pi}) = \begin{cases} 2e^{in\omega_0 t} & \text{if } n \text{ is odd}, \\ 0 & \text{if } n \text{ is even}. \end{cases} \]  \hspace{1cm} (4-2)
<table>
<thead>
<tr>
<th>Crystal family</th>
<th>Primitive</th>
<th>Base-centered</th>
<th>Body-centered</th>
<th>Face-centered</th>
</tr>
</thead>
<tbody>
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<td><img src="image2" alt="Cubic Base-centered" /></td>
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</tr>
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<td><img src="image27" alt="Hexagonal Body-centered" /></td>
<td><img src="image28" alt="Hexagonal Face-centered" /></td>
</tr>
</tbody>
</table>

Table 4-1: Crystal Families and Their Bravais Lattice

All 7 crystal families and their corresponding 14 Bravais lattice structures are presented
The emission of even harmonics as a result of broken inversion symmetry is a particular instance of more fundamental understanding of the effect of spatio-temporal symmetries in selection rules in high harmonics emission. In both classical and quantum physics, symmetry of a system is associated with the invariance in the equations of motion and corresponds to conservation laws and selection rules. Transformations can be incorporated into a unitary operator, and as long as the operator commutes with the Hamiltonian of a system, it defines a symmetry. To understand the influence of symmetry on the HHG in more generalized context, dynamical symmetry [93] offers a framework to investigate the spatio-temporal properties of the light-matter system. More specifically, the rules for the generation of harmonics can be extracted from the dynamical symmetry of the Hamiltonian [94] which describes the interaction of strong light field with the target. If we dismiss the spin-orbit interaction, nuclear spin energy, and inter-nuclear repulsions (Born-Oppenheimer approximation), the Hamiltonian of the light-matter interaction can be defined as $H_{HHG} = E_{kin} + V_{ij} + V_j + V_L$ where $E$ is the kinetic energy, $V_{ij}$ is the electron-electron interaction, $V_j$ is the Coulomb potential, and $V_L$ is the term related to the light matter interaction (with dipole approximation).

By substituting the microscopic definitions into the Hamiltonian, we have

$$H_{HHG}(t) = -\frac{1}{2} \sum_j \nabla_j^2 + \frac{1}{2} \sum_{i,j} \frac{1}{r_i - r_j} + \sum_j V(r_j) + \sum_j E(t) \cdot r_j$$

(4-3)

Where $r_j$ is the coordinate of the $j$’th electron, $\nabla_j^2$ is the Laplacian operator with respect to $r_j$, $V(r)$ is the potential energy, and $E(t)$ is the electric field of the driving laser.

As mentioned earlier, a dynamical symmetry which commutes with the Hamiltonian gives rise to selection rules. By reviewing Equation 4-3, it is clear that the first three parts in the
Hamiltonian are time-independent and the laser–matter interaction term is the only time-dependent part of the Hamiltonian. Hence, the time symmetry of the laser field, \( E(t) \) has a definitive role the dynamical symmetry of the system. Following the same approach for the special symmetries, the kinetic and electron–electron interaction terms, are both invariant under all possible rotations and reflections. Hence, the spatial symmetries of \( V(\mathbf{r}) \) corresponds to the selection rules in the harmonic spectrum.

The above description links high harmonics generation rules to the time symmetry of the driving field as well as the spatial symmetry the medium. In the following section, the role of special symmetry and the atomic orientation in the lattice, and in particular, the reflection symmetry of the target in HHG spectral features from ZnO is investigated.

4.2.1 Symmetry and HHG Spectrum in Zinc Oxide

In this section, the orientation dependence of emitted harmonics to the three-dimensional structure of the ZnO crystal is investigated, with the use of same experimental configuration that has been used to generate high harmonics in the previous chapter.

**Figure 4-1: Orientation Dependent Properties of Emitted Harmonics**

Panel a) represents the 3D crystal Structure of ZnO. Panel b) shows the laser polarization direction normal to the propagation direction, laying within the crystal’s a-plane (11-20). Panel c) demonstrates the orientation dependent spectra of emitted harmonics.
The crystal is mounted in the rotation stage to enable the rotation of crystal plane about its normal. Since the beam propagates along the normal of the crystal plane, the laser polarization lies within the surface a-plane of ZnO.

Figure 4-1c confirms that odd harmonics are emitted for every $\pi/2$ rotation of the laser polarization direction with respect to c-axis whereas even harmonics are generated when laser polarization direction is along the high symmetry axis of the crystal (every $\pi$ rotation), for which the inversion symmetry is broken. In the next step, the crystal is mounted in the adaptor with a slight tilt to create a non-zero projection of the polarization on the c-plane (Figure 4-2a). In this case, odd harmonics exhibit different periodicity; a six-fold periodicity in the spectrum of odd orders was observed and maxima appears in periods of $\pi/3$. This feature can be view as the effect of hexagonal arrangement of atoms in the c-plane in wurtzite ZnO. The measurements support sensitivity of HHG process to the 3D structure of the crystal, due to electron trajectories driven outside the plane of the crystal surface.

Figure 4-2: Orientation Dependent High Harmonics from a Tilted Plane

As shown in panel a), the laser polarization normal to the propagation direction has a component in the crystal’s c-plane (0001). Panel b) shows the plotted orientation-dependent spectra of emitted harmonics.
As discussed earlier, for the generation of even harmonics, the broken inversion symmetry of the system needs to be broken. In the theoretical framework, a number of approaches have been employed to incorporate the broken symmetry into the simulation. One way is to include the effect of multiple bands in the calculation, which in turn, lengthens the theoretical efforts. The other adaptation has been to apply a weak second harmonic field in addition to the fundamental driving field to break the dynamical symmetry of the system [95,96]. Still, the appropriate treatment of the dipole matrix elements had been overlooked for so long. The harmonic generation spectrum is obtained by taking the Fourier transform of the time-dependent expectation value of the dipole moment operator in the resonance state if the Hamiltonian is written in the length gauge [97]. However, in almost all of the simulations of high harmonics spectrum, only the magnitude of dipole moment has been considered the phase has been overlooked, until recently when Jiang et. al. [81,98] accounted for both amplitude and phase of the transition dipole elements. This complementary approach has allowed for the first time the replica of most features in the spectra of even harmonics in ZnO obtained from the experiment.

Figure 4-3 illustrates the zinc and oxygen arrangement for the a-cut sample. As the laser focuses at the target and its polarization is rotated with respect to optic axis of the crystal, harmonics exhibit orientation dependent in their spectrum. Here, panel b) shows the zoomed color-scale plot of Figure 4-1 b). Additional weak peaks at $\theta=60^\circ$ an $\theta=120^\circ$ is present in the spectra of even harmonics. These weak symmetry features reproduced in the theoretical model by Jiang et. al. [81] are reliant of both the amplitude and phase of dipole matrix element. As illustrated in Figure 4-4, at $\theta=72^\circ$ an $\theta=108^\circ$ where laser is parallel to Zn-O bond direction, the square of absolute value of the dipole moment in the calculation increases, and the spectrum of $11^{th}$ (odd)
harmonic is maximized in this region. Similarly, when the magnitude of transition dipole multiplied by the square of absolute value of phase maximizes in the calculation, the spectrum of $12^{th}$ (even) harmonic exhibits peaks at $\theta=60^\circ$ and $\theta=120^\circ$. By switching the phase term of the transition dipole on/off, the weak features appear/vanish in the orientation dependent spectrum of even harmonics.

![Image of crystal structure and measurement setup]

**figure 4-3: Strong and Weak Symmetry Features of HHG**

The arrangement of zinc and oxygen atoms in the crystal’s a-plane has been illustrated in panel a). $P_{MIR}$ shows the laser polarization direction while $C$ shows the direction of the optical axis. $\theta$ is the relative angle between the laser polarization and c-axis. In panel b), strong and weak symmetry dependent features in the orientation dependence of above-gap harmonics arises from the variation of $\theta$.

The orientation dependent spectral measurements which are presented here do not discriminated between parallel and perpendicularly polarized harmonics. However, as previous studies point out, the polarization states of the emitted harmonics originates from different mechanism [43,44,63,64]. In the following section, I discuss different aspects of polarization techniques in Gases and solid harmonics.
Figure 4-4: Theoretical and Experimental Orientation Dependence Harmonics

Panels a, b) illustrates the comparison of theoretical and experimental orientation-dependent harmonic strength of the 11th and the 12th harmonics, respectively. Panel c) shows the growth of the transition dipole magnitude between $\theta=72^\circ$, and $\theta=108^\circ$, along Zn and O bonds direction. Panel d) includes the transition dipole magnitude multiplied by the square of the phase of the transition dipole at $k=0.2$. Panels e) and f) respectively show once the square of absolute value of phase is turned on, and off in the definition of transition dipole term reproduced from the experimental data in [58] and simulations in [81].

4.3 Symmetry and Polarization Properties of HHG

For decades, polarization techniques have been applied to nonlinear measurements and were used as spectroscopic methods to probe the spatial symmetry of different nonlinear media[99]. Recently, polarization resolved measurements have been extended into the highly nonlinear phenomena, such as high harmonic generation, both in gases [43,44] and solids [63,64]
suggesting a novel way to resolve the spatial symmetry properties of molecular orbitals as well as the structural properties of solid targets.

To explain the role of polarization resolved measurements of emitted harmonics, it is worthwhile establish the link between symmetry and polarization properties of HHG from atomic gases. Generally, high harmonics are emitted when an atomic gas is ionized by intense ultrafast laser pulses. As studies suggest, when the ellipticity of the driving field changes, the polarization distribution of the emitted harmonics largely depends on the change in the angle of the recollision electrons in real space rather than the electronic structure [100-102]. In the study of molecular gas target, the amplitude and relative phase of high harmonics are known to depend on the structure of the molecule and on its orientation with respect to the polarization of the incident beam [103-106]. It appears that the structure and symmetry of the highest occupied molecular orbitals (HOMO) governs this dependence [12,107,108]. This has led to developing the tomographic imaging technique to probe the orbital structure of N₂ molecules via recording high harmonic spectra as a function of molecular alignment [11]. This probing technique has been restricted to the measurement of the amplitudes of harmonics spectra, thus relying on the assumptions of the molecular symmetry to include the relative phase and the polarization of the imaged orbitals. This in turn, limits the technique to simple molecular gases, for which the assumptions remain valid. To overcome such limitation, the polarization state of high harmonics can be utilized, as they carry information about the relative phase between the \( x \) and \( y \) components of the free-bound transition dipole moment [43]. For such measurements, the polarization state of the driving beam was kept linear, and instead, several different generation media was investigated. High harmonic spectrum from each of the aligned N₂, O₂, and CO₂ molecular targets shows distinctive polarization
behavior, providing more insight towards imaging of complex molecules. For instance, in N₂, all emitted harmonics were found to be linearly polarized. Yet, for each particular alignment angle (e.g. alignment angle of 45 degree with respect to the laser polarization direction), the polarization rotation of emitted harmonics were found to be different for 23rd and higher orders than that of below 23rd order [43]. Further studies confirmed the ellipticity in the polarization states for the emitted harmonics from N₂ due to enhancement in the pump alignment as well as the improvement in the signal to noise ratio in the HHG process[44].

