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Traditio et Innovatio

Single-cycle probing of the dynamics of the insulator-to-metal phase transition in VO_2

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Abstract

This thesis takes advantage of both the ultrashort duration and high peak power of femtosecond laser pulses to explore two essential frontiers in condensed-matter and strong-field physics. First, it resolves the long-debated insulator-to-metal transition mechanism in monoclinic (M1 phase) vanadium dioxide (VO_2) by using a single-cycle optical pulse excitation. The optical pulse first drives the system to an excited metallic rutile state, followed by electron thermalization and lattice relaxation that unfold over tens to hundreds of femtoseconds. Isolation of the structural and electronic dynamics of the system is achieved through this methodology. The extracted pure population dynamics allow for the first time to visualize the highly anharmonic vanadium–vanadium bond oscillations, which play a key role in the physics of the insulating monoclinic to metallic rutile phase transition. Second, the thesis demonstrates the development of an advanced solid-state high harmonic generation and spectroscopy apparatus, which combines stable broadband harmonic detection under precisely characterized light fields. This capability enables for the first time, the precise study of the transition from perturbative to nonperturbative or extreme nonlinear optics in bulk crystals. The transition to the extreme regime is probed by tracking the scaling of the harmonic yield with the applied field strength over a broad range of crystalline solids—including diamond, MgO , MgF_2 , CaF_2 , and LiF , thereby providing a platform for investigating the physics of this transition.

Zusammenfassung

Diese Arbeit nutzt sowohl die ultrakurze Dauer als auch die hohe Spitzenleistung von Femtosekunden-Laserpulsen, um zwei wesentliche Grenzbereiche der Physik kondensierter Materie und der Starkfeldphysik zu erforschen. Erstens wird der seit langem diskutierte Mechanismus des Übergangs vom Isolator zum Metall in monoklinem (M1-Phase) Vanadiumdioxid (VO_2) mit Hilfe einer optischen Einzelpulsanregung aufgeklärt. Der optische Puls bringt das System zunächst in einen angeregten metallischen Rutilzustand, gefolgt von Elektronenthermalisierung und Gitterrelaxation, die sich über Dutzende bis Hunderte von Femtosekunden entfalten. Durch diese Methode wird die strukturelle und elektronische Dynamik des Systems isoliert. Die extrahierten reinen Populationsdynamiken ermöglichen zum ersten Mal die Visualisierung der stark anharmonischen Vanadium-Vanadium-Bindungsschwingungen, die eine Schlüsselrolle in der Physik des isolierenden monoklinen zu rutilen Metallphasenübergangs spielen. Zweitens wird in dieser Arbeit die Entwicklung einer fortschrittlichen Festkörperapparatur zur Erzeugung von Oberwellen und zur Spektroskopie demonstriert, die eine stabile breitbandige Detektion von Oberwellen unter präzise charakterisierten Lichtfeldern ermöglicht. Diese Fähigkeit ermöglicht zum ersten Mal die genaue Untersuchung des Übergangs von perturbativen zum nichtperturbativen oder extremer nichtlinearer Optik in Massenkristallen. Der Übergang in den extremen Bereich wird durch die Verfolgung der Skalierung der harmonischen Ausbeute mit der angelegten Feldstärke über eine breite Palette von kristallinen Festkörpern - einschließlich Diamant, MgO , MgF_2 , CaF_2 und LiF - untersucht, wodurch eine Plattform für die Erforschung der Physik dieses Übergangs geschaffen wird.

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Introduction

From discovering the wave-particle duality of light with ordinary light sources to control the electron dynamics with modern laser systems, the research in light-matter interactions has traversed a long path. The nature of light intrigued ancient philosophers; they started guessing about light's nature, but Isaac Newton and Christiaan Huygens were among the first ones who scientifically advanced this study [1, 2, 3]. Thomas Young (double slit experiment), Augustin-Jean Fresnel (wave theory of light), Max Planck (quantization of light's energy to explain black body radiation), and Albert Einstein (explanation of photoelectric effect) added their experimental and theoretical contributions to establish the wave-particle dual nature of light [4, 5, 6, 7]. The aforementioned works, together with spectroscopic discoveries like atomic absorption, atomic emission, the Raman effect, etc., had relied on incoherent and low intensity ordinary light sources [8, 9, 10].

With the discovery of the laser [11] by Theodore Maiman in 1960, the long-awaited goal of coherent, tabletop, intense light sources became a reality. Since its invention, the laser technology has been continuously upgraded to achieve higher power and shorter pulse durations so that it could probe strong-field and ultrafast phenomena. Two years later, McClung and Hellwarth produced nanosecond (10^{-9} s) pulses with the Q-switching technique [12]. Later, mode-locked lasers generated picosecond (10^{-12} s) and femtosecond (10^{-15} s) optical pulses [13, 14]. Although ultrafast laser pulses were available in the 80's, their peak power was not strong owing to laser-induced damage of the gain medium in the amplification process. Chirped pulse amplification (Nobel prize 2018) solved this problem in 1985 [15], and femtosecond petawatt level lasers became available. The reduction of laser pulse duration continued further and in 2001 femtosecond laser pulses facilitated extreme ultraviolet (EUV) attosecond pulse generation (Nobel prize in 2023) possible through the process of high harmonic generation in gaseous systems [16, 17]. After the successful generation of EUV attosecond optical pulses, the next big challenge in laser technology was to synthesize custom optical pulses of femtosecond and attosecond durations. The light field synthesizer achieved this goal by controlling the spectral and temporal properties of broadband light pulses [18, 19].

The above-mentioned advances in laser technology has paved the way for the study of nonlinear and strong field light-matter interactions. When the laser intensity is low, such that it cannot alter the electrostatic potential of matter significantly, laser-matter interactions fall under the realm of perturbative nonlinear optics, where the laser

interaction is treated as a perturbation to the original system. Under these low-intensity fields, the laser-induced polarization is dominated by linear and weakly nonlinear terms [20]. In contrast, ultrafast lasers with amplified pulses can achieve peak intensities whose fields are high enough to approach or even exceed the binding fields within matter to induce strong nonlinear effects. Since ordinary perturbation theory fails to explain the strong-field effects, this regime is defined as the nonperturbative or strong-field regime. The study of strong-field effects has led to discoveries like high harmonic generation [21, 22, 23, 24], above-threshold ionization [25], attosecond light pulse generation [16, 17], attosecond electron pulse generation [26], etc.

Aside from facilitating the research in strong-field laser-matter interactions, high-intensity ultrashort pulses enable to track the phenomena occurring on ultrafast timescales in time-resolved experiments. Thanks to these ultrashort pulses, rotational and vibrational dynamics of molecules, which occur in picosecond and femtosecond regimes are now accessible. Time-resolved dynamics work on a pump-probe scheme, where a strong pump pulse excites the system, and a delayed weak pulse (probe) monitors the pump-induced responses of the system as a function of time. Ahmed Zewail followed the pump-probe method to examine the time-resolved chemical dynamics with femtosecond laser pulses. His work on femtochemistry [27, 28] earned him the Nobel Prize in 1999. With the progress of both ultrashort pulse technology and probing techniques over the years, pump-probe methods have become a powerful tool for probing several phenomena such as recording chemical reaction dynamics [29, 30], imaging molecular orbital [31], directly measuring light field waveform [32], studying electron transport in solids [33], observing real-time valence electron motion [34], tracking photoinduced phase transitions [35, 36], etc.

Photoinduced phase transition (PIPT)

Phase transitions are usually driven by external stimuli such as temperature [37], pressure [38], or doping [39]. However, light can also induce non-thermal, nonequilibrium changes in the material’s structural [35, 40], electronic [35, 36], or magnetic [41] properties to alter its phase. Ultrafast laser-driven phase transitions can modify material properties in a controlled way on ultrafast timescales. In PIPT with the pump-probe method, ultrafast lasers can probe the properties of the unperturbed state or drive the system into a new phase depending on whether the laser excitation is weak or strong respectively [42, 43].

Monoclinic vanadium dioxide (M1-VO_2) is one of the most important candidates that shows PIPT when exposed to ultrashort laser pulses [35, 42]. Due to its near room temperature (67°C) [37, 44] insulator-to-metal phase transition (IMT) accompanied by a monoclinic to rutile (R-VO_2) structural change, this material has been extensively studied. Over the last 25 years, several ultrafast experiments [35, 45, 40, 46, 42, 47, 48, 49, 50, 51] have been performed to elucidate the transition dynamics and mechanism of PIPT

in VO₂. However, most of these studies are limited by the durations of the pump and probe pulses as well as the type of samples (thin film) used. Thin film samples introduce unwanted issues like interfacial effect, thickness effect, polycrystallinity, defects, and strain effect.

Ultrafast optical pump-probe techniques like transient reflection, transmission, absorption and photoelectron emission provide high temporal resolution and sensitivity to both electron and atomic dynamics in M1-VO₂ [35, 45, 46, 42, 48, 49, 47, 50]. However, these studies have so far produced a range of often conflicting conclusions regarding both the timescale and the nature of the IMT. On one hand, early femtosecond-scale studies emphasized on structural mechanism [35, 45], associating the transition timescale with the vibrational period of the vanadium-vanadium (V–V) mode in M1-VO₂ [52]. On the other hand, later investigations supported the idea of a instantaneous electronic Mott localization mechanism [47, 50, 49]. Nevertheless, these techniques are not able to provide the transient structure of the material after optical excitation. In contrast, time-resolved X-ray and electron diffraction probing methods can track the laser-excited dynamics of the atomic structures [35, 40, 46], but they lack both the sensitivity to electronic dynamics and the temporal resolution of optical probing methods. Overcoming these limitations requires a new approach that combines the high temporal resolution of the optical techniques and the real-time, phase-resolved detection of the transition dynamics.

High harmonic generation (HHG)

The interactions of intense laser pulses with gas, liquid, or solid generate high energy radiation of multiple frequencies, namely high harmonics (HHs) of the driving pulse. HHG was first discovered in gaseous systems, and the generation mechanism is well understood with the three-step model [53, 54]. Attosecond pulse generation [17, 55, 56], electron dynamics investigation [57, 58] and molecular orbital examination [31, 59] are a few examples of the applications of HHG in atoms and molecules.