With the first realization of high harmonics in bulk crystals, the motivation to explore the electron dynamics and the structural properties of solids encouraged the application of polarization techniques in addition to the orientation dependent spectral measurements of high harmonics. As recent studies indicated, in centrosymmetric crystals, the anisotropy in the dependence of the high harmonic spectrum on the driving laser polarization has been attributed to the real-space electron trajectories in periodic crystals [52] and to coupling between inter- and intra-band generation mechanisms [49]. For crystals lacking inversion symmetry, such as α-quartz, the generation of even harmonics can be attributed to various underlying mechanisms responsible for the emission of high harmonics, the effects of which are evident in measurements of the polarization states of the emitted harmonics [63]. Particularly in the case of α-quartz, the measurements of polarization distribution of the emitted harmonics have been carried out for two various band directions; Along Γ – K direction, emitted even harmonics were parallel to the driving laser polarization and pointed out to strong coupling between bands [64] or asymmetric dipole matrix elements [81], whereas along Γ – M direction, perpendicularly-polarized even harmonics with respect to the laser field have been observed and have been described as a manifestation of Berry curvature [63].
In the following sections, by means of both experimental measurements and theoretical calculations, the polarization properties of emitted harmonics from ZnO are explored. Using one-dimensional two-band Semiconductor Bloch Equations (1D SBE) in combination with the Linearly-Coupled Excitation (LCE) model [64] successfully reproduces the major features of the polarization-resolved experimental HHG spectrum and the polarization states of emitted harmonics, suggesting that the polarization-dependent features can be mainly explained by symmetry.

4.3.1 Polarization Properties of HHG in Zinc Oxide

As mentioned earlier in the chapter, the orientation dependent spectral measurements do not differentiate parallel and perpendicularly polarized harmonics relative to the laser polarization. One way to account for such orientations is to generalize the SBEs model to 2D or 3D. Nonetheless, this generalization requires extensive numerical work. Recently, Linearly Coupled Excitation (LCE) model has been shown success to analyze parallel and perpendicularly polarized harmonics in Gallium Selenide exposed to the THz pulses [64]. To apply this method, first, 1D SBEs is solved and the induced current along the direction of each Zn-O bond is calculated. The orientation of the bonds encodes the symmetry properties of the system. After finding the corresponding currents for the parallel and perpendicular emissions along each bond, they can both be combined to result in the polarization integrated harmonic spectra, as it has been shown in figure 4-5.
Figure 4-5: Atomic Structure of a-plane ZnO in the Real Space

\( \mathbf{e} \) is the unit vector defining the excitation along a particular bond direction. \( \theta \) is the relative angle between the polarization of the mid-IR beam and x-axis whereas \( \alpha \) is the relative angle between the polarization angle of the harmonic and the mid-IR polarization direction. Parallel and perpendicular emission directions are shown by the green dashed arrows.

To examine LCE model’s accuracy in describing the polarization-sensitive measurements, it is practical to define the direction of the excitation components associated with three bonds with the help of unit vectors \( \mathbf{e}_1, \mathbf{e}_2 \) and \( \mathbf{e}_3 \), as shown in Figure 4-5. \( \theta \) defines the relative angle between the laser polarization and c-axis (which is along \( \mathbf{e}_3 \) in this case). In order to obtain the polarization distribution, a new unit vector \( \mathbf{e}(\alpha) \) pointing in the direction of \( \alpha \) is defined. It can be written in terms of \( \mathbf{e}_1, \mathbf{e}_2 \) as:

\[
\mathbf{e}(\alpha) = \frac{\sin(\alpha + \theta)}{2\cos(18^\circ)}(\mathbf{e}_1 - \mathbf{e}_2) - \frac{\cos(\alpha + \theta)}{2\cos(72^\circ)}(\mathbf{e}_1 + \mathbf{e}_2)
\]

(4-4)

This way, the polarization direction of harmonics is measured with their parallel and perpendicular components with respect to the laser polarization axis, hence the current along \( \mathbf{e}(\alpha) \) is written as

\[
J(\theta, \alpha, t) = \left[ J_1(t)\mathbf{e}_1 + J_2(t)\mathbf{e}_2 + J_3(t)\mathbf{e}_3 \right] \mathbf{e}(\alpha)
\]

(4-5)

where \( J_1(t) \) is the current along direction \( \mathbf{e}_i \). The intensity of the generated harmonics polarized along the direction with angle \( \alpha \) can be calculated by projection.
\[ I(\theta, \alpha, \omega) = \left| (E_1(\omega)e_1 + E_2(\omega)e_2 + E_3(\omega)e_3)e(\alpha) \right|^2 \] (4-6)

where \( E_1(\omega) \) is the Fourier transform of the current along direction \( e_1 \).

In the following measurements, 90 fs pulses were focused onto the exit plane of the a-cut zinc oxide crystal. The generated harmonics passed through two different polarizers to cover the total range of the emitted harmonics up to 17th order. The polarizer sheet (450-750 nm) is transparent to below-gap harmonics and a broadband wire grid polarizer (250-4000 nm) is used to pass the above-gap harmonics (\( \Delta \varepsilon_{\text{ZnO}} = 3.3 \text{ eV} \)).

Two types of measurements were carried out to explore the polarization behavior of the generated harmonics: First, we fix the angle between the laser polarization and the crystal optic axis and rotate the polarizer to analyze the polarization states of the emitted harmonics. The schematics of the experimental set up is described in Figure 4-6 where the angle \( \theta \) indicates the direction of the c-axis relative to the laser polarization and the polarization distribution for below- and above-gap harmonics for particular orientation of c-axis: parallel (\( \theta = 0 \)) and perpendicular (\( \theta \)) to the laser polarization direction.

Panels (a-h) indicate the qualitative agreement between theory and simulation for each harmonic. Along the c-axis (panels a, c, e, f) the polarization states of even and odd harmonics are parallel to one another. With the laser polarization perpendicular to the c-axis (b, d, g, h), weak even harmonics exist with polarization perpendicular to the driving beam polarization direction. Though theory predicts similar behavior for the above-gap even harmonics (with close to perpendicular polarization, such perpendicularly polarized even harmonics are not observed in the experiment, mainly because of the weak emission and low signal to noise ratio. The perpendicularly emitted even harmonics has been attributed to the presence of geometrical (Berry)
phase in the previous study, and has been measured using Berry curvature [63]. The obtained results show that harmonic polarization states predicted here by using symmetry properties are identical to those predicted before using Berry curvature. The accumulated phase due to the adiabatic parallel transport of the wave vector in the momentum space, can actually be incorporated into the dipole phase and be included in the calculation of HHG spectrum [27].

Figure 4-6: Polarization States of Below- and Above-gap Harmonics

For laser polarization parallel to c-axis, panels (a, e) present the findings from experiment while panels (c, f) show the theoretical HHG spectrum. For laser polarization perpendicular to c-axis, panels (b, g) present experimental results while panels (d, h) show the theoretical HHG spectrum.

Next, we fix the polarizer and vary the relative angle between crystal axis and laser polarization direction (indicated by $\theta$). The harmonic spectra are measured as a function of the crystal orientation for two particular direction of the polarizer axis: 1-the polarizer is set to pass the portion of harmonics emission with polarization parallel to the driving laser polarization, and
2- the polarization passes the perpendicularly polarized component of the harmonics relative to the laser polarization direction. The result of these measurements in comparison with the theoretical findings is shown in Figure 4-7. For the straightforward visual comparison in the orientation dependent features, the theory has been scaled for each harmonic (each harmonic has the same scaling factor for parallel and perpendicular components).

**Figure 4-7: Polarization-resolved Harmonics Spectrum**

Top panels report the orientation dependence of emitted harmonics which are polarized parallel to the laser polarization direction: panels (a, e) refer to the experiment, and panels (b, f) refer to theoretical calculations. Bottom panels report the orientation dependent of harmonics emission perpendicular to the laser polarization direction, panels (c, g) refer to the experimental results and panels (d, h) refers to the theoretical calculations.

Most of the orientation dependent features in the experimental data and the theoretical model look similar. We find that odd harmonics mainly remain parallel to the driving beam polarization for $\theta =0^\circ$, $\theta =90^\circ$, and $\theta =180^\circ$, whereas weak odd harmonics appear with perpendicular polarization with respect to the laser polarization at $\theta=15^\circ$ and $\theta=165^\circ$, as well as
\( \theta = 72^\circ \) and \( \theta = 108^\circ \), consistent with the theoretical calculations. On the other hand, even harmonics are emitted parallel to the laser polarization along the optic axis, and likewise for the observed peaks at \( \theta = 65^\circ \) and \( \theta = 115^\circ \). In agreement with the result of polarization state of harmonics, at \( \theta = 90^\circ \), all the parallel even harmonics vanish, and even orders with polarization perpendicular to the laser polarization are visible in the spectrum of below-gap harmonics though they are not detected above the band gap frequency, perhaps due to the attenuation in the emission strength.

Additionally, we observe strong emission of the perpendicularly polarized even harmonics at \( \theta = 15^\circ \) and \( \theta = 165^\circ \) as well as relatively weak maxima at \( \theta = 65^\circ \) and \( \theta = 115^\circ \) as well in the experiment which are reproduced at slightly different angles of \( \theta = 35^\circ \), \( \theta = 145^\circ \) in the calculated spectra.

To better understand and compare the orientation dependent experimental spectrum with the result of LCE model, the polarization-resolved orientation-dependent spectra of below- (5\(^{\text{th}}\) and 6\(^{\text{th}}\)) and above-(11\(^{\text{th}}\) and 12\(^{\text{th}}\)) harmonics are integrated from the color fill plots in Figure 4-7 and shown in Figure 4-8.

The top frames are for the parallel components and the bottom frames are for the perpendicular components. The additional peaks observed at \( \theta = 45^\circ \) and \( \theta = 135^\circ \) and are absent in simulation may be due to birefringent effect. For the perpendicular polarization, the positions of the maxima for odd harmonics in the experiment and simulation are identical, but the relative magnitude of the peaks differs. The maxima of even harmonics slightly differ in theory compared to the experiment.
Figure 4-8: Polarization-resolved Orientation Dependence of Integrated Harmonics

Top panels report the orientation dependence of emitted odd (5th and 11th) versus even (6th and 12th) harmonics which are polarized parallel to the laser polarization direction: panels (a, e) refer to the experiment, and panels (b, f) refer to theoretical calculations. Bottom panels report the orientation dependence of odd (5th and 11th) versus even (6th and 12th) harmonics emission perpendicular to the laser polarization direction, panels (c, g) refer to the experimental results and panels (d, h) refer to the theoretical calculations.

In general, the obtained results confirm that LCE model successfully reproduces the dependence of the odd and even harmonics yield and their polarizations on the input laser orientation, emphasizing that the polarization properties of HHG is largely governed by symmetry. Similar studies confirm the universal features in polarization states of harmonics and that the polarization of harmonics follow the main symmetry-imposed rules:

1- With laser polarization parallel to the mirror plane, all odd and even harmonics are polarized parallel to the laser polarization direction.

2- With the laser polarization perpendicular to the mirror plane, odd harmonics are emitted parallel, and even harmonics are emitted perpendicular to the laser polarization direction.
Such universal behavior can establish the polarization of harmonics as an all-optical sensitive probe of the structural changes in crystals such as phase transition, complementing ultrafast x-ray techniques and electron diffraction imaging methods for probing the dynamics of solids.

Figure 4-9: Measured and Calculated Ellipticity of Harmonics

Panels (a-c) show the measurement of ellipticity using the polarizer, and panels (c-e) is the calculated ellipticity using SBEs together with LCE model. Harmonics are linearly polarized for laser polarization parallel/perpendicular to c-axis, and elliptically polarized for laser along Zn-O bond direction.

For a complete information on the polarization states of emitted harmonics, the ellipticity of the above gap harmonic are studied in experiment and theory by using the prior measurements of the polarization states of the harmonics. As shown in Figure 4-9, for laser polarization along high symmetry axes, harmonics are emitted with linear polarization, whereas along the orientation of Zn-O bonds, harmonics are emitted with elliptical polarization while their major ellipse axis remains along the laser polarization direction. A reasonable agreement between the theory and experiment validates the role of bonds direction in the generation of non-perturbative harmonics.
4.3.2 Birefringence effect in Zinc Oxide

In thick crystals, harmonics can be generated throughout the bulk. Due to their long absorption length, below gap harmonics can propagate in the crystal and be detected. Hence, they may have the fingerprint of the propagation effect in their spectral and polarization properties. In contrast, above-gap harmonics have relatively short absorption length and only ones which are generated close to the exit plan of the target can be detected. Since Zinc Oxide is a birefringent material, the driving laser polarization state alters during the propagation, and becomes elliptical for crystal orientation angles close to 45° and 135°. Such changes in the polarization state of the driving beam has been shown to influence the emitted harmonics yield [13], and may lead to unexpected changes in their polarization states. To avoid this, harmonics from thin ZnO film, or in the reflection geometry have been proposed. However, monocrystalline films of a-plane ZnO are not available at this time. Here, the ellipticity of the driving laser after propagation through the crystal under the experimental conditions is investigated and the result is shown in Figure 4-10. As indicated in the plot, once the orientation angle \( \theta \) varies from 0° to 90°, the driving laser ellipticity grows from 0 to 0.8, and then decreases back to 0, with its maximum value at \( \theta=45° \). The outcome is consistent with the known linear birefringence properties of ZnO, indicating that nonlinear propagation effects are negligible in this case, and that the effects of driving beam propagation on the polarization of harmonics is minor for crystal axis parallel (\( \theta=0° \)) and perpendicular (\( \theta=90° \)) to the laser polarization direction.
The gray solid line shows the calculated ellipticity for 0.3 mm thick ZnO. Both theory and experiment suggest that the ellipticity is maximized for crystal orientation of $\theta=45^\circ/135^\circ$ with respect to the driving beam polarization.

For other crystal orientations, the yield of harmonics has been measured as the function of driving beam’s ellipticity. This is shown in Figure 4-11. The laser ellipticity was varied using a set of a half-wave plate and a quarter-wave plate, and the data were corrected for propagation of the mid-IR laser through the birefringent crystal by measuring the mid-IR ellipticity after propagation.

For the a-plane measurements, corrections to the ellipticity values is made to account for the driving laser propagation. For the c-plane, the polarization state does not change during propagation.
Due to the crystal birefringence, the maximum obtained ellipticity is roughly 0.4, and is consistent with the measured ellipticity dependence of the 11th harmonic from c-cut ZnO, for which there is no birefringence. In both cases, the ellipticity dependence behaves similarly. While the harmonic generation efficiency drops substantially at relatively large values of ellipticity, it remains above 50% for ellipticity values ≤0.35, corresponding to crystal orientation angles between 0° -20°, 70° -110°, and 160° -180°. Therefore, the discrepancies between theory and experiments close to 45° and 135° might result from the elliptically-polarized driving laser at the exit of the crystal. On one hand, to further confirm this hypothesis, the measurement in the reflection geometry [54,109] is suggested. On the other hand, reflection geometry introduces uncertainty in the measurements due to nonlinear reflection coefficients [109]. To tackle this, HHG is pursued in transmission geometry with a slightly different method, that is to generate and measure harmonics from bulk crystals based on the Jones calculus [110] approach to polarization. In this approach, the bulk crystal with known (measured) birefringence is treated as a phase retarder, allowing for the calculation of the input polarization required to obtain the desired polarization state at the exit of the crystal for any orientation of the crystal’s optic axis relative to the driving laser polarization.

To explain this approach in more details, the Jones calculus technique is illustrated in the following section and is examined to simulate and predict the orientation dependent spectral features arising from a supposedly a-cut ZnO thin layer. After compensating for the birefringence, the ellipticity dependent and rotationally sensitive features in the harmonics are observed.
4.3.3 Jones Calculus Approach to Polarization

In Jones calculus, the polarization of light is represented by a vector, and its alteration due to propagation through the optical elements (e.g., polarizer, wave-plate) is incorporated into a 2x2 matrix. Hence, an entire optical system can be written as a single matrix (resultant from multiplication of different matrices) representing the total effect on polarization of light traveling through the system.

From Jones Calculus, a matrix for an arbitrary phase retarder mimics the birefringent crystal ZnO, as

\[
J_{ZnO} = \begin{bmatrix}
\cos^2 \theta_{ZnO} + e^{i\Delta \phi} \sin^2 \theta_{ZnO} & (1 - e^{i\Delta \phi}) \cos \theta_{ZnO} \sin \theta_{ZnO} \\
(1 - e^{i\Delta \phi}) \cos \theta_{ZnO} \sin \theta_{ZnO} & \sin^2 \theta_{ZnO} + e^{i\Delta \phi} \cos^2 \theta_{ZnO}
\end{bmatrix}
\] (4-7)

where \( \theta_{ZnO} \) is the orientation of the c-axis and the phase retardation due to the difference between the ordinary and extraordinary refractive indices is \( \Delta \phi = \frac{2 \pi d}{\lambda} (n_e - n_o) \) with \( d \) as the crystal thickness, \( \lambda \) as wavelength, \( n_e/n_o \) as extraordinary/ordinary refractive index.

To compensate for the alteration of the ellipticity caused by ZnO, a set of half wave-plate (HWP) and a quarter wave-plate (QWP) can be used, with Jones matrices as:

\[
J_{HWP} = \begin{bmatrix}
\cos(2\theta_{HWP}) & \sin(2\theta_{HWP}) \\
\sin(2\theta_{HWP}) & -\cos(2\theta_{HWP})
\end{bmatrix}
\] (4-8)

\[
J_{QWP} = \begin{bmatrix}
\cos^2 \theta_{QWP} + i \sin^2 \theta_{QWP} & (1 - i) \cos \theta_{QWP} \sin \theta_{QWP} \\
(1 - i) \cos \theta_{QWP} \sin \theta_{QWP} & \sin^2 \theta_{QWP} + i \cos^2 \theta_{QWP}
\end{bmatrix}
\] (4-9)

These matrices are more particular form of a phase retarder with their phase delay defined as \( \Delta \phi_{HWP} = \pi \pm 2m\pi \) for HWP, and \( \Delta \phi_{QWP} = \pi/2 \pm 2m\pi \) for QWP.
To obtain the linear polarization at the exit of the crystal, the following resultant equation should be solved for $\theta_{HWP}$ and $\theta_{QWP}$.

$$\hat{P}_{out} = J_{ZnO} J_{QWP} J_{HWP} \hat{P}_{in}$$  \hspace{1cm} (4-10)

With $P_{out}$ as being linearly polarized in the plane of the crystal parallel to c-axis.

Calculations were done in Python. The combination of HWP and QWP angles for which the ellipticity of the output beam turns out to be negligible ($\varepsilon < 0.0125$) were selected. Among these selected angles, the ones which give rise to the output polarization in the plane of ZnO and along c-axis were carefully chosen to be used in the experimental setup. Where multiple possible angle combinations exist, the combination that is simplest to transition the setup into is chosen. Regardless, all combinations result in effectively equivalent outcome.

![Normalized Intensity](image)

**Figure 4-12: Ellipticity of Mid-IR at the Exit Plane of ZnO for All Configurations of HWP and QWP**

The crystal axis is along the input laser polarization. Dark lines present the location of vertical polarization with ellipticity less than 0.01.

Figure 4-12 shows the ellipticity of mid-IR after propagation through ZnO ($d=0.3$ mm, $\lambda=3.4$ $\mu$m) for c-axis along the laser polarization. The minima (dark regions) on the plot stands for the
set of HWP and QWP angles corresponding to linear output polarization ($\varepsilon < 0.01$) of the beam. As expected from the characteristics of the wave-plates, the periodicity of the dark region is $\pi/4$ for half wave-plate (y-axis on the plot), and $\pi/2$ for quarter wave-plate (x-axis).

### 4.3.3.1 Experiment and Results

The driving wavelength for this part of the experiment is $\lambda = 3.4 \, \mu m$ to well match the wave-plates’ specifications. After passing through HWP and QWP, the beam is focused on the exit a-plane of ZnO and collected afterwards using the same focusing and detection geometries as has been used in the previous chapter.

![Experimental Setup for Simulating HHG from Thin film a-cut ZnO](image)

*Figure 4-13: Experimental Setup for Simulating HHG from Thin film a-cut ZnO*

*The geometry is similar to the previous HHG setup, with the added HWP and QWP to control the input polarization state and ultimately generate linear polarization parallel to the crystal optics axis.*

Using Malus’ law, the polarization state of mid-IR beam after propagating through ZnO is measured for different crystal orientation. Initially, the mid-IR polarization should be fixed along c-axis, and a polarizer is set after the crystal. Next, the transmitted mid-IR power after the polarizer is recorded as the polarizer rotate. This step should be repeated for different orientation of c-axis. Figure 4-14 shows the fraction of incident power transmitted through a polarizer for various
orientations of the crystal, compared to a calculation performed using the same crystal thickness and table values for the ZnO refractive indices.

![Graph showing polarization state of Mid-IR at the Exit Plane of ZnO at Different Orientations](image)

**Figure 4-14: Polarization State of Mid-IR at the Exit Plane of ZnO at Different Orientations**

*When the curve ranges from 0 to 1, the polarization is linear. Smaller ranges correspond to a more elliptical light. Therefore, when the crystal orientation is at 0 or 90 degrees, the output light is linear; when the crystal is at 45 degrees the light is elliptical.*

These measurements together with the comparison of the obtained ellipticity from experiment to the theoretical calculation verifies the efficiency of Jones Calculus in predicting the correct combination of HWP and QWP to adjust the birefringence effect from ZnO.

As illustrated in figure 4-15 b), the polarization angle varied from -20° to 20° with respect to the input polarization. The discrepancy between the calculated and measured values around 0 and 90 degrees is most likely due to the precision of the power measurements (milliwatt precision). The good agreement between the experiment and simulation confirm the validity of the technique and in properly accounting for ZnO’s phase retardation.
Figure 4-15: Polarization Characterization of Mid-IR Beam at the Crystal Exit

Panels show the experimental results as well as the simulations for (a) the ellipticity of mid-IR at the exit while panel, and (b) the angle of the major ellipse axis with respect to the incoming beam.

To experimentally confirm the validity of the optical system in setting polarization of mid-IR beam to linear at the exit of the crystal, we carry out the measurement of mid-IR power after the crystal and rotating polarizer, this time with the designated angles of HWP and QWP. As seen in figure 4-16, the output polarization is linear for almost all the crystal angles with minima at 90, showing that the polarization is set along initial orientation of c-axis (vertical). For crystal orientations near 45° and 135°, the output polarization is not perfectly linear, and these two orientations experience the most polarization change from ZnO.

All the results until now, confirms that implementing Jones calculus approach to polarization effectively counteracts the birefringence of ZnO and that it is experimentally feasible to exclude the propagation effect from the orientation dependent features from ZnO by correctly accounting for the bulk effects.
Figure 4-16: Corrected Polarization State of Mid-IR at the Exit Plane of ZnO at Different Orientations.

For the measured curves ranging 0 to 1, the polarization is linear. While for some angles, the minimum power is nonzero, the small ellipticity is due to the performance of the waveplates and the precision of the calculated angles.