Despite the success of HHG in the gas phase, it was challenging to generate higher-order harmonics from solids due to laser-induced damage. Meanwhile, this shortcoming was addressed by incorporating two main strategies: (i) reducing the solid target thickness and (ii) using laser pulses having photon energies lower than the bandgap of the target materials. Ghimire et al. generated higher-order harmonics in a solid sample for the first time in 2011 using a 500 μm -thick ZnO crystal and a mid-infrared driving laser of central energy ~ 0.32 eV [23]. Since then, solid-state HHG has been widely studied. High harmonic generation mechanisms in solids are different from those in gaseous media because they depend on factors such as electronic band structure [24, 60], valence potential [61] and symmetry [62, 61] of the solids. These characteristics make solid-state HHG an efficient tool for capturing band dispersion [24, 63] and valence electron potential [61] of solids. Extensive studies of solid-state HHG in materials like semiconductors [23, 64, 65],

dielectrics [24, 60, 62, 66], and nanostructured [67, 68] materials help to understand several aspects of the strong-field light-matter interactions.

In spite of the rapid advancements in solid-state HHG and spectroscopy over the last decade, the experimental apparatus have not been significantly upgraded. Consequently, there has not been much progress in addressing the experimental factors that contribute to the non-perfectly symmetric generation of HHs during orientation-dependent measurements in crystalline solids. Furthermore, techniques like laser picoscopy of solids [61] require experimental apparatus capable of not only simultaneous recording HHs spanning from the lowest to the highest measurable orders but also the incorporation of absolute driving field calibration. Such advancement are also necessary for laser field-dependent or crystal orientation-dependent HH spectroscopy [24, 23, 69]. Thus, solid-state HH spectroscopy would experience a massive boost once all these developments will be combined in a single setup.

In strong-field physics, the transition from perturbative to nonperturbative nonlinearity marks the onset of extreme nonlinearity or extreme photonics regime [70]: the regime where the response of a system to an external field becomes highly nonlinear [65, 71]. Understanding this transition is important for controlling HHG efficiency, manipulating harmonic spectra, and utilizing the nonperturbative regime for applications in attosecond pulse generation and ultrafast electron dynamics study. Even though solid-state high harmonics spectroscopy has been explored in various materials utilizing mid-infrared [23, 72], near-infrared [69, 62] or visible [24, 60, 61] laser pulses, to the best of our knowledge, no systematic study has measured the nonlinearity of harmonics in a wide range of materials. As a result, it becomes difficult to identify a general onset condition. Although the Keldysh parameter γ is usually used to define the onset of strong-field effects in gaseous media [73], no analogous parameter has been experimentally confirmed to characterize the perturbative to nonperturbative transition in solids across a variety of materials. This project needs the technical advancement of the high harmonic experimental apparatus as discussed in the previous paragraph.

In this thesis, I have contributed to uncover the population dynamics and electronic response during the photoinduced phase transition of monoclinic VO_2 utilizing broadband transient reflectivity measurements. An advanced experimental apparatus has also been developed for the generation and spectroscopy of high harmonics in bulk solids. This thesis also presents an experimental and theoretical investigation of the onset of extreme nonlinearity across various solids using high harmonic generation. Furthermore, a general summary of the thesis is as follows:

- As the primary objective, I have described the broadband probing of the ultrafast phase transition of M1-VO_2 using a ~ 2.4 fs single-cycle visible light pulse. The broadband probing spanning from 415 nm to 950 nm uncovers two characteristic decay time scales, previously assumed to be the outcomes of electronic Mott mechanism and structural mechanism of the phase transition [45, 47, 49, 50]. However, experiments presented in this dissertation suggest that the different timescales are

wavelength-dependent optical responses of the material. While researching the origins of these time scales, it can be concluded that the electronic response of the excited rutile phase elongates the transition time in one spectral region and reduces it in the other region. This observation can be used as a marker for the phase-resolved study with optical pulses. The time-resolved response of the thermally excited rutile phase are obtained by first elevating the temperature of M1-VO₂ crystal above the insulator-to-metal transition temperature and then carrying out a set of pump-probe experiments. This excited rutile phase response together with the transient reflectivity measurements of M1-VO₂ has enabled to disentangle the population dynamics of the M1-VO₂ during the phase transition. The wavelength-independent transition rate corresponding to monoclinic to rutile VO₂ phase transition is evaluated from the laser-excited population dynamics of the M1-VO₂. Accordingly, the transition rate and population dynamics are utilized to extract the anharmonic vanadium-vanadium bond length alternation dynamics [74] associated with the monoclinic to rutile phase transition. Thus the broadband probing of M1-VO₂ and R-VO₂ using our ultrashort optical pulses bridge the essential gap of combining the high temporal resolution of the optical techniques with the phase-resolved detection of the transition dynamics. Real-time TDDFT simulation further supports the experimental observation implying that the anharmonic motion of the V-V dimer triggered by the optical pulse is responsible for the phase transition.

- An advanced experimental setup for high harmonic generation and spectroscopy in solids has been developed, comprising several technical advancements. Three important features of the setup are: Firstly, the setup minimizes the effect of uneven surface roughness of the crystalline sample on the high harmonic yields in laser field strength- and crystal orientation-dependent high harmonic generation by utilizing a state of the art goniometer with 5 degrees of freedom and a chirped-mirror-based pulse compressor. This arrangement results in nearly symmetrical harmonic yields consistent with the crystal's intrinsic symmetry during a 360° rotational scan. Secondly, a custom-built dual spectrometer allows for the simultaneous measurement of high harmonics over a broad spectrum, from the lowest to the highest measurable orders, spanning the ultraviolet (UV) to extreme ultraviolet domains. The third feature is the calibration of the absolute laser field strength using EUV gas attosecond streaking measurements [32, 56] for the purpose of determining the precise driving field strength during high harmonic generation in the developed system. The experimental setup is optimized for operation with laser pulses having carrier photon energies of 2.0 eV and 1.5 eV respectively. These advancements are further needed for determining the onset of the extreme nonlinearity discussed in the next paragraph.
- In a systematic study of perturbative and nonperturbative high harmonic generation, the onset of extreme nonlinearity is examined for a wide range of materials. As the sources of HHG in this study, five bulk crystalline materials with distinct bandgaps: diamond (C), magnesium oxide (MgO), magnesium fluoride (MgF₂), cal-

cium fluoride (CaF_2) and lithium fluoride (LiF) are used. The electric fields for all the experiments are calibrated with EUV attosecond streaking, ensuring an accurate evaluation of the onset fields. While the nonlinearity of the third harmonic yield has primarily been used to capture the onset field for each material, the nonlinearity of the higher-order harmonic yields has also been presented to support the onset field determined by the third harmonic. A simulation of the ionization rates for fused silica is presented to clarify the significance of Keldysh's theory [73] in differentiating between the multiphoton and tunneling regimes and consequently, the perturbative and nonperturbative regimes. The experimental onset field amplitudes for all the materials do not agree with those predicted by the Keldysh parameter [73], leading to propose a new model to explain the results.

The thesis is arranged as follows

- Chapter 1 discusses about the physics of phase transitions in the strongly correlated material, vanadium dioxide.
- Chapter 2 gives a brief introduction to the high harmonic generation in solids.
- Chapter 3 provides an overview of the experimental attosecond (AS) beamline employed for all the experiments detailed in this thesis.
- Chapter 4 discusses in detail the experimental setup designed for conducting broadband transient reflection experiments on bulk single crystalline M1-VO_2 . This chapter also describes the technique used to achieve a polished surface from the bulk crystal.
- Chapter 5 presents the broadband probing of photoinduced phase transition in M1-VO_2 with two sets of transient reflection measurements, at room temperature and at 80°C . In addition, the importance of laser spectral intensity stabilization and laser pulse pedestal effect during broadband optical measurements are also highlighted here.
- Chapter 6 of this thesis presents the disentanglement of the monoclinic VO_2 population dynamics and excited rutile phase VO_2 electronic (thermalization and relaxation) response during the photoinduced phase transition of M1-VO_2 . The derived population dynamics are used to extract the vanadium-vanadium bond length alternation related to the ultrafast phase transition of M1-VO_2 . Results of real-time TDDFT simulation has been presented to support our experimental findings.
- Chapter 7 describes the development of the advanced experimental apparatus for high harmonic generation and spectroscopy in bulk solids.
- Chapter 8 presents an experimental investigation of the onset of extreme nonlinearity in bulk solids through high harmonic generation.

- Chapter 9 discusses the conclusions and outlook.

List of publications during the PhD period:

1. S. Mandal, P. Kumar, H.Y. Kim, Z. Pi, J. Xu, D. Chen, D. Kazenwadel, P. Baum, S. Meng and E. Goulielmakis, "Deciphering the dynamics of the light-induced phase transition in VO₂", (submitted).
2. S. Mandal, P. Kumar, Z. Pi, H.Y. Kim, M. Zhan and E. Goulielmakis, "Development of a state of the art solid-state high harmonic spectroscopy apparatus", (in preparation).
3. S. Mandal, P. Kumar, H. Y. Kim and E. Goulielmakis, "Onset of extreme nonlinearity in bulk solids", (in preparation).
4. H. Y. Kim, M. Garg, S. Mandal, L. Seiffert, T. Fennel, and E. Goulielmakis. "Attosecond field emission." Nature 613, no. 7945 (2023): 662-666.

Conference contributions during the PhD period:

1. S. Mandal et al., "Broadband probing of ultrafast phase transition in VO₂", LiMatI2024, September 2024, Rostock, Germany, (Poster presentation).
2. S. Mandal et al., "Onset of extreme nonlinearity in bulk solids", ECLIM 2024, September 2024, Lisbon, Portugal, (Poster presentation).
3. S. Mandal et al., "Attosecond field emission", AttoChem 2023, September 2023, Vienna, Austria, (Invited talk).