4.3.3.2 Modified Orientation Dependent Spectrum from ZnO

Now it is possible to apply the analysis in the measurement of harmonics generated from ZnO to obtain orientation dependent spectrum. Figure 4-17 compares the HHG spectrum from bulk ZnO to the spectrum which is not affected by the propagation of mid-IR. The major symmetry-imposed features are seen in both spectra: both odd and even harmonics are generated along the crystal c-axis, while only odd harmonics are emitted for polarization perpendicular to the c-axis. However, the additional peaks of both odd and even harmonics at 45° in the corrected form of the spectrum is missing in the previous experiments in transmission geometry. The weak symmetry features in the even harmonics is absent in the corrected form of the spectrum (figure 4-17(b)), and suggesting that the origin of the signal may be related to the polarization of the light at the exit of the bulk crystal. The differences between spectra requires further study, potentially with comparison to reflection geometry measurements or complementary theoretical calculations.
Figure 4-17: Experimental HHG Spectra with/without Propagation Effect

Panel (a) shows HHG spectrum using the wave-plates and ZnO at calculated angles. Panel (b) shows HHG spectrum affected by the propagation of Mid-IR through ZnO.

The new setup does result in a lower signal-to-noise ratio in comparison to the previous orientation dependent measurement. This might be due to use of low-order wave-plates that introduce reflection losses which, in turn, reduce the intensity at the crystal’s exit plane. Additionally, since both wave-plates were mounted in the mechanical rotation mount, automating the wave-plates rotation process will most likely improve the measurement quality.
CHAPTER 5: FIELD-CONTROL OF HHG FROM FERROELECTRICS

In this chapter, I present the measurements of high harmonics from ferroelectrics crystals. Ferroelectric crystals are materials with a spontaneous permanent dipole moment, which can be controlled via external fields, which makes these types of crystals attractive for studying the effects of symmetry in high harmonic emission. First, I describe ferroelectricity, and introduce two ferroelectric perovskite materials used for HHG measurements: barium titanate (BaTiO$_3$) and lithium niobate (LiNbO$_3$). Next, I measure the orientation-dependent spectral features and polarization states of emitted harmonics from these two crystals. I explain the exciting features arising from symmetry of the medium and compare the results with the theoretical calculations that has been carried out using time-dependent density functional theory (TDDFT). Finally, I examine the idea of controlling high harmonics from perovskite ferroelectric materials by controlling symmetry of the medium via an applied DC field.

5.1 Ferroelectric Materials

Ferroelectrics crystals are materials that exhibit spontaneous polarization, the magnitude of which can be controlled through an external stimulation, such as applied electric field or temperature change. As shown in Figure 5-1, below the Curie temperature, ferroelectricity can be defined in terms of the behavior of the induced polarization in the presences of an electric field. In dielectrics, the induced polarization caused by the external electric field is linearly proportional to the applied field, the slope of which represents the permittivity of the dielectric (Figure 5-1(a)). In nonlinear dielectrics, the permittivity is not constant, and changes as a function of the electric field, resulting in the nonlinear polarization behavior. Dielectrics exhibiting such behavior are known as
paraelectric materials (Figure 5-1(b)). In ferroelectrics, in addition to the nonlinear behavior, a non-zero polarization exist in the absence of electric field, the amount of which can be controlled, or reversed when the applied field is varied (Figure 5-1(c)). The spontaneous polarization follows the hysteresis behavior below Curie temperature, in analogy to ferromagnetic materials which exhibit hysteresis in applied magnetic fields.

![Figure 5-1: Polarization-electric Field Hysteresis](https://example.com/figure5.png)

Different categories of materials based on the induced polarization in an external field. (a) Dielectrics, for which the polarization is zero in the absence of an external field, and increases linearly with the applied field strength. (b) Paraelectrics for which the polarization increases nonlinearly with the applied field, and saturates at large field strengths. (c) Ferroelectrics, which show similar behavior as paraelectrics although a permanent polarization remains even for zero field strength, and the polarization follows a hysteresis curve-loop. The remnant polarization $P_r$ indicates the remaining amount of polarization in the material once the electric field becomes zero, and coercive field $E_c$ refers to the existence of nonzero field effect when the polarization is set back to zero.

The hysteresis behavior in ferroelectric crystals originates from their microscopic properties. A ferroelectric crystal consists of volumes of uniform polarization, known as domains, with local structural changes at their interfaces, known as the domain walls [111]. In ferroelectrics, at least two equilibrium orientations of spontaneous polarization exist in the absence of an electric field [112]. Domain walls can present physical local properties slightly different from those of the
domains. One example of that is the effect of strain variation, which is enhanced for the nanoscale thin film ferroelectrics, and causes fluctuations in the local polarization of the wall [113]. In the presence of a strong electric field, domain dipoles are reoriented, summing to a large polarization, the magnitude of which depends of the electric field strength. In general, domain and phase activities in ferroelectric materials give rise to nonlinear and hysteretic response [114]. Hysteresis below the Curie temperature is mainly caused by domain wall movements [115].

![Hysteresis Loop](image)

**Figure 5-2: Polarization Configurations under an Applied Electric Field**

The configuration of the domain polarization is shown along hysteresis curve. With zero polarization, domains are polarized in different directions, such that the total polarization becomes zero. When the polarization growth reaches the saturation, with zero electric field, domains polarizations are readjusted to some extent, but still show a remnant polarization effect.

5.2 Symmetry and Dipole Moment in Ferroelectrics

The role of symmetry in the properties of ferroelectric crystals arises from the connection between the internal electric dipole of a ferroelectric material and the crystal lattice structure. The strength and the orientation of the domain dipoles, i.e. the spontaneous polarization, is impacted by structural phase transitions. These phase transitions can occur due change in the temperature or
several other external change of variables such as chemical doping, pressure, electrical and mechanical stress fields [116,117]. The phase diagram of a ferroelectric barium titanate (BaTiO$_3$) is presented in Figure 5-3. As shown, 4 different phases of BaTiO$_3$ is presented in the phase diagram [118].

![Phase Diagram for BaTiO$_3$](image)

**Figure 5-3: Phase Diagram for BaTiO$_3$**

All four phases of BaTiO$_3$ are shown in the diagram. At room temperature and atmospheric pressure, BaTiO$_3$ has tetragonal structure.

Above Curie temperature, $T_c$, the crystal exists in its symmetric cubic state. At room temperature and atmospheric pressure, (Below $T_c$), Phase transition distorts the cubic structure to the tetragonal structure, following a slight displacement of titanium atom from the center of the cube. This displacement gives rise to a change in the angle of the titanium-oxygen bond, and the formation of permanent dipole moment along c-axis of the crystal, which are the signatures of the broken inversion symmetry in the crystal configuration.
The study of phase transition in ferroelectric materials had been done using nuclear magnetic resonance [119], neutron diffraction [120], and x-ray diffraction combined with the structural analysis [119]. The advancement in the ultrafast technology allowed for ultrafast x-ray diffraction techniques [5,121], and time-resolved study of dynamical phase transitions [122]. We expect that high harmonic spectroscopy may allow for new insight into these complex and highly-correlated ferroelectric systems. With the merit of sub-cycle pulse duration, high harmonics enable probing of electron-electron interaction that so far has been hidden in the strongly correlated materials. In particular, polarization-resolved high harmonic spectroscopy may shed light on structural dynamics during phase transitions. The entrainment of polarization through applying DC electric field enables control and manipulation of symmetry in ferroelectric crystals, the signature of which may be evident in the spectral intensity of the harmonics.

![Figure 5-4: Structural Transition in BaTiO$_3$](image)

BaTiO$_3$ unit cell (a) Perovskite-type barium titanate (BaTiO$_3$) unit cell in the symmetric cubic state above $T_c$ (b) Tetragonally distorted unit cell below $T_c$.

In the following section, our goal is to demonstrate HHG from ferroelectrics, and investigate their potential for studies of tunable HHG under applied fields. If successful, our work
would open a new path for studies of ultrafast structural phase transitions in these materials (BaTiO$_3$/LiNbO$_3$).

### 5.3 HHG in Bulk Ferroelectric Barium Titanate (BaTiO$_3$)

BaTiO$_3$ was the first discovered polycrystalline ceramic material that demonstrated ferroelectricity. The study of temperature-dependent structural transitions in BaTiO$_3$ revealed the phase transitions at relatively low temperature, making them attractive for probing the phase transition mechanisms with the technologically available lab facilities. As mentioned in the prior chapter, BaTiO$_3$ belongs to the tetragonal lattice class at room temperature, shown in Figure 5-4. Increasing the temperature at atmospheric pressure allows the tetragonal-cubic phase transition.

In this section, I investigate the generation of high harmonics from the ferroelectric crystal BaTiO$_3$ driven by intense mid-IR laser pulses. Through laser polarization-dependent measurements, I find that odd and even harmonics are optimized for different polarization directions, unlike previously studied crystals. Furthermore, I observe that the harmonic yield from different ferroelectric domains, with randomly oriented polarization due to the lack of applied field, varies significantly. This suggests that the domain-dependent properties of the ferroelectrics can be probed using ultrafast pulses of high harmonics.

#### 5.3.1 Experimental Setup

For the measurements in this section, mid-IR pulses of 90 fs are focused by a spherical mirror ($f=100$ mm) into a bulk BaTiO$_3$ crystal (111) with thickness of 0.5 mm. The harmonic spectra, with spectra extending to the near-UV, are measured using a high-resolution spectrometer (Ocean Optics HR2000+ES).
Figure 5-5: The Experimental Setup and Spectrum of Emitted Harmonics from BaTiO$_3$

Panel (a) shows the experimental setup, and panel (b) shows harmonics generation up to 17$^{th}$ orders are generated.

The existing broad feature in the spectrum limits the detection of 13$^{th}$ to 16$^{th}$ harmonics.

5.3.2 Results and Discussion

As illustrated in Figure 5-5, harmonics up to 17$^{th}$ order are detected, for crystal c-axis perpendicular to the laser polarization direction. The spectrum is stretched to the detection limit, and the observation of cut-off is restricted by the spectrometer range (200-1100 nm). A broad feature that exist in the spectrum of harmonics covers the detection range of 13$^{th}$-16$^{th}$ harmonics. Interestingly, although the laser is polarized perpendicular to the crystal’s c-axis and we expect to probe only odd harmonics, both odd and even harmonics are observed with comparable intensity, unlike ZnO and other semiconductors.

To confirm the nature of the emissions, the spectra for different driving laser wavelengths are measured and indicated in Figure 5-6. For these measurements, the driving laser intensity and the Si thickness were optimized for the idler central wavelength of 3.8 µm and not varied during the experiments. Harmonic signals are identified by the peaks that shift with the driving laser wavelength. No notable features corresponding to band fluorescence is observed. The broad
feature centered around 250 nm in the spectrum of HHG also shifts with the change of driving wavelength, suggesting the generation follows a nonlinear mechanism and does not originate from band emission or excitation.

![Harmonic Wavelength Graph](image)

**Figure 5-6: Wavelength Dependence of Generated Harmonics from BaTiO$_3$**

All emitted harmonics and the broad features at harmonic wavelength $\lambda=250$ nm shift as the driving mid-IR wavelength changes. The silicon thickness is optimized for $\lambda=250$ µm idler beam.

To further investigate the orientation-dependent spectral features, the crystal axis should be rotated, and the spectral intensity of harmonics recorded as the function of relative angle between the driving beam polarization and c-axis. However, in the case of BaTiO$_3$, the domains of the ferroelectric correspond to dipoles with different orientation and magnitude, resulting in the loss of homogeneity in the modulation of the harmonics intensity and loss of consistency in the measurement. This phenomenon is illustrated in Figure 5-7. The laser polarization is initially fixed along the c-axis for zero degrees. As the crystal is rotated, and the position of the focal spot on the crystal is varied accordingly. Figure 5-7(b) shows the orientation-dependent harmonic spectra
when the laser focal spot is located near the center of the target, and the focus experiences few
domain boundaries. Moving the focal spot closer to the edge of the crystal allows the focus to cross
multiple domain boundaries of the crystal during a complete rotation, as shown in Figure 5-7(c).
In this case, the observed spectrum and yield of HHG is strongly modulated. The change in the
quality of the harmonic signals, as well as the lack of a clear symmetry is attributed to random
orientation and strength of dipoles in different domains.

![Harmonic wavelength vs Angle](image)

**Figure 5-7: Influence of Multiple Domains in HHG from BaTiO₃**

*Panel show (a) rotating the laser polarization by using a half-waveplate, (b) rotating the crystal orientation with laser focal spot near-center. The strong modulation in the harmonics spectra is caused by contributions from multiple domains.*

From Figure 5-7 it is interpreted that the domains prevent the measurements from being
performed by rotating the crystal, due to the difficulty in keeping the focal spot on a single domain.
Instead, we can carry out the orientation-dependent spectral measurements by rotating the laser
polarization while keeping the crystal fixed. We accomplish this by using a low-order half-wave
plate for the mid-IR (WPLH05M-4000). The result of the measurement is shown in Figure 5-8.
Figure 5-8: Orientation Dependence of Harmonics from BaTiO$_3$

In these panels, 0, $\pi$, and 2$\pi$ radians correspond to laser polarization along the c-axis. (a) The maximum of 4$^{th}$ and the minimum of 5$^{th}$ harmonic are shown by dashed and dotted lines respectively. (b) The yield of 4$^{th}$ and 5$^{th}$ harmonic as a function of input polarization direction. The double peak structure of the odd harmonic with a local minimum is identified.

Two surprising feature arises from the measurements of orientation-dependent spectral intensity of harmonics, indicated in the figure:

1- For laser polarization perpendicular to c-axis, even harmonics are maximized, unlike the previous experiments [51,58,59,64] for which only odd harmonics existed at such orientation. In addition, for laser polarization along c-axis, no odd and even harmonics are generated, in contrast to the previously observed behavior where both odd and even harmonics were generated at such orientation.

2- The spectrum of odd harmonics consists of double-hump shaped harmonics with two maxima and a local minimum in between the observed maxima, for laser polarization perpendicular to c-axis (shown by dashed line). The orientation for the observed local
minima of odd harmonics coincides with the maximum of even harmonics. The double peaks of odd harmonics (shown by dotted line) are located ± 10 degree from the location of local minimum.

Figure 5-9: Measured and Calculated Orientation-Dependent Spectrum

(a) Experimental harmonic spectra (b) Preliminary TDDFT calculations (courtesy of V. Turkowski). Based on the calculations, with respect to the driving beam polarization, the crystal orientation for which even harmonics are maximized, differs ±6 degrees from the orientation of the crystal that maximizes odd harmonics.

To theoretically investigate generation of high harmonics ferroelectric BaTiO₃, and understand the effect of ferroelectricity and strong correlation in the more complex materials, Time Dependent Density Functional Theory has been implemented in simulations based on time-dependent density functional theory. The calculations were carried out by Dr. Volodymyr Turkowsky and Naseem Ud Din. The orientation-dependent spectrum obtain from the calculation is presented in comparison to the experimental result in Figure 5-9. The calculations show orientation-dependent spectral features which are in harmony with the outcome of the experiment.
From the simulation, the calculated orientation difference between the peaks and the local minimum is ± 6 degree.

From the phase diagram and the structural features of BaTiO₃, it is possible to interpret the resultant deviation in the peak of odd harmonics relative to the maximum on even harmonics arises from the displacement of titanium due to the cubic-tetragonal phase transition. This has been shown in Figure 5-10. The calculated value for the deviation from the calculation matches the angle of the Ti-O bond (± 6 degrees) in the crystal structure used for the calculations, demonstrating the role of structural symmetry and real space trajectories in the generation of odd harmonics. However, the anomaly in the orientation-dependent spectral intensity of even harmonics as opposed to previously studied materials still needs further understanding about the role of symmetry and excitation dynamics in BaTiO₃ exposed to the strong-field regime of nonlinear optics.

![Diagram of BaTiO₃ structure and harmonic generation](image)

**Figure 5-10: Measured and Calculated Orientation-Dependent Spectrum**

As shown in the figure, the calculated spectrum of 5th harmonics show maxima ±6 degrees deviation from the maximum of even harmonics, corresponding to the shift in the angle of Ti-O in the tetragonal lattice of BaTiO₃.
To measure the polarization state of emitted harmonics, we continue our method for single domain focusing geometry, and record the polarization distribution of harmonics by utilizing a sheet polarizer for each orientation of the crystal optics axis relative to the laser polarization direction. Here, we mainly focus on two orientations; (a) the one for which the yield of even harmonics is maximized (for laser polarization perpendicular to c-axis), and (b) the one for which the yield of odd harmonics is maximized (for laser polarization 80 degrees rotated relative to c-axis. Figure 5-11 shows the result of the polarization states of harmonics for these two specific orientations.

![Polarization States of Emitted Harmonics for Particular Crystal Orientation](image)

**Figure 5-11: Polarization States of Emitted Harmonics for Particular Crystal Orientation**

Panels show the polarization states of harmonics. x-axis presents the polarizer angle with respect to c-axis, such that degree polarizer angle corresponds to laser polarization along c-axis. (a) input polarization is perpendicular to c-axis, maximizing the emission of even harmonics (b) input polarization ~80, 100 degrees relative to c-axis, maximizing the emission of odd harmonics.

As it is followed from the panels, on one hand, odd and even harmonics are both emitted almost parallel to the laser when laser polarization is rotated 80 degrees with respect to the optics axis. On the other hand, for laser polarization perpendicular to c-axis, emitted even harmonics are perpendicularly polarized with respect to the laser polarization direction. The perpendicularly
polarized even harmonics has been recently attributed to the presence of geometrical (Berry) phase [63] in the momentum space due to nontrivial band shape. The effect of geometrical phase in polarization measurement in anisotropic media, known as Pancharatnam-Berry phase [123,124] can result in the rotation of the polarization plane due to curvature of the parameter space (Rytov-Vladimirskii law [125,126]), and has contributed to the harmonics intra-band emission in MoS$_2$ in the strong field regime. Such geometrical interpretation needs more detailed experiments and calculations which are currently under investigation.

Although the polarization-resolved orientation-dependent measurement can shed light towards the understanding of different behavior in the generation mechanism of even harmonics, and the role of curvature of the bands in the geometrical picture, and the propagation effect from the birefringent bulk BaTiO$_3$ can cause uncertainty in the interpretations from the polarization-resolved spectral features. Our explanation for the generation mechanism in these experiments is that harmonics are mainly generated via nonlinear optical process (sum frequency generation and cascaded process) throughout the bulk. To avoid the lower order nonlinear processes, bulk target is substituted with thin film BaTiO$_3$. Thin films of BaTiO$_3$ grown with pulsed laser deposition are examined, but it is found that the growth results in nano-domains that does not allow orientation-dependent spectral measurements. Since other thin-films of BaTiO$_3$ are not commercially available, we decide to test high harmonics generation from ferroelectric LiNbO$_3$ for which a thin film crystal is commercially available, and explore spectral features that arise from LiNbO$_3$. In the following section, we discuss the emission of harmonics from x-cut 600nm thin-film LiNbO$_3$ on fused silica substrate (Nano LN).
5.4 HHG in Thin Film Ferroelectric Lithium Niobate (LiNbO$_3$)

LiNbO$_3$ is an artificially made ferroelectric crystal and an attractive platform for nonlinear optics owing to its high optical nonlinear coefficients and broadband optical transmission [127]. It is widely used in integrated and guided-wave optics.

LiNbO$_3$ is a uniaxial crystal with band-gap of 4 eV. The paraelectric phase at high temperature ($T_c = 1145$) possesses inversion symmetry. Below Currie temperature, the crystal structure is trigonal [128]. Figure 5-12. Shows the crystal structure at room temperature for x-plane which is used in our experiment.

![Crystal Structure](image)

**Figure 5-12: x-cut LiNbO$_3$ Crystal Structure at Room Temperature**

*The configuration of Li, O, and Nb atoms in x-plane of the crystal, used for HHG experiment is shown*

The experimental set up that is used to generated harmonics from LiNbO$_3$ is similar to that for BaTiO$_3$, and the detection schematics has been optimized to optimized the intensity of the emitted harmonics. Due to realignment of our OPA system and characterizing the idler spectral bandwidth the chosen idler wavelength for these measurements are 3.4 µm. The optimized thickness of silicon to overcome the dispersion is now 6 mm for the chosen wavelength. The thin-
film is placed in the rotation mount such that the mid-IR pulses are focused on the exit plane of the crystal. No notable feature related to band excitation and no domain dependent effect from rotation of the crystal with respect to the input polarization direction is observed from thin-film sample.

Figure 5-13: Orientation-dependent Measurement HHG in LiNbO₃

Panels (a) show the orientation dependent spectrum of harmonics from LiNbO₃, in panel (b) same measurements with a different color-scaling has been shown to better demonstrate the behavior of high harmonics. All odd and even harmonics show double peak spectral features. Panels (c-f) show the integrated harmonics intensity for odd and even harmonics with various orders. It is shown that even harmonics maxima are less distant than odd harmonics. As well, for all harmonics, higher orders have less distant maxima than lower orders.
The orientation dependence of harmonics is measured with respect to the polarization of the laser, and shown in Figure 5-13. Panels (c-f) shows the integrated intensity over the spectral bandwidth of each harmonics.

First, it is evident that the spectral features of the harmonics qualitatively follow the same manner that is observed from BaTiO₃, with odd and even harmonics, being maximized for different orientation. It is interesting to notice that, different from BaTiO₃, in the case of LiNbO₃, both even and odd harmonics present the double-hump structure in their orientation dependent spectra. Although the peaks are maximized differently for even harmonics in comparison to odd harmonics, the minima of even orders coincide with the ones from odd orders. Based on measurements, the following conclusions can be extracted from Figure 5-13 (a-f):

1- All the minima are observed for the laser polarization perpendicular to the optics axis.
2- As Figure 5-13 (c-f) shows, the peaks of the even harmonics are less distant from one another than the peaks of odd harmonics.
3- Through Figure 5-13 (c-f), it is shown that for both odd and even harmonics, the peaks become less distant from one another for higher orders.
4- As shown in Figure 5-13 (a), 4th harmonic show a different orientation-dependence compared to all other harmonics which can be attributed to a nonlinear optical harmonic generation.

To interpret the results from the orientation-dependent spectrum, the effect of crystal structural dynamics and symmetry should be taken into account, and requires input from theoretical calculations. Calculations of the influence of LiNbO₃ structural dynamics on HHG spectrum for different orientations of the crystal are currently being investigated.
To further understand if these features are imposed by the symmetry of the system, the polarization-resolved orientation-dependent measurements are carried out by using the wire grid polarizer before the detection set up, and further investigate the orientation dependence of harmonics. The axis of polarizer is fixed, first, parallel, and next, perpendicular to the laser polarization direction, and the crystal is rotated with respect to the laser polarization.

![Figure 5-14: Polarization-resolved Orientation Dependent HHG Spectrum](image)

Panels (a, b) show the parallel and perpendicular components of the high harmonic spectrum and their dependence on the orientation of c-axis with respect to the laser polarization. Panels (c, d) refer to the integrated spectrum intensity for 5th and 6th harmonics for their parallel and perpendicular component, respectively.