Chapter 1

Physics of vanadium dioxide

Transition metal oxides exhibit unique and interesting properties that emerge from the interaction of lattice, electronic, and magnetic degrees of freedom [75, 76]. Vanadium dioxide is an important example of a transition metal oxide due to its use in fundamental research and technological applications [77, 78, 79]. F. J. Morin discovered a reversible insulator-to-metal transition (IMT) of VO_2 at $\sim 67^\circ\text{C}$ [37] in 1959. Two years later, S. Westman et al. showed that this IMT is accompanied by a structural change from monoclinic (M1-VO_2) to rutile (R-VO_2) tetragonal phase [44] (Figure 1.1). Notably, the driving mechanism or the cause of the phase transition has been under debate since then. It was unexpected to observe the insulating behavior in VO_2 because of the presence of a partially filled band originating from the valency of vanadium (V) and oxygen (O). J. B. Goodenough published the first work on this topic in 1971 [80], and described that a Peierls-like distortion in the structure causes the formation of insulating phase, which should otherwise be metallic. He concluded that the primary mechanism behind this phase transition is the dimerization of the V atoms. However, Zylbersztein & Mott put forward a model [81] in 1975, also known as Mott-Hubbard model, which proposed that electronic correlations have the main contribution in creating the experimentally measured energy gap of the monoclinic phase. These conflicting ideas of Goodenough and Mott gave rise to the famed debate between structural distortion and electron correlation being competing pathways for the phase transition of VO_2 .

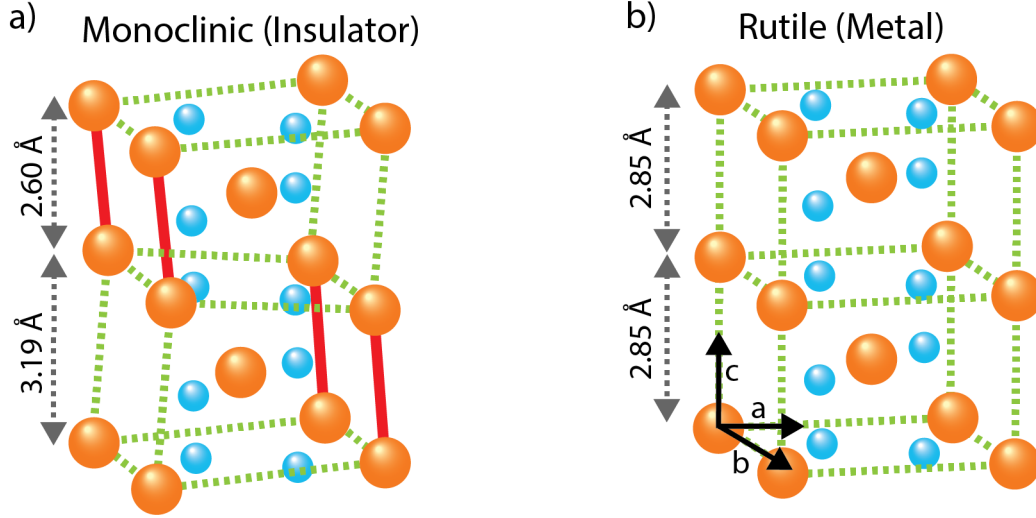


Figure 1.1: **Schematic of the VO_2 structure in the monoclinic and rutile phases.** a), b) Schematic of the crystal structure of (a) monoclinic (insulator) and (b) rutile (metal) VO_2 . Orange balls and cyan balls represent vanadium atoms and oxygen atoms respectively.

1.1 Crystal field theory and Goodenough model

The transition metal vanadium is present in the d-block of the periodic table and its electron configuration is: $[\text{Ar}]4s^23d^3$, with vanadium having five d-orbitals: $d_{3z^2-r^2}$, d_{xy} , $d_{x^2-y^2}$, d_{xz} , and d_{yz} (Figure 1.2). Five d-orbitals are degenerate in a spherical potential (Figure 1.3.a); owing to the high symmetric field, all the d-orbitals experience the same repulsion from the surrounding charges. However, in octahedral potentials (Figure 1.3.b), as in VO_2 , the metal ion is symmetrically surrounded by six oxygen ions or ligands. This octahedral crystal potential breaks the degeneracy as a result of the electrostatic repulsion between the metal d-electrons and ligands. Here, the rule is that the closer the d-electrons are to the anions, the higher their energies are. Crystal field theory describes that the hybridization of V_{3d} and O_{2p} orbitals facilitates σ and π type overlaps and creates states with σ and π characters. $d_{3z^2-r^2}$ and d_{xy} orbitals (Figure 1.2) point towards the oxygen anions of the octahedron and hybridize strongly with O_{2p} orbitals to raise the energy of these two d-orbitals, which are collectively referred as e_g^σ or σ^* states (Figure 1.3.d). Meanwhile, the other three d-orbitals $d_{x^2-y^2}$, d_{xz} , and d_{yz} experience less repulsion because of their orientation between the oxygen anions (Figure 1.2). As a consequence, they are shifted to lower energy levels and form a threefold degenerate t_{2g} state (Figure 1.3.d).

The octahedral potential of rutile VO_2 exhibits a tetragonal distortion, characterized by the distortion of the octahedron along the z-axis, as shown in Figure 1.3.c. The

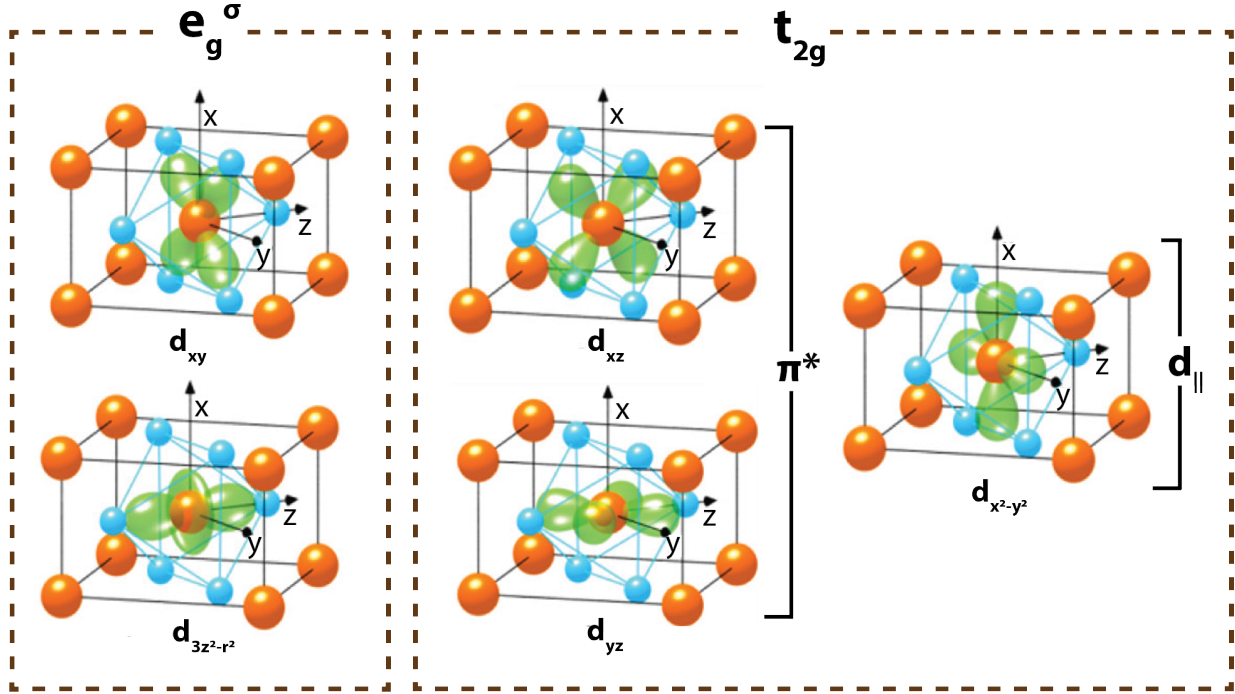


Figure 1.2: **Vanadium d-orbitals within oxygen octahedron of a rutile VO_2 structure.** The $d_{3z^2-r^2}$ and d_{xy} orbitals form e_g^σ state, while the $d_{x^2-y^2}$, d_{xz} and d_{yz} orbitals create t_{2g} state. Here green lobes describe the d-orbitals, orange balls illustrate the vanadium atoms and cyan balls represent the oxygen atoms. Adopted from ref. [82]

tetragonal symmetry of the crystal potential breaks the degeneracy of the t_{2g} state into π^* and $d_{||}$ states (Figure 1.3.d). Relatively non-bonding $d_{x^2-y^2}$ orbital ($d_{||}$ state), which lies along the rutile x-axis (Figure 1.2), shifts to a lower energy level compared to the d_{xz} and d_{yz} orbitals (π^* state), which orient between the oxygen anions (Figure 1.2). Figure 1.4 illustrates separately the tetragonal potential of oxygen anions within the VO_2 rutile structure.