The spectrum of even and odd harmonics are shown for both parallel and perpendicular components of the emitted harmonics in Figure 5-14. Panels (c, d) refer to the integrated spectrum intensity for 5th and 6th harmonics for their parallel and perpendicular component, respectively.
The comparison between Figure 5-14 (a,c) and Figure 5-13 (a,c) demonstrates that harmonics are mostly emitted parallel to the laser polarization, but there is a fraction of harmonics that are emitted with perpendicular polarization. Further interpretation of the results of orientation dependence of parallel, and perpendicular harmonics requires the theoretical TDDFT calculations to be merged with the orientation dependent calculations to predict the origin of such angle dependence.

Measurements of polarization states of harmonics for laser orientation relative to c-axis at two different angles is performed: The relative angle that maximizes the intensity of even harmonics ($\theta=58^\circ$, shown by dashed line in Figure 5-13 (e)), and along the local minima of all harmonics ($\theta=77^\circ$, shown by dotted line in Figure 5-13 (c-f)), . The results of these measurements are shown in Figure 5-15.

**Figure 5-15: Polarization States of High Harmonics from LiNbO$_3$**

With respect to the laser polarization, panel (a) refers to crystal orientation for which even harmonics are maximized, and panel (b) refers to the crystal orientation for which all harmonics are minimized. Harmonics are polarized parallel to the laser polarization in both measurements.

From the measurements, it is seen that Harmonics are polarized parallel to the laser polarization for both orientation of the lasers relative to the crystal that maximized even harmonics, or
following the local minima. It is interpreted that harmonics from BaTiO$_3$ were generated, at least partially, from cascaded process, while harmonics from LiNbO$_3$ are emitted through non-perturbative process.

We further explore the possibility to control the symmetry of ferroelectric materials and observe the behavior that might arise from the generated harmonics in both bulk BaTiO$_3$ and thin film LiNbO$_3$.

5.5 Symmetry and Field-control of High Harmonics
Ferroelectric crystals belong to polar non-centrosymmetric crystal group, with the polarization along the polar axis. Via an externally applied electric field, the magnitude and direction of spontaneous permanent dipole moment within the crystal can be continuously modified along a hysteresis curve. Therefore, the polarization in this class of materials can serve as a “knob” to tune the symmetry properties, and to control the properties of the emitted HHG. Controlling HHG from ferroelectrics potentially benefit strong-field optoelectronics [129] in multiferroic devices. Breaking the inversion symmetry in the centrosymmetric plane of ZnO (c-plane) through an externally applied field has been demonstrated recently[129]. Here, I examine the idea of reorienting the domains of the thin-film LiNbO$_3$ and bulk BaTiO$_3$ through applying a strong constant electric field.
Gold layers are deposited on the sample using adhesive layer of chromium (Cr). The thickness of conductive contacts (including Cr) is 80 nm, and the distance between them is 0.5 mm.

Figure 5-16 shows the design of the target for the purpose of symmetry control of high harmonics from ferroelectrics, the designed electrical contacts, include nano-scale gold plates (70 nm thick) that are deposited on the ferroelectric LiNbO$_3$ and BaTiO$_3$ thin films using Chromium (10 nm thick) as the adhesive intermediate layer (few nanometer thick). The thickness of the mask between the plates ($\Delta=0.5$ mm) allows an applied DC voltage of up to 6 kV between the plates considering the electrical breakdown in air ($E=3$ kV/mm). The breakdown value is much larger for LiNbO$_3$ ($E=21$ kV/mm) and BaTiO$_3$ ($E=18$kV/mm) in their ferroelectric phase. For BaTiO$_3$ crystal, the contacts are used on both sides of the sample to allow for the applied electric field in the bulk.

5.5.1 Controlling HHG from LiNbO$_3$

Idler wavelength of 3.4 $\mu$m is focused at the exit of LiNbO$_3$ target in the region between two conductive contacts using a silicon lens ($f=100$ mm). The high voltage is applied to the target and is increased with the increments of 50 V. The breakdown occurred at 1.5 kV, different from
what the calculated breakdown suggests. For this reason, we limit our measurements to this range, and subsequently apply the voltage in the increments of 100 V in two different setting.

In the first setting, DC field is set parallel to the crystal axis. In this setting, the laser polarization can be set parallel or perpendicular to the crystal optics axis. In the second setting, DC field is set perpendicular to the crystal optics axis. Accordingly, laser polarization parallel, and perpendicular, to c-axis are examined. We do not observe any effects in the emitted harmonics spectral intensity from the applied field. However, we notice the decrease in the intensity of harmonics even with no applied voltage. No similar behavior has been observed for high harmonic measurements when the laser is focused in the center of the sample where no contact is close to the focal region. This behavior can be interpreted as the local thermal effects caused by the existence of gold in the vicinity of the focal region. Reducing the repetition rate of the idler beam from 10 kHz to 5 kHz, and subsequently to 2 kHz resolves the thermal issue. The result of laser-induced thermal for DC field parallel to the laser polarization (setting 1) is shown in Figure 5-17. Due to the high Curie high temperature for LiNbO₃, we do not believe that there is any phase transition induced by the laser. The spectral features in the orientation-dependent features of the spectrum for the focus in the vicinity of the gold contacts does not differ from the prior measurements. Our interpretation is the optically induced change in the photorefractive index [130].

We examine the influence of applied DC field this time with the driving laser beam at 2 kHz. However, even with 2 kHz repetition rate of mid-IR beam, no change in the spectral intensity of the emitted harmonics is observed as the result of applied DC field. There is a chance that the
needed voltage for the observation of change in the spectral intensity is much more than the applied voltage in the experiment.

**Figure 5-17: Laser-induced Thermal Effects at the Focal Spot**

*Panels show the laser-induced thermal effects for (a-c) laser polarization parallel (∥) to c-axis, and for (d-f) the laser polarization perpendicular (∥) to c-axis. In panel a, the focal spot is located at the center of the sample, and no thermal influence on the harmonics are noticed. Panels (b,c) show the thermal effects for 5 kHz and 2 kHz, respectively. Panels (d-f) show the thermal effects for 10 kHz, 5kHz, and 2kHz, respectively.*

To investigate the field control over harmonics from LiNbO$_3$, we compare our parameter space to the result of Rao et. al. [131] design of nano-periodically poled LiNbO$_3$ waveguide, for which highly efficient second harmonic from LiNbO$_3$ is achieved through quasi-phase matching (QPM) process. The design of the electrodes length for the polling process is such that the electrodes’ contact length matches the length required for quasi-phase matching (QPM), resulting in the enhancement of second harmonic yield. The LiNbO$_3$ waveguide is sandwiched between the electrodes with engineered contacts, and the AC voltage is applied to every other contacts, to
reorient the ferroelectric domains. The schematic of the designed can be found in Figure 1 of reference [131]. The results of the Figure 2 in reference [131] shows that for the repeated applied voltage, the efficiency of the generated second harmonic increases as the poling process is repeated, suggesting that the domain reorientation re-orientation needs multiple poling trials. As well as higher applied electric field. Since in their measurement, voltage is applied through LiNbO$_3$ medium and not with the air interface, it was possible to experimentally apply the field close to the electrical breakdown field. The examination of the applied electric field influence on HHG from LiNbO$_3$ needs more complex design more in depth investigation.

5.5.2 Controlling HHG from BaTiO$_3$

In this experiment, we try the same idea for high harmonics control through an applied DC field for (100) plane BaTiO$_3$. As shown in Figure 5-18, the orientation-dependent spectral features are the same as it has been observed from (111) plane due to symmetry. The preparation of contact is similar to the procedure described for LiNbO$_3$, with electrical contacts being deposited on both side of the sample to apply the effect of electric field in the bulk of the crystal. With the experimental trial, the electrical breakdown occurred at 900 V.

The same settings for the experiment used in the trials of LiNbO$_3$ is applied to BaTiO$_3$: The first setting corresponds to DC field parallel to c-axis, and the second setting refers to DC field perpendicular to c-axis. The laser polarization can be set parallel or perpendicular to c-axis in each setting.
In comparison to HHG in bulk BaTiO$_3$ (111), similar features have been observed which includes the double peak structure in the spectrum of odd harmonics with local minimum that coincides with the maximum of even harmonics.

In both settings, as the applied voltage changes with the increments of 50 V, all harmonics exhibit strong modulation, and become very weak with the applied voltage of 300 V. The rate of modulation changes for parallel and perpendicularly polarized laser with respect to c-axis.

To try the reversibility of the process, the voltage is scanned from 300 V back to 0 V and the intensity of harmonics are recorded. The noticeable growth in the intensity of harmonics is observed. This behavior is the similar for both positive and negative polarity of the field, can be repeated mainly for the second setting. In the first setting, fluctuations in the modulated intensity is observed while applying voltage. This, in turn, disrupts the measurement and influences the quality of the recorded spectra. In the second setting, the modulated spectra remain stable and it is possible to better extract the hysteresis behavior of different harmonics orders. Figure 5-19 demonstrates the configurations of the laser polarization parallel to c-axis when DC field is also parallel to c-axis, and the related measurements of harmonics intensity as the function of applied
voltage. It is shown in panels (a) through (c) that switching the polarity and reversing the voltage change produce almost the same behavior in the intensity change of $5^{th}$-$7^{th}$ harmonics, and that the measurements can be repeated with agreeable results to a good extent.

![Figure 5-19: HHG Hysteresis Loop Retrieved Through Applied DC Field](image)

In this configuration, Laser polarization and c-axis are parallel to one another, and both perpendicular to the DC field. Panels (a-c) represent hysteresis loop for different odd and even harmonics order.

The difference in the growth of voltage in for each round of measurement might be due a remnant polarization in the sample when the field is set back to zero, that can, in turn, affect the propagation of harmonics throughout the bulk.

In Figure 5-20, the measurement of harmonics intensity as a function of voltage is shown for the other orientation of the lase, that is perpendicularly polarized to c-axis, with DC field remaining parallel to c-axis. For these measurements, as observed in panels (a) through (c), with reversing the voltage, the harmonics do not grow back to the same intensity, probably due to summing of laser polarization and DC field. However, harmonics show more precise hysteresis.
behavior in this configuration. When switching the polarity, the measurements show that the modulation in the intensity of harmonics agrees well between the first and second rounds of polling, confirming the potential to further tune harmonics repeatedly to obtain the hysteresis loop.

![Diagram of laser polarization and DC field](image)

**Figure 5-20: HHG Hysteresis Loop Retrieved Through Applied DC Field**

In this configuration, Laser polarization is perpendicular to both c-axis and the DC field. Panels (a-c) represent hysteresis loop for different odd and even harmonics order

It is surprising to see the effect of symmetry control on the intensity of all harmonics instead of only even harmonics [129]. However, if the harmonics from BaTiO$_3$ are generated through SFG process throughout the bulk, the change in the generation of even harmonics can influence the cascaded generation of odd harmonics as well, and the control of symmetry will affect all harmonics. To avoid such generation mechanism and to be able to control the non-perturbative harmonics, an alternative way of doing the measurements is to use reflection geometry to generate harmonics, which will be attempted in future experiments.
CHAPTER 6: FEW-CYCLE COMPRESSED MID-IR PULSES

Part of this section have been reproduced using reference [28] with the permission of OSA Publishing.

In the current chapter, I highlight the importance of few-cycle laser pulses for spectroscopy and imaging application, and as the main route for development of isolated attosecond sources. The few-cycle pulses are accessible through nonlinear pulse compression techniques, some of which are attainable following the amplification step, such as the propagation in the nonlinear gas or transparent solid medium. Here, I demonstrate the self-compression of the mid-infrared pulses down to the few-cycle regime via filamentation in bulk medium, and study the parameter space that allows such compression factor. I characterize the compressed pulses and exploit them to generate high harmonics in ZnO with enhanced yield. The potential for further compression using microstructured fibers is proposed by the means of simulation, providing the parameter space for further experimental studies.