The Goodenough model [80] takes into account the crystal field effects, as well as the interactions between V–V pairs (dimerization) to explain both the appearance and disappearance of the bandgap in low temperature insulating and high temperature metallic phases of VO_2 respectively. Vanadium atoms align linearly along the c-axis (Figure 1.5.a) of the rutile structure; the V–V distance becomes uniform, and no dimerization occurs. This results in partial overlap of $d_{||}$ and π^* states—the material is expected to be metallic as the electrons can move freely in the empty states above the Fermi level (E_F) (Figure 1.5.c). However, during the phase transition from rutile to monoclinic, VO_2 undergoes a Peierls distortion where the V atoms form V–V dimers along the c-axis (Figure 1.5.b). Dimerization creates bonding and antibonding states by doubling the unit cell and bringing

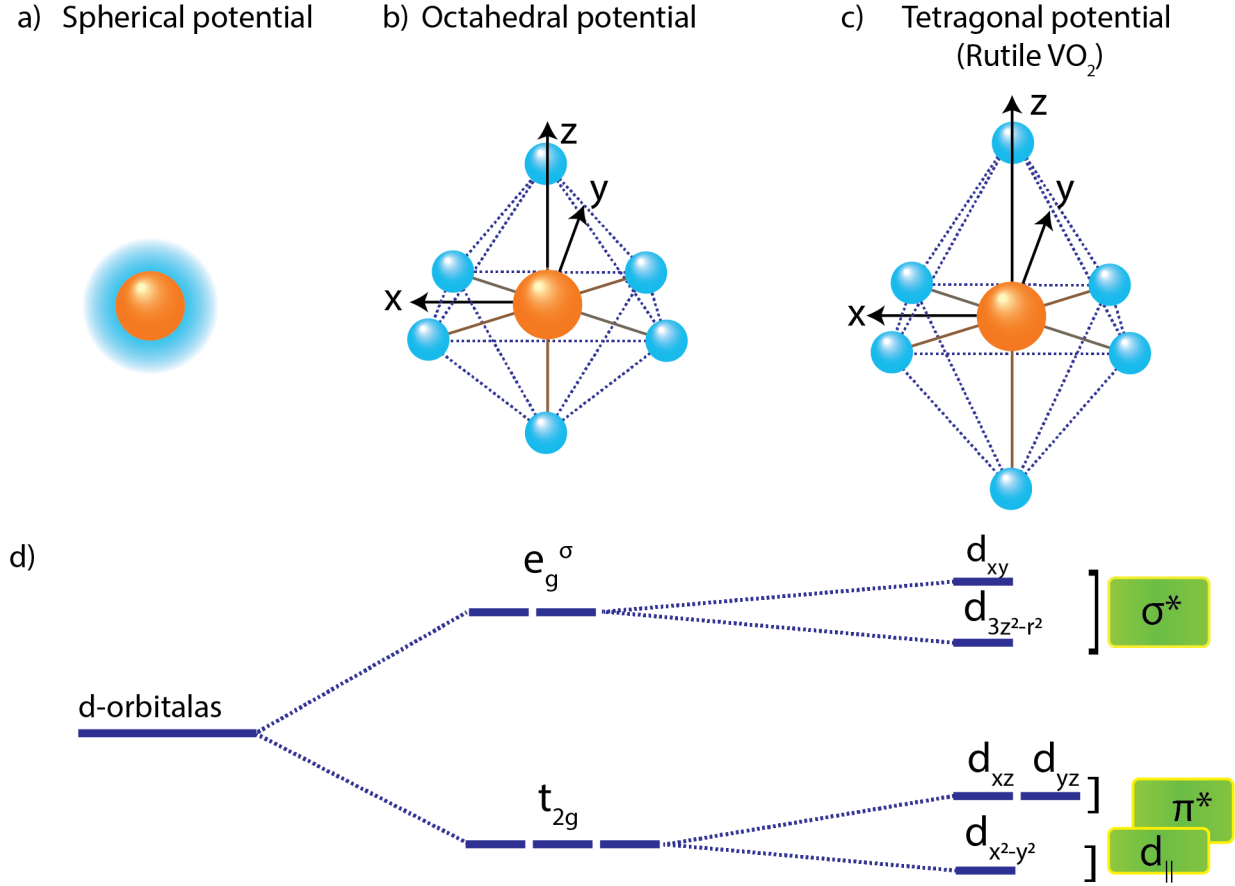


Figure 1.3: **Energy level splitting of d-orbitals of V ion under three different crystal potentials.** a), d) In a spherical potential, the degeneracy of the five d-orbitals remains intact. b), d) The degeneracy breaks into two-fold e_g^σ and three-fold t_{2g} orbitals under an octahedral potential. c) In a tetragonal potential, like rutile VO_2 , additional splitting of the orbital degeneracies occurs. Adopted from refs. [83, 84]

the V atoms in each dimer closer. The $d_{||}$ band, which was responsible for the metallic behavior in the rutile phase, splits into a bonding ($d_{||}$) and an anti-bonding ($d_{||}^*$) component (Figure 1.5.d). The bonding $d_{||}$ band becomes fully occupied, and the anti-bonding $d_{||}^*$ band moves up in energy above the Fermi level. The tilting of V-V dimers and deformation of vanadium-oxygen octahedra strengthen the interaction between vanadium d-orbitals and oxygen p-orbitals such that the π^* band rises above the Fermi level (Figure 1.5.d). Thus, the insulating phase of the monoclinic structure in the Goodenough model can be explained by the combined effects of dimerization, vanadium-vanadium tilting, and deformation of the vanadium-oxygen octahedra.

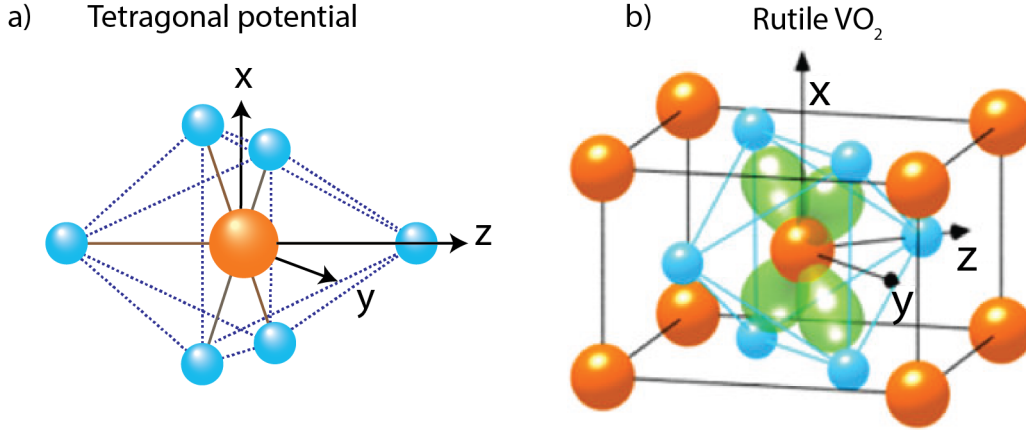


Figure 1.4: **Visualization of the tetragonal potential within rutile VO₂ structure.** a) Tetragonal potential rotated by 90°, compared to the one presented in Figure 1.3.c. b) Rutile VO₂ structure with d_{xy} orbital (green). The cyan balls (oxygen anions) in a) and b) mark identical arrangements of tetragonal structure.

1.2 Mott-Hubbard model

The Mott-Hubbard (MH) phase transition cannot be understood through single electron interaction. This model considers the electron hopping between neighboring sites and the repulsion of electrons due to the Coulomb potential U within the same site. The Hubbard's Hamiltonian [85] for a system with interacting particles is given by,

$$H = -t \sum_{\langle ij \rangle \sigma} \left(c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma} \right) + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (1.1)$$

Here, U is the onsite intra-atomic Coulomb potential (e^2/r_{12}), and t is the hopping integral (kinetic energy), which represents the ability of an electron to hop between neighboring sites i and j . The bracket $\langle ij \rangle$ constrains the summation to nearest-neighbor pairs (i, j) . $c_{i\sigma}^\dagger$ and $c_{j\sigma}$ represent the creation and annihilation operators of electron with spin σ on site i and j respectively. The operator $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ measures the occupancy of site i with electrons of spin σ . In the non-interacting case ($U=0$), the MH model simplifies to the tight binding model and exhibits metallic behavior if there is one electron per site. However, in the strong interacting case ($U>t$), one can expect an insulating behavior due to the localization of charges from electronic repulsion. Mott insulators are basically materials that possess these properties. Therefore, according to the MH model, competition between Coulomb repulsion and hopping integral of the metal d electrons leads to the insulating behavior in the monoclinic phase.

The metallic behavior in rutile phase (above $\sim 67^\circ\text{C}$) arises from the delocalization of electrons across the lattice through partially filled $d_{||}$ states. Mobile conduction

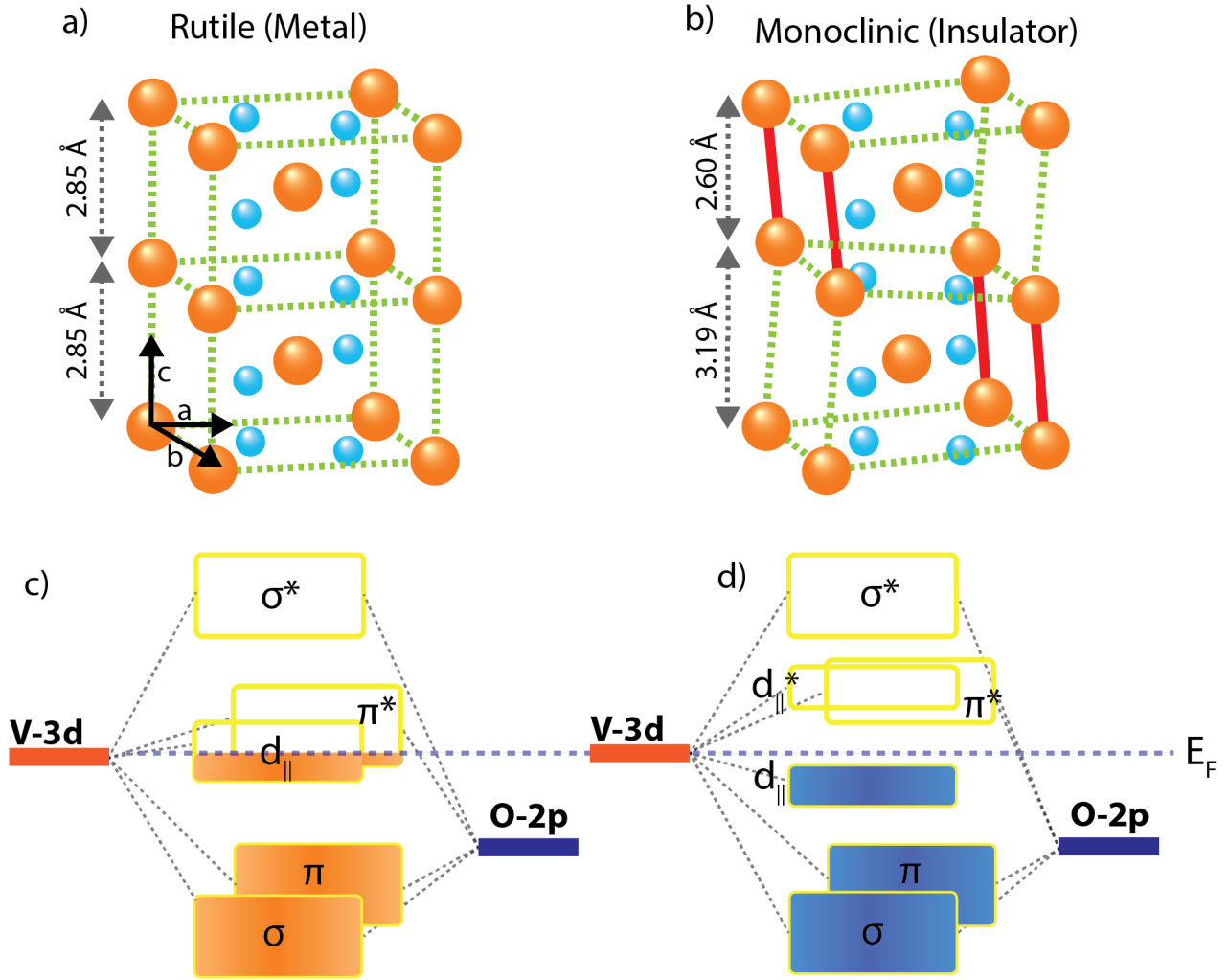


Figure 1.5: **Schematic of the band structure in the metallic and insulating phases of VO₂.** a), b) Schematic of the crystal structure of (a) rutile (metal) and (b) monoclinic (insulator) VO₂. Orange balls: vanadium atoms; cyan balls: oxygen atoms. c), d) Schematic of the band structures in the metallic (c) and insulating states (d) of VO₂ based on crystal field theory.

electrons reduce the on-site (within the same $d_{||}$) Coulomb repulsion U by screening the interactions between localized electrons. The system remains metallic since the kinetic energy dominates the Coulomb repulsion U , allowing the electrons to move freely. In contrast, when the system is cooled below the phase transition temperature, the electron mobility and consequently, the screening diminishes. The unscreened repulsive force between electrons in the same orbital becomes stronger, which increases the effective Coulomb repulsion U felt by the electrons. The electrons are trapped in individual $d_{||}$ orbitals because the repulsive interaction does not allow two electrons to share the same orbital or to hop be-

tween sites. This strong electron-electron repulsion within the $d_{||}$ orbitals splits the band into lower (containing the localized, lower energy electrons) and upper (unoccupied high energy states) Hubbard bands. The gap between the lower and upper Hubbard bands is responsible for the insulating behavior of VO₂.

Over the last few decades, a variety of experiments, especially ultrafast measurements have been carried out using different techniques to understand the phase transition mechanism of VO₂ and the related transition pathways.

1.3 Ultrafast experiments on VO₂

In order to characterize the equilibrium monoclinic and rutile phases of VO₂, researchers use static techniques like X-ray diffraction [86, 87], Raman spectroscopy [88, 89], reflectance spectroscopy [90], and photoemission spectroscopy [90]. However, the static techniques have to be combined with ultrafast methods to probe the nonequilibrium states during the phase transition— optical excitation by ultrafast laser pulses [91] can track the phase transition dynamics on femtoseconds (fs) or picoseconds (ps) timescale.

The two main objectives of the ultrafast VO₂ experiments have been: (i) determining the timescale of the phase transition and (ii) identifying the mechanism behind the phase transition whether due to electron correlations (Mott mechanism) or structural distortions (Peierls mechanism). According to the current understanding, the laser-driven phase transition in the Mott picture begins with the generation of photoexcited holes, which reduces V_{3d} electron population and alters the screening, that finally leads to the collapse of the band gap and an instantaneous insulator-to-metal transition without structural changes [49]. On the other hand, if structural distortions alone drive the transition process, the electronic temperature first rises by the absorption of laser photons and the phonon modes generated from this process control the atomic movement, which ultimately results in the rutile metal phase. The duration of such transitions is longer than the Mott transition because the final state can only be identified once the structural changes are complete [49].

There are a number of significant experiments in this topic. Cavalleri et al. conducted the first time-resolved phase transition experiment of VO₂ in 2001 [35], where they observed a sub-picosecond transformation to the high-temperature phase (rutile metal) using femtosecond X-ray and visible pulses as probes for structural and electronic dynamics respectively. Cavalleri et al. [45] carried out another experiment in 2004 utilizing ultrafast reflectance spectroscopy with a driving pulse having 15 fs duration to show that the phase transition is not pulse duration limited; instead, it takes a time of ~ 80 fs. The 80-fs time delay was described as a "*structural bottleneck*" related to the optical phonon period that links monoclinic and rutile structures. These two experiments triggered several new studies in following years focusing on identifying the roles of electronic and structural contributions. Among these, the main experimental techniques utilized to investi-

gate the photoinduced phase transition dynamics of VO_2 are ultrafast optical spectroscopy [35, 45, 92, 42, 49, 48], terahertz time-domain spectroscopy [93, 94, 95, 96], ultrafast electron diffraction [40, 46, 97, 98], ultrafast X-ray diffraction [35, 99, 51, 100], time-resolved X-ray absorption spectroscopy (XAS) [101], time-resolved photoelectron spectroscopy [47], EUV transient absorption spectroscopy [50], etc.

Interestingly, the *structural bottleneck* was not observed in ultrafast experiments of photoemission [47], THz conductivity [95], infrared transmission [49], and EUV transient absorption [50] spectroscopy. Although the transition times in the first three studies [47, 95, 49] were constrained by pulse durations or instrument responses (40 fs, 60 fs, and 20-35 fs, respectively), the fourth study [50] exhibited 26 ± 6 fs transition time which was not limited by the instrument response (5.6 fs) but three times shorter than the *structural bottleneck* time. Thus, these experiments suggest that IMT in VO_2 is driven by the Mott mechanism. Moreover, the ultrafast reflectance measurement in VO_2 microcrystals showed that the IMT time can vary from 40 fs (pulse duration limited) to 200 fs (not pulse duration limited) [48], indicating the dependence of ultrafast IMT on the type or size of the sample used. However, all these approaches are not sensitive to the transient structure of the material.

Furthermore, ultrafast X-ray [35, 99, 51, 100] and electron diffraction [40, 46] measurements examined the structural changes during the phase transition. Baum et al. [40] used electron diffraction to demonstrate that V-V dimer dilation occurs within 300 fs, whereas the atomic displacements take picoseconds. By using electron diffraction and optical absorption measurement, Morrison et al. [46] concluded that photoexcitation results in a transient monoclinic metal-like phase. This experiment supports the ultrafast optical measurements mentioned in the previous paragraph. Nevertheless, studies with X-ray absorption spectroscopy have shown that there is no monoclinic metallic phase during photoinduced phase transition [101]. Recent experiments using ultrafast diffuse scattering found that the structural transformation takes around 100 fs without any long-range transition [51, 100]. Figure 1.6 describes the ultrafast time scales (in femtoseconds) of the phase transition of M1-VO_2 measured by different transient experiments over the last 25 years [35, 45, 102, 94, 40, 47, 48, 50, 49, 51, 103, 100].

Therefore, the inconsistent timescales (different time scales reported in the literature) on light-induced phase transitions of VO_2 have further increased the challenges on understanding the physics of ultrafast phase transitions. However, both recent and earlier works indicate two main timescales of the ultrafast phase transition: the first set of studies suggests the IMT transition takes place in ~ 25 -40 fs, and the second class of studies demands a structural phase transition time of ~ 100 fs. Although the techniques discussed in the previous paragraph are sensitive to structural changes, they are neither sensitive to electronic response nor attain the temporal resolution of optical probing techniques. In order to resolve these issues, we need an approach which can use the temporal resolution of the optical techniques and can resolve the phase of the transition in real-time. Ultrashort optical pulses with broad bandwidth have this potential of tracking ultrafast IMT and probe

the phase-specific responses in transient reflectivity measurements, since the broadband transient signal can serve as spectroscopic markers for identifying the features of the new phase.