6.1 Few-cycle Pulses

As the time resolution in pump-probe spectroscopy is associated with the duration of the pump and probe pulses, the generation of few-cycle laser pulses has had immense benefits to time-resolved spectroscopy [132-135] and imaging techniques [136,137] and coherent control [138-140] experiments. Moreover, few-cycle pulse compression has also enabled the generation of isolated attosecond pulses [4,24,25,85,141]. However, intense few-cycle pulses are challenging to obtain directly from a high-energy laser amplifier, primarily due to limitations in the gain bandwidth [142]. As the remedy to this problem, additional nonlinear spectral broadening techniques [143-145] associated with self-phase modulation followed by subsequent compression
with chirped mirrors [146] or bulk materials [147] have been demonstrated to support few- [148] and even single-cycle [149] pulse durations in a wide range of wavelength regions. An interesting alternative to the spectral broadening and subsequent post compression schemes is the self-compression of ultrafast pulses [150,151], which can be achieved by balancing the accumulation of phases associated with the nonlinear refractive index and linear propagation. Typically, such schemes require a medium with anomalous dispersion to balance the (normal) dispersion associated with self-phase modulation. Compression schemes based on microstructured fibers with properly engineered dispersion for a specified wavelength regime can lead to the successful self-compression. Bulk media have made self-compression of ultrafast pulses feasible in their anomalous dispersion regime of the wavelength as well. The choice of medium usually depends on its nonlinear properties in the laser parameter space.

The focus of this chapter is the demonstration of HHG in solids with few-cycle mid-IR pulses, which are generated by taking advantage of nonlinear self-compression through filamentation in the anomalous dispersion regime [152]. While the achieved pulse durations are too long to support isolated attosecond pulse generation, the work presented in this chapter serves as a first step towards a compact, solid-state attosecond source.

6.2 Nonlinear Self-compression of Mid-IR Pulses

Few-cycle mid-IR pulses have benefited the state-of-the-art HHG sources since higher photon energies can be been obtained from laser sources performing in the mid-IR wavelength regime [16,17,153]. This can be explained through cut-off law (equation 1-8) and that the ponderomotive energy is proportional to the driving wavelength [84]. However, it is very
challenging to achieve high-energy few-cycle mid-IR pulses directly from the laser amplifiers due to limited gain bandwidth support and thermal lensing in the amplifier crystal.

On one hand, OPCPAs allow for aiming high energies (up to 100 millijoules) and better beam quality without much thermal effects and power loss that is associated with laser amplifiers. However, there are challenges that arises from such complex design. First, the ultra-broad gain bandwidth requires the phase matching condition to be met very well. Second, the ratio of pump and seed pulse durations is a determining parameter in temporal optimization, and the pump laser and seed needs to be well synchronized. Third, the nonlinearity and transparency of the crystal can be limiting factors, and thus the nonlinear crystal must be chosen specific to the wavelength regime. Nowadays, the major restriction in signal energy scaling of OPCPAs is amplified noise (superfluorescence).

On the other hand, solid-state HHG requires relatively lower pulse energies (a few-microjoule regime), and therefore do not require such a complex scheme as OPCPA. Instead, one promising route for achieving few-cycle pulses with few-microjoule pulse energies involves nonlinear self-compression via filamentation in bulk materials [154-156].

Figure 6-1 shows a typical picture of a filament formation. During the propagation of strong laser field throughout the medium, the nonlinear response of the material to the intense field adds an intensity-dependent term to the refractive index (nonlinear index of refraction):

\[ n(r) = n_0 + \Delta n = n_0 + n_2 I(r) \]  \hspace{1cm} (5-1)

\[ \Delta n = n_2 I(r) \]  \hspace{1cm} (5-2)

This dependence is known as Kerr effect. Table 5-1 shows the nonlinear index of refraction for some of the bulk solids transparent to mid-IR wavelengths, using reference [157].
Figure 6-1: Filamentation in an Optically Transparent Medium

Panel shows the filamentation process: self-focusing of a beam by optical Kerr effect as the power exceeds the critical power $p_{cr}$ and subsequent defocusing as the result of reduction in the nonlinear refractive index. Focusing-defocusing interplay can form a long propagation path of light filaments.

When the intense laser pulses surpass the critical peak power ($p_{cr} \approx 3.77\frac{\lambda_0^2}{8\pi n_0 n_2}$ for a Gaussian pulse), the intensity-dependent refractive index allows for overcoming diffraction and the pulse begins to self-focus. Kerr effect, causes a nonlinear change in the refractive index, leading to a lens-like focusing effect which curves the wave-front shape. This phenomena is known as kerr lens or kerr self-focusing effect and ultimately generates self-focusing [158]. During self-focusing, the intensity close to the pulse center increase, allowing for the multiphoton ionization process and the formation of plasma. High electron density in the vicinity of ionizing region reduces the index of refraction. And cause a self-induced counteracting diffraction. The balance between the effect of self-focusing, and self-diffraction effect ultimately forms the filament(s) channel inside the medium. During filamentation process, self-focusing and ionizing processes cause the pulses to undergo spatio-temporal effects, the prominent of which is the nonlinear spectral broadening.
Material | $n_2 \times 10^{-13}$ asu, at 1.06 $\mu m$
--- | ---
YAG | 2.7
Fused silica | 0.85
CaF$_2$ | 0.43
Sapphire | 1.23

Table 6-1: Nonlinear Refractive Index in Bulk Materials Transparent to Mid-IR Pulses

The table is reproduced from the data in reference [157].

Adding to that, the pulse will be affected by the dispersion of the material, which is associated with the linear refractive index. The spectral phase can in general be expanded as:

$$\beta(\omega) = \beta(\omega_0) + \left. \frac{d\beta}{d\omega} \right|_{\omega_0} (\omega - \omega_0) + \frac{1}{2} \left. \frac{d^2\beta}{d\omega^2} \right|_{\omega_0} (\omega - \omega_0)^2 + ...$$  \hspace{1cm} (5-3)

Where \( \frac{d\beta}{d\omega} \mid_{\omega_0} \) is linear dispersion, and \( \frac{d^2\beta}{d\omega^2} \mid_{\omega_0} \) is the group velocity dispersion (GVD) which can be written as the function of the wavelength as

$$\left. \frac{d^2\beta}{d\omega^2} \right|_{\omega_0} = \frac{\lambda_0^2}{2\pi c} \frac{dn}{d\lambda^2} \mid_{\lambda_0}$$  \hspace{1cm} (5-4)

The refractive index as the function of wavelength can be found using Sellmeier equation:
\[ n^2(\lambda) = 1 + \frac{B_1 \lambda^2}{\lambda^2 - C_1} + \frac{B_2 \lambda^2}{\lambda^2 - C_2} + \frac{B_3 \lambda^2}{\lambda^2 - C_3} \] (5-5)

Figure 6-2 presents the amount of anomalous group velocity dispersion (GVD) for the same materials in the mid-IR wavelength regime where they have the potential to balance the spectral phase arising from self-phase modulation.

The plot shows GVD of fused silica [151,159], Sapphire [160], CaF2 [161] and YAG [162]. For each material, the gray area indicates the anomalous dispersion region.

Among such materials, yttrium aluminum garnet (YAG, Y₃Al₅O₁₂) is a good candidate, for its availability, high nonlinear coefficient (~1.76 at 3.8 µm [163]), and extended IR transparency. As shown in Figure 6-1, the slope of GVD is sharper than in fused Silica, and calcium fluoride (CaF₂). Darginavičius et al. [156] compared the supercontinuum spectra generated from microjoule-level pulses with duration of 15 fs with central wavelength near 2 µm and in each of the mentioned materials. In Figure 2 of their manuscript [156], they demonstrated that YAG demands much less pulse energy to generate broadband supercontinuum spectra than other materials. The supercontinuum spectrum spans about 1 to 2.5 µm. For this reason, we choose YAG.
as the nonlinear medium for self-compression in our experiments. The amount of GVD at 3.8 μm, the spectral broadening range, and the need for lower pulse energy suggests the choice of YAG over other bulk solids for the goal of self-compression.

### 6.3 Self-compression of Mid-IR Femtosecond Pulses from 50 kHz OPA

#### 6.3.1 Self-compression Setup

In the experiment, the central wavelength of the idler pulses is chosen to be \( \lambda_{\text{idler}} = 3.8 \mu m \), for which a maximum pulse energy of 14 μJ was obtained. Since the idler pulses emerge from the OPA with a negative chirp, they should first be compressed close to their transform-limited duration. This is achieved via linear propagation in bulk silicon, after which pulses with duration of 90 fs were measured using a home-built dispersion-free FROG setup with surface third-harmonic generation as the nonlinear process [164]. Figure 6-3 shows the schematic of the self-compression set up together with the HHG set up.

![Figure 6-3: Self-compression and HHG Setup](image)

*CM: curved mirror; Dashed thick line: movable mirror. Mid-IR pulses are directed first to the FROG for characterization and further to the HHG setup [28].*

Next, the beam is focused YAG window oriented at Brewster’s angle (to minimize the reflection loss) using a focusing mirror \( f = 100 \text{ mm} \). The estimated thickness of YAG is chosen
between 1 mm to 4 mm, based on the required GVD to balance out the self-phase modulation and the added dispersion from the optics in the set up (dispersion from silicon lens and CaF$_2$ lens has been accounted for). Filament formation occurs in the vicinity of the geometric focus. Once the anomalous dispersion of YAG is equivalent to the accumulated nonlinear phase, the optimal self-compression can be achieved. Towards this, for different window thicknesses (1 mm to 4 mm windows), we scan the position of YAG with 0.5 mm increments with respect to the focal spot position along the beam’s propagation direction to find both the appropriate thickness and suitable window position. A systematic measurement of the pulse duration for each thickness is carried out using FROG. When the 2 mm YAG plate is placed about 3 mm ahead of the focus, the shortest pulse duration of $\tau=34$ fs is obtained, with no measurable loss in the energy within the precision of the power-meter. Thinner plates showed best compression closer to the focus (2 mm ahead of the focus for 1 mm YAG thickness), but the minimum pulse duration was still longer ($\tau=69$ fs for 1 mm YAG thickness).

In Figure 6-4, the uncompressed and shortened pulses are both characterized. Panels (a, b) refer to the measured and retrieved FROG traces of the uncompressed pulses respectively, and panels (c, d) present experimental and reconstructed FROG traces for the shortened pulses. In panel (e) the retrieved temporal profiles for 90 fs and 34 fs pulses are shown. The result of self-compression corresponds to sub-three-cycle duration. The retrieved spectral profiles in panel (f) indicates the spectral broadening of mid-IR driving beam, stretched mostly to shorter wavelengths due to self-steepening in the self-compression process [165].
6.3.2 Few-cycle Driven HHG Setup

To focus the pulses to the exit plane of a-cut ZnO crystal, the lens is replaced by a focusing mirror to avoid introducing dispersion to the self-compressed pulses. The path from self-compression set up to HHG set up is the same distance as it is to the FROG set up. Therefore, we believe that propagation path does not add more dispersion that has been already considered in the pulse measurements. Hence, the compressed pulse duration at the interface of air/target is 34 fs.
Using the measured pulse energy, pulse duration, and focal spot size, the vacuum peak intensities corresponding to the 90 fs pulse is 0.6 TW/cm$^2$ and for the compressed pulses of 34 fs, the intensity increases to 1.6 TW/cm$^2$. The crystal is oriented perpendicular to the crystal axis, resulting in only odd harmonics.