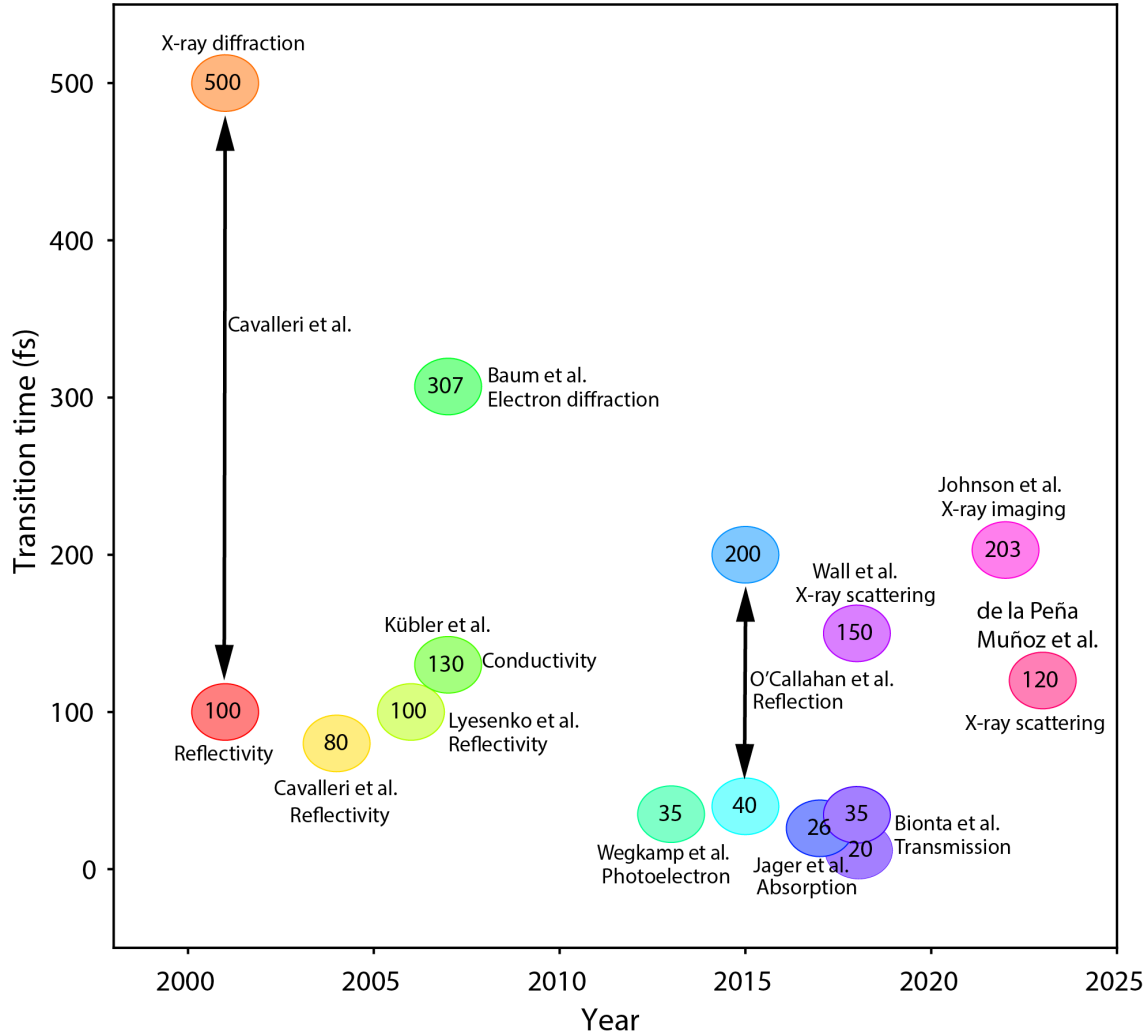


Figure 1.6: Measured transition time of photoexcited insulating M1-VO₂ to metallic R-VO₂ over the last 25 years. The values inside the circles correspond to the transition time in femtoseconds measured by different transient probing techniques.

Chapter 2

An overview of the high harmonic generation

This chapter summarizes the research conducted on high harmonic generation (HHG). An introduction to HHG in gases and solids is essential for this thesis. Gas-phase HHG is utilized for EUV attosecond streaking measurements to characterize field waveforms used in experiments presented in this thesis, whereas solid-state HHG helps to explore the onset of nonperturbative regime in bulk solids.

2.1 Introduction to high harmonic generation

Basic optical phenomena such as reflection, refraction, absorption and transmission are linear light-matter interactions, where the polarization induced in the material is proportional to the amplitude of the applied field (E). However, soon after the invention of laser [11], it was found that the linearity does not persist when the laser intensity exceeds a certain threshold. The laser field induced polarization $P(E)$ can be described as,

$$P(E) = \epsilon_0 (\chi^{(1)} E^1 + \chi^{(2)} E^2 + \chi^{(3)} E^3 + + \chi^{(N)} E^N) \quad (2.1)$$

$\chi^{(N)}$ are the electric susceptibility of order N and ϵ_0 is the vacuum permittivity. At higher field intensities the contribution of the higher-order terms of susceptibility becomes important.

The discovery of second harmonic generation in quartz by Franken et al. [104] in 1964 and two-photon absorption in $\text{CaF}_2:\text{Eu}^{2+}$ by Kaiser et al. [105] in the same year opened the era of nonlinear light-matter interactions. In 1967, the third harmonic was generated in gases like helium, neon, argon, krypton and xenon with a Q-switched ruby laser [106]. The development of laser technologies in the subsequent years provided shorter and intense pulses, which enabled the generation of higher-order harmonics in gases [107, 21, 22]

in the late 1980s. The characteristics of high harmonics are categorized into three regions (Figure 2.1.a): (1) Perturbative regime: with mainly the lower order harmonics whose intensities drop as the order increases and scale perturbatively with the driving laser intensity; (2) Plateau regime: where higher order harmonics show a plateau-like behavior and the harmonic yield scales nonperturbatively with the driving laser intensity; (3) Cutoff regime: where very high-order harmonic (higher than the plateau harmonics) intensities drop as the harmonic order increases, like in the perturbative regime, but eventually vanishing to zero.

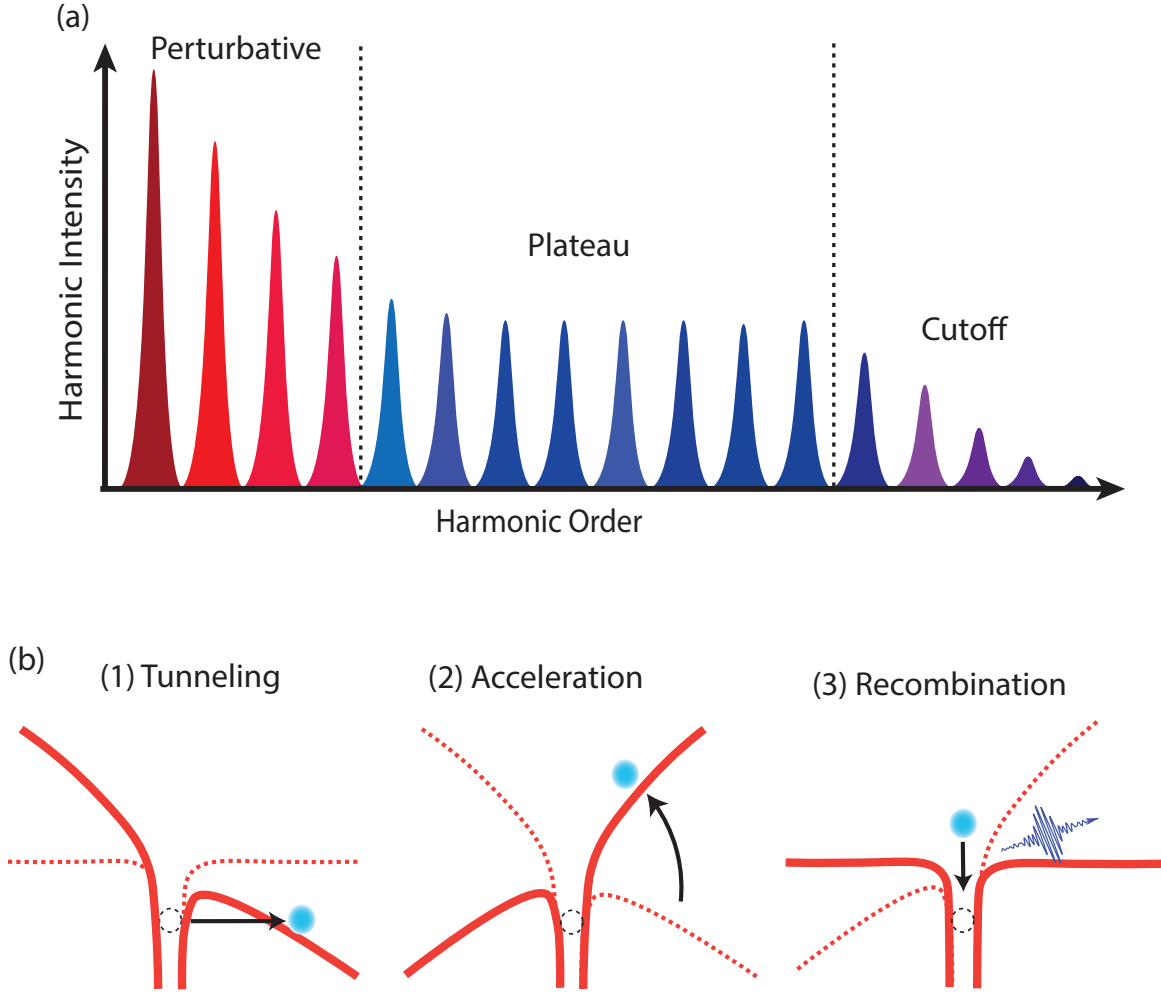


Figure 2.1: (a) Schematic of the gas high harmonic spectrum. (b) Visualization of the three-step model of the HHG in gaseous system.

The perturbative theory of optical harmonic generation could not explain the plateau-like spectrum of the high-order harmonics. However, a three-step model (Figure 2.1.b), which was developed in 1993 for describing the high harmonic generation process in gas [53, 54], successfully explains the observed high harmonic spectra. The steps are:

(1) **Tunnel ionization:** when the electric field of the pulse interacting with the gas atoms is strong enough to lower the atomic potential, there is a finite probability for an electron to tunnel through the potential barrier.

(2) **Acceleration:** this partially free electron wave packet is then accelerated away from the parent ion by the electric field of the driving pulse.

(3) **Recombination:** as soon as the driving electric field changes sign the wave packet is accelerated back, hence can recombine with the parent ion by emitting the energy (K.E.) gained during the acceleration process as higher energy photons.

The cutoff energy of the emitted photon is given by [108, 109],

$$E_{cutoff} = I_p + K.E. = I_p + 3.17U_p \quad (2.2)$$

where, I_p is the Ionization potential of the atom and U_p is the pondermotive energy of the electron. The pondermotive energy depends on the frequency (ω) and intensity (I) of the driving laser field as, $U_p = e^2 I / 4m\omega^2$. e and m are the charge and mass of electron respectively. Each sufficiently intense half cycle of the driving laser pulse can generate a burst of EUV photons. It is possible to create an isolated attosecond pulse required for the attosecond streaking with the proper adjustment of the carrier-envelope phase of the driving field and the application of appropriate spectral filtering near the cutoff region [56].