![HHG Spectrum from Few- and Multi-cycle Driving Pulses](image)

**Figure 6-5: HHG Spectrum from Few- and Multi-cycle Driving Pulses**

*Corresponding HHG spectrum from few-cycle (dark blue) compared to HHG spectrum from multicycle (red) driving pulses. The vacuum intensities are estimated to be 1.6 and 0.6 TW/cm$^2$ and 0.6 TW/cm$^2$ for the few- and multicycle pulses, respectively [28].*

Shown in Figure 6-5 are both multi- and few-cycle driven high harmonic spectra. Compared to the multi-cycle spectrum, the yield of few-cycle HHG is enhanced by a factor of approximately two for above-gap plateau harmonics. Moreover, the harmonic cutoff energy appears to be extended from $\sim 4.8$ eV (the 15$^{\text{th}}$ order) to more than 5.5 eV (beyond the 17$^{\text{th}}$ order). Because of the limitation in the spectrometer range, the real cut-off, and the extension of it due to few-cycle driven harmonics is not observable. The simulations, described below, suggest that both the increase in the harmonics yield and the cut-off extension occurs as the result of the increased
intensity of the few-cycle pulses. The relative broadening in the harmonics spectral bandwidth is another signature of the few-cycle-driven HHG and verifies a temporal gating of the HHG process in the shorter pulse, reducing the duration of the harmonic pulse train.

6.3.3 Theoretical Analysis

To simulate the experiments, a one-dimensional (1D) model of ZnO with two bands is accurate enough to describe the main features of the HHG process in semiconductors [166]. The mid-IR beam’s polarization is perpendicular to c-axis (along $I' - M$ direction) suggesting that electron-hole dynamics are restricted in this direction. For the energy dispersion and dipole matrix elements of ZnO, the structural data described in [74,167] is utilized, and the calculations are based on the idler wavelength ($\lambda_{\text{idler}}=3.8 \ \mu\text{m}$), and the measured temporal pulse profile extracted from the FROG measurements. The vacuum peak intensities are modified to reflect the intensity inside the crystal. 0.76 TW/cm$^2$ and 0.29 TW/cm$^2$ were used for the few- and multicycle pulses, respectively. Other parameters that are implemented in the simulations are band gap of 3.3 eV, dephasing time of 1.582 fs, and time steps of 1.2 attoseconds. The emitted radiation spectrum is then calculated via the Fourier transform of $\mathbf{J}(t)$. The harmonic spectra were calculated over a range of intensities within the focus and coherently averaged based on the experimentally measured intensity distribution within the focal plane [167].

Figure 6-6 shows the total calculated spectra (yield of the inter- and intraband contributions) for the multi- and few-cycle driving pulses, after intensity averaging. As illustrated in the figure, near- and above-gap harmonics form a plateau for both multi- and few-cycle driving beams. By comparing the peaks of harmonics generated by self-compressed pulses, and the multicycle pulses, it is clear that the harmonics become broadened for the shorter driving pulses,
supporting the result of experiment. This effect is shown in detail in the inset for the 15\textsuperscript{th} harmonic. The yield of the 15\textsuperscript{th} harmonic is additionally increased by approximately an order of magnitude for the compressed pulses. The discrepancies between the experimental results and the theoretical calculations originates most likely from the propagation effects in the bulk crystal, and the limitation of the detector to measure the actual harmonics spectrum cut off.

![Simulated Harmonic Spectra Driven by Uncompressed and Compressed Pulses](image)

**Figure 6-6: Simulated Harmonic Spectra Driven by Uncompressed and Compressed Pulses**

*Simulated harmonic spectrum driven by $\sim$8 cycles and $\sim$3 cycles pulses, shown by a solid red line and a solid blue line, respectively. The inset shows the normalized yields of the 15\textsuperscript{th} harmonic on a linear scale, to more clearly show the broadening of the spectrum.*

In conclusion, few-cycle mid-IR pulses generated through nonlinear self-compression have been utilized to generate high harmonics in ZnO crystals. The increase in the harmonic yield by a factor of two, and an apparent increase of the cutoff energy from the 15\textsuperscript{th} to beyond the 17\textsuperscript{th} harmonic is demonstrated, and the qualitative features in the experimental spectrum is supported by the simulation based on a 1D two-band model. Our results suggest the potential of using...
nonlinear self-compression to produce a few-cycle mid-IR laser source for solid-state attosecond science from commercially available Yb laser technology.

6.4 Anti-resonant Hollow-core Fiber

As the route to single-cycle pulse generation, we have additionally explored the use of anti-resonant hollow-core fiber (AR-HCF) pulse compression through collaboration with Dr. Correa’s group at CREOL. In such fibers, the wave guide dispersion can be engineered to provide anomalous dispersion and self-compression in a particular spectral range. In addition, the confined geometry can provide enhanced nonlinear interactions. The optimal fiber dimensions for nonlinear propagation and self-compression of our mid-IR pulses were obtained from simulations, and a gas-filled microstructured fibers setup [89,168,169] was designed and fabricated, as shown in Figure 6-7. The result of simulation for the spectrum and pulse duration are shown in Figure 6-8 and Figure 6-9.

![Figure 6-7: Design of Anti-resonant Fiber and High Pressure Durable Chamber](image)

Figure show the experimental scheme for the compression of idler mid-IR pulses with wavelength of $\lambda=3.5 \, \mu m$ and pulse duration of 90 fs
Figure 6-8: Simulation of Power Spectral Density and Spectral Evolution

Calculated power spectral density (PSD) at $z=0$ and $z=10$ cm (top) and spectral evolution (bottom) for a 73 μm core HC-AR fiber under 10 bar Xe, pulse energy 8 μJ, pulse duration 90 fs pumping in the anomalous dispersion regime at 3.5 μm. DW: dispersive wave.

Figure 6-9: Simulation of Temporal Evolution and Maximum Pulse Compression

Calculated temporal evolution (left) and maximum pulse compression at $z=7.7$ cm (right) for a 73 μm core HC-AR fiber under 10 bar Xe, pulse energy 8 μJ, pulse duration 90 fs pumping in the anomalous dispersion regime at 3.5 μm. The pulse is compressed down to ~2.1 fs.

The focal spot size at the tip of the fiber is checked with mid-IR camera (Boson 320 LWIR thermal camera). The measurement of focal spot for checking the coupling geometry has been
done by moving the camera in the vicinity of focus and measure the focus spot size for each 0.025 mm displacement of camera. The measurements are shown in Table 2.

<table>
<thead>
<tr>
<th>Position (mm)</th>
<th>Radius in x direction (pixels)</th>
<th>Radius in y direction (pixels)</th>
<th>Overall beam radius (pixels)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.550</td>
<td>5.95</td>
<td>8.57</td>
<td>7.14</td>
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<tr>
<td>0.575</td>
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<td>0.600</td>
<td>3.90</td>
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<td>4.32</td>
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<tr>
<td>0.625</td>
<td>4.00</td>
<td>3.73</td>
<td>3.86</td>
</tr>
<tr>
<td>0.650</td>
<td>5.63</td>
<td>3.86</td>
<td>4.66</td>
</tr>
<tr>
<td>0.675</td>
<td>8.12</td>
<td>5.54</td>
<td>5.70</td>
</tr>
</tbody>
</table>

Table 6-2: Measurement of Focal Spot Size

With scanning the position of the camera with respect to the lens, the number of camera pixels in $x$, and $y$ dimension in the transverse plane of the propagation which corresponds to the focal image is calculated. The image of the focal spot and its zoomed version are both shown in Figure 6-10.

![Focal Spot Size Measurements Based on the Pixel Size of Image](image)

Figure 6-10: Focal Spot Size Measurements Based on the Pixel Size of Image

Each pixel corresponds to 6 $\mu$m and the focal diameter is found by fitting the calculated focal spot at each step of measurement. Based on these measurements, we find the Rayleigh length to be
approximately 0.5 mm. The beam diameter is 46.32 µm, which is an appropriate size relative to the inner diameter of the fiber (74 µm). The measurement suggests that high coupling efficiency can be obtained. The plotted data and FWHM of the fitting function is shown in Figure 6-10.

Measurements of the fiber coupling and spectral broadening are planned. Pulse compression remains a challenge for sub-cycle pulses, and we intend to perform measurements using the TIPTOE technique [170,171].

![Figure 6-11: Measured and Fitted Data for Transverse Plane of the Beam](image)

*The number of pixels and FWHM of the fitted function results in 4 pixels (24 µm radius) for x direction, and (3.72 pixels (22.38 µm radius) in y direction.*
CHAPTER 7: SUMMARY AND OUTLOOK

In this dissertation I investigated orientation dependence of emitted harmonics from a-cut bulk ZnO driven by intense femtosecond mid-IR pulses. Aside from the intense harmonic emission observed for driving laser polarizations along the high symmetry axes, the polarization-resolved harmonic signal reveals structural features when the driving laser is polarized along other angles corresponding to Zn-O bonds. Using one-dimensional two-band Semiconductor Bloch Equations in combination with the Linearly-Coupled Excitation model, I explained how the symmetry of the medium can be incorporated into the dipole amplitude and phase. While the proposed model effectively replicates the major features of the polarization-resolved HHG spectrum observed in the experiment, the dependence of parallel and perpendicularly polarized harmonics on the crystal orientation, as well as the polarization states of emitted harmonics for particular crystal orientations, were found to be quite different from one another, suggesting that the polarization-dependent features are primarily governed by structural symmetry rather than the excitation dynamics.

As an application of symmetry to control harmonic generation process, I investigated the generation of high harmonics from the ferroelectric crystals, which have ‘tunable’ symmetry properties due to the ability to control the magnitude and direction of spontaneous permanent dipole moments using an external electric field. Through studies of the orientation dependence of odd and even harmonics and their relative polarization states, I observed that the harmonic signal depends strongly on the ferroelectric polarization. Future study of HHG in ferroelectric and multiferroic crystals opens the pathway towards emergent optoelectronic devices based on HHG
and promotes solid-state high harmonic spectroscopy as an all-optical technique to probe the fundamental limits to light-induced switching in ferroics.

Although the focus of the dissertation remained mainly on the orientation dependence and polarization properties of ZnO and ferroelectrics, these properties are universal feature of strong field physics and has been observed in several solids. Therefore, time-resolved spectroscopy driven by high harmonics is an inclusive technique with the potential for sub-cycle temporal resolution to study the carrier correlation and dynamical phase transition in solid state of matter.

Finally, I demonstrated the generation of high harmonics in ZnO crystals with few-cycle mid-IR pulses generated through nonlinear self-compression. I demonstrated that the harmonics yield would increase by factor of two, and the cut-off energy, originally observed up to 15th harmonics, would extend to beyond the 15th harmonic. The results propose pulse compression via filamentation in the anomalous dispersion regime as promising techniques for development of few-cycle mid-IR laser sources and will further improve solid-state attosecond science.

As the route to single-cycle pulse generation, gas-filled microstructured fiber [89,168,169] compression scheme is developed through collaboration with Dr. Correa’s group at CREOL, and the optimal fiber dimensions that would enhance the nonlinear propagation of the pulses in the mid-infrared regime is obtained from simulations. Subsequently, the fiber is fabricated and the prospects of spectral broadening of 3.5 μm idler wavelength followed by effective post compensation setup is discussed. Future plan is to experimentally test and control the strength of the nonlinearity by varying the average power and gas pressure. Further investigation will pave the way to developing high-power high-repetition attosecond source in the mid-IR regime.
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