2.2 High harmonic generation in solids

High harmonic generation in gases has been known for nearly four decades, but HHG in solid-state has only been uncovered over the past decade. The irreversible damage of solids under strong laser fields limited the generation of higher-order (nonperturbative) harmonic in solids. However, new generation laser systems with ultrashort pulses in the terahertz [110], mid-infrared [111, 112], and visible regions [19] have paved the way for high harmonic generation in solids. After several predictions [113, 114] of high-order harmonic generation in crystal structures, Ghimire et al. [23] discovered harmonics up to the 25th order in 2011 by illuminating a 500 μm thick zinc oxide (ZnO) crystal with a 3.25 μm laser. Solid-state high harmonic generation and spectroscopy have undergone rapid advancement after this discovery. Terahertz [64], mid-infrared [23] and optical [24] fields have been able to generate harmonics across a wide spectral range: with energies below the bandgap in GaSe [64], above the bandgap up to 7 eV in ZnO [23], and in the EUV region up to 40 eV in SiO₂ [24] respectively. High harmonics (HHs) have also been generated from solid systems like semiconductors [23, 64, 65], large-bandgap materials [24, 60, 62, 66, 61], 2D materials [72], nanostructured solids [67, 68], metasurfaces [115], rare gas solids [69] and even in metal [116]. The solid-state high harmonics exhibit specific characteristics that are different from those generated in gaseous media.

1. **Crystal orientation:** Solid-state HH yield depends on the orientation of the crystal with respect to the laser polarization [62, 61, 117]. This dependence arises due to the anisotropic nature of the crystal's electronic structure and the symmetry properties of the material. An n -fold symmetric crystal generates n -fold symmetric harmonic yields if the crystal or the polarization of the driving laser is rotated by 360° with respect to each other. The orientation dependence is stronger in higher-order harmonics compared to lower-order harmonics.
2. **Crystal symmetry:** Gaseous systems generate only odd harmonics due to the inversion symmetry of the medium, whereas solids can generate only odd or both odd and even harmonics, depending on whether the inversion symmetry of the solid is centrosymmetric or noncentrosymmetric respectively [23, 118, 119].
3. **Cutoff:** Solid-state HHs generated with different driving laser fields exhibit a non-exponential drop of the yields with the increase in harmonic order and a linear dependence of cutoff energy with the increase in driving field strength [23, 64, 24, 61]. The cutoff energy of the gas phase HHs, on the other hand, scales quadratically with the driving field strength. Notably, HHs from solid Argon have exhibited multiple plateaus [69].
4. **Laser ellipticity:** HHG efficiency for gaseous medium is zero for circularly polarized laser fields. In contrast, HHs in solids can be generated using elliptical or circularly polarized lasers with lower efficiency than linearly polarized fields [62, 120].
5. **Damage threshold:** One of the main limitations of HHG in solids is the irreversible damage of the solid sample irradiated by very high intensities. The threshold intensity of this damage depends on the laser parameters and crystal properties. Usually, large bandgap materials [24, 62] can withstand higher laser intensities than low bandgap semiconductors [117, 121]. Laser pulses with a central energy lower than the material's bandgap reduce the damaging effect and lasers having KHz repetition rate are preferred over MHz lasers to optimize the laser-induced heat dissipation.
6. **Carrier-envelope phase (CEP) dependence:** For few-cycle laser pulses, the CEP effect becomes important when the high harmonic emission takes place within a fraction of the field cycle. Although several studies have indicated the presence of carrier-envelope phase effects in solid-state high harmonic generation [24, 67, 122], the influence of CEP is much weaker compared to that in the gaseous phase [123].

2.3 HHG models

To understand the HHG mechanism and explain the observed characteristics of HHG in solids various models and approaches have been proposed: intraband Bloch oscillation [23, 24], semiconductor Bloch equations [64, 124], three-step model like gas-phase HHG

[125, 126], scattering approximation [61] and time-dependent density functional theory (TDDFT)[127, 128]. Here, I briefly summarize the HHG models based on band and scattering pictures.

2.3.1 Band picture

Figure 2.2 illustrates the band picture of high harmonic generation in solids. The band structure of a crystalline solid consists of occupied valence bands and unoccupied conduction bands such that the top of the valence bands and the bottom of the conduction bands are separated by the band gap (E_g). A strong laser field excites the electrons from valence bands to unoccupied conduction bands and leaves holes in the valence bands. The applied field drives the electrons and holes within their band dispersion in opposite directions to generate intraband high harmonics (intraband current).

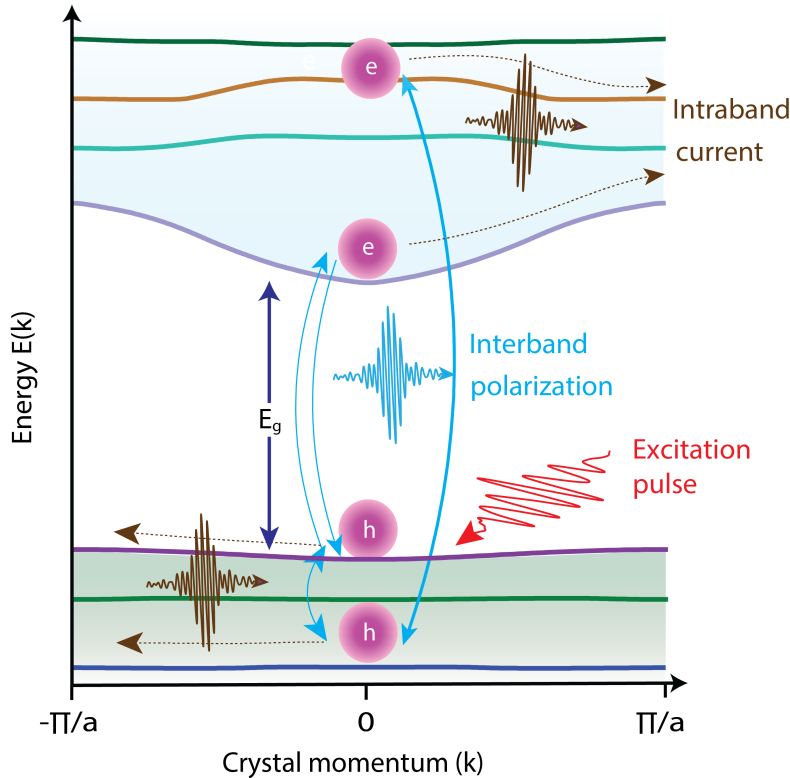


Figure 2.2: **Band picture of HHG in solids.** The arrows present the excitation pulse (red) induced motion of charge carriers (electrons (e) and holes (h)). The cyan arrows show the interband transitions, which give interband polarization. The grey arrows mark the motion of carriers within a single band, which is the source of intraband currents. The green-shaded area denotes the density of states in the valence band, while the cyan-shaded area represents the density of states in the conduction band. Figure adapted from ref. [60]

The polarization induced by the excitation of charge carriers between bands and their consequent recombination generates interband high harmonics (interband polarization). Dominant contributions between intraband and interband HHG in solid are still under debate. Some support the intraband mechanism [23, 24, 60], while others prefer the interband contributions [129, 130].

2.3.2 Semiclassical model

This approach assumes pre-excited charge carriers are present in the conduction band of solids [23, 24], i.e., it doesn't take into consideration the laser-excited transition of electrons from the valence band to the conduction band. Thus, in semiclassical model the harmonics originate from the intraband motion (current) of the charge carriers. The motion of the electron with wave vector k in reciprocal space under the constant field E_0 can be described by the "acceleration theorem" [131] as,

$$\hbar \frac{dk}{dt} = -eE_0 \quad (2.3)$$

The group velocity $v_g(k)$ of the electron in the conduction band having dispersion $\mathcal{E}(k)$ is given by,

$$v_g(k) = \frac{1}{\hbar} \frac{d\mathcal{E}(k)}{dk} = -\frac{\Delta a}{\hbar} \sin(ka) \quad (2.4)$$

The band dispersion $\mathcal{E}(k) = \Delta \cos(ka)$, is defined from the tight binding model with nearest neighbor approximation. Here, Δ is the bandwidth and 'a' is the lattice constant. The dynamic position $x(t)$ of the charge carrier can be obtained by integrating the equation 2.4 as,

$$x(t) = x(0) - \frac{\Delta}{eE_0} \cos\left(\frac{aeE_0}{\hbar}t\right) \quad (2.5)$$

This oscillation of the electron with frequency $\omega_B = aE_0e/\hbar$, under the constant applied field E_0 is known as Bloch oscillation.

In the presence of a time-dependent electric field of the form $E(t) = E_0 \cos(\omega t)$, the time-dependent momentum can be written as,

$$k(t) - k(0) = -\frac{e}{\hbar} \int_0^t E(t') dt' = \frac{e}{\hbar} A(t) = -\frac{eE_0}{\omega\hbar} \sin(\omega t) \quad (2.6)$$

where, $A(t) = -\int_0^t E(t') dt'$ is the vector potential of the electric field.

The above equation shows the maximum momentum of an electron can be, $k_{max} = \frac{eE_0}{\omega\hbar}$. The Boltzmann equation[132] gives the time evolution of the electron momentum distribution $u(k, t)$ as,

$$\frac{\partial}{\partial t}u(k, t) = \frac{\partial}{\partial k}u(k, t)\frac{dk}{dt} = -\frac{eE(t)}{\hbar}\frac{\partial}{\partial k}u(k, t) \quad (2.7)$$

Now, in the semiclassical approach, considering an initial electron distribution, $u(k, 0)$, the analytical solution of the following equation becomes:

$$u(k, t) = u\left(k + \frac{e}{\hbar}A(t), 0\right) \quad (2.8)$$

Therefore, the electric field drives the electron wave packet in the anharmonic dispersion profile of the conduction band without affecting the shape of the electron distribution. The current generated from the acceleration of the wave packet is given by,

$$j(t) \propto \int_{BZ} v_g(k)u(k, t)dk$$

The integration is over the first Brillouin Zone ($-\pi/a$ to π/a). Since the high harmonic radiation amplitude is proportional to the rate of change of current, $E_{HH}(t) \propto \frac{d}{dt}j(t)$, the spectrum of the emitted high harmonic signal in this intraband case is given by,

$$I(\omega) \propto |\omega j(\omega)|^2 \quad (2.9)$$

Now, if we consider beyond the nearest neighbor approximation case, the energy dispersion of the i^{th} conduction band can be decomposed into the Fourier components as:

$$\mathcal{E}(k) = \sum_{n=0}^{n_{max}} \epsilon_{i,n} \cos(nka) \quad (2.10)$$

where, $\epsilon_{i,n}$ are the Fourier coefficients of the i^{th} band, n is the lattice side number and n_{max} is the maximum number of distant neighbors considered in the model. The highest characteristics distance (R_{max}) and the maximum energy (E_{max}) acquired by the electron wave packet from the laser field (E_0) are determined by the n_{max} .

$$R_{max} = n_{max}a \text{ and } E_{max} = eE_0R_{max} = n_{max}\hbar\omega_B$$

Based on this, the high harmonic yields is defined by Luu et al.[24] as,

$$I_N(\omega, E_0) \propto (N\omega)^2 \left| \sum_{n=1}^{n_{max}} n\epsilon_{i,n} J_N \left[\frac{n\omega_B}{\omega} \right] \right|^2 \quad (2.11)$$

Here, N is the harmonic number, ω and E_0 are the carrier frequency and field amplitude of the driving laser and J_N is the Bessel function of first kind of order N . The cutoff harmonic order is obtained by maximizing the Bessel function i.e. when $N = n_{cutoff}\omega_B/\omega$. Where, n_{cutoff} is the highest order Fourier coefficient. The cutoff energy of the high harmonic is defined as,

$$E_{cutoff} = \hbar N\omega = \hbar n_{cutoff}\omega_B = n_{cutoff}aeE_0$$

This model correctly predicts the linear scaling of the HH cutoff energy (as discussed in the HH properties 3) with driving laser field strength (E_0).

2.3.3 Quantum mechanical approach- semiconductor Bloch equations

The Semiconductor Bloch Equations (SBEs) are a set of equations that are used to represent the quantum mechanical dynamics of electron-hole pairs in a semiconductor or solid under an external electric field [133, 134]. SBEs account for the interband excitations of the charge carriers as well as their intraband dynamics. The time evolution of the interband polarization (p_k) and populations of electrons ($f_{e,k}$) and holes ($f_{h,k}$) in the absence of Coulomb interaction can be written as,

$$i\hbar \frac{\partial p_k}{\partial t} = \left(\mathcal{E}_{e,k} + \mathcal{E}_{h,k} - i\frac{\hbar}{T_2} \right) p_k - (1 - f_{e,k} - f_{h,k}) d_k E(t) + ieE(t) \nabla_k p_k \quad (2.12)$$

$$\hbar \frac{\partial f_{e,k}}{\partial t} = -2Im |d_k E(t) p_k^*| + eE(t) \nabla_k f_{e,k} \quad (2.13)$$

$$\hbar \frac{\partial f_{h,k}}{\partial t} = -2Im |d_k E(t) p_k^*| + eE(t) \nabla_k f_{h,k} \quad (2.14)$$

$\mathcal{E}_{e,k}$ and $\mathcal{E}_{h,k}$ are the energies of the electrons and holes respectively, T_2 is the dephasing time, and d_k is the dipole matrix element representing the transition between bands. The first term in the R.H.S of equation 2.12 describes the phase dynamics of the wavepacket with dephasing factor, the second term describes the creation of interband polarization (interband transitions) because of the coupling of laser field $E(t)$ with the dipole; and the last term stands for the time-dependent transportation of the polarization (intra-band excitations) in momentum space. The first term of equations 2.13 and 2.14 represents optical interband transitions, and the second term represents intraband excitations.

The accumulated interband polarization $P(t)$ is given by,

$$P(t) = \sum_k d_k p_k(t) \quad (2.15)$$

The total intraband current $J(t)$ from all the populated bands is given by,

$$J(t) = \frac{|e|\hbar}{\hbar} \left[\sum_k \sum_e \nabla_k \mathcal{E}_{e,k} f_{e,k} + \sum_k \sum_h \nabla_k \mathcal{E}_{h,k} f_{h,k} \right] \quad (2.16)$$

Here, $\frac{1}{\hbar} (\nabla_k \mathcal{E}_{e,k})$ and $\frac{1}{\hbar} (\nabla_k \mathcal{E}_{h,k})$ are the group velocities of the electrons and holes respectively, in the corresponding bands. The source of the radiation is given by, $\frac{d}{dt} \left[\frac{dP}{dt} + J(t) \right]$ and hence the spectrum of the emitted radiation is

$$I(\omega) \propto |\omega^2 P(\omega) + i\omega J(\omega)|^2 \quad (2.17)$$

This model could also be used to investigate the interband, $I_{inter}(\omega) = |\omega^2 P(\omega)|^2$ and intraband $I_{intra}(\omega) = |\omega J(\omega)|^2$ contributions separately. According to current understanding, the high harmonic generation in solids originates from the complex interaction between the interband and intraband contributions.

2.3.4 Scattering picture of HHG

The scattering model [61] interprets HHG as the outcome of strong laser-driven scattering of quasi-free electron motion on the valence potential of solids. The interaction of valence potential, $V(r) = \sum_k V_k e^{ikr}$ with a strong laser field $E(t) = E_0 \sin(\omega t)$ of frequency ω creates an effective crystal potential of the form,

$$U_{eff}(r, E_0) = \sum_k V_k J_0 \left(\frac{k E_0}{\omega^2} \right) e^{ikr} \quad (2.18)$$

Here, V_k , and J_0 are the Fourier component of the crystal potential and the Bessel function of the first kind of zero order respectively. The properties of this crystal potential can be modified by the laser field amplitude (E_0). For example, when the laser field is strong enough, the crystal potential can be suppressed completely so that the electron wave packets become quasi-free (Figure 2.3).

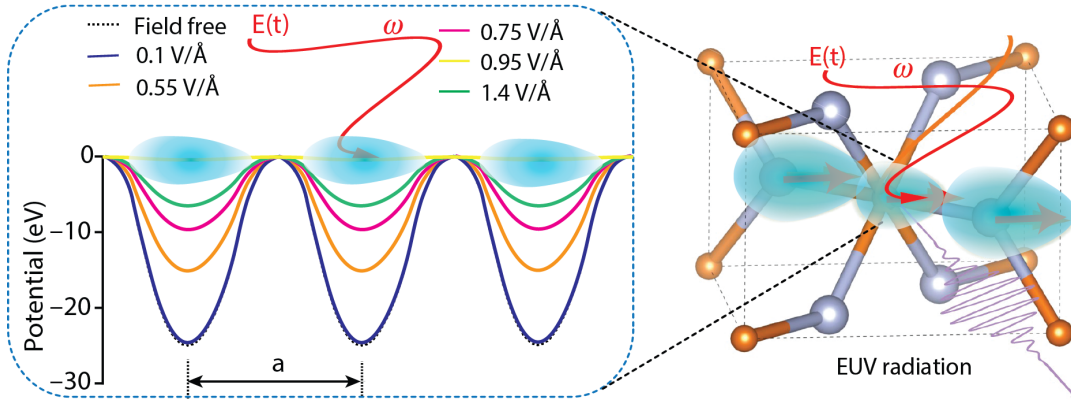


Figure 2.3: **Scattering picture of HHG in solids.** Deformation of effective crystal potential under strong laser fields (red) of frequency ω . The blue-shaded areas represent valence electron clouds. The suppression of crystal potential under strong laser field can result in a nearly free electron. Adopted from ref. [61]

The dynamics of quasi-free electron wave packets on the periodic potential of solids offer to describe high harmonic generation through scattering pictures [61].

The harmonic radiation along the laser polarization $\mathbf{e}_{\parallel}$ can be obtained through this model as,

$$I_N(E_0, \omega, \mathbf{e}_{\parallel}) \propto \left| N_e \sum_k \mathbf{k} \cdot \mathbf{e}_{\parallel} V_k J_N \left(\mathbf{k} \cdot \mathbf{e}_{\parallel} \frac{E_0}{\omega^2} \right) \right|^2 \quad (2.19)$$

Here, N is the harmonic number, V_k s are the Fourier coefficients of the crystal potential, ω and E_0 are the carrier frequency and field amplitude of the driving laser and J_N is the

Bessel function of first kind of order N . This equation can be simplified to a projected 1D problem by summing over the V_k 's in the perpendicular direction ($\mathbf{e}_\perp$) of the laser polarization.

$$I_N(E_0, \omega, \mathbf{e}_\parallel) \propto \left| N_e \sum_{k_\parallel} k_\parallel V_{proj} J_N \left(k_\parallel \frac{E_0}{\omega^2} \right) \right|^2 \quad (2.20)$$

where, $V_{proj} = \sum_{k_\perp} V_k$ are the Fourier components of the potential projected along the laser polarization ($\mathbf{e}_\parallel$) and $\mathbf{k} = \mathbf{k}_\perp + \mathbf{k}_\parallel$ with $k_\perp = \mathbf{k} \cdot \mathbf{e}_\perp$ and $k_\parallel = \mathbf{k} \cdot \mathbf{e}_\parallel$.

According to the Fourier projection-slice theorem, the Fourier transform of this projected Fourier component, V_{proj} is directly linked to the slice of the valence potential in real space. This scattering model was used to : (i) capture the valence electron distribution in crystalline solids [61]; (ii) show the linear cutoff (E_{cutoff}) dependence of HHs with the driving electric field strength (E_0) [61]; and (iii) determine the valence radius (r_h) of the smallest atom in crystals (ZnO, SiO₂, MgF₂, SiC and Diamond) according to the formula [61],

$$E_{cutoff} = \frac{2\pi E_0}{r_h \omega}. \quad (2.21)$$

Chapter 3

Experimental tools - attosecond beamline

This chapter outlines the experimental facility available in the Attosecond (AS) beamline of our laboratory. The experiments described throughout this thesis are carried out in this AS beamline. Additional information regarding each specific experiment shall be presented in the relevant chapters.

3.1 Laser system

An ultra-broadband, Kerr-lens mode locked oscillator is pumped by a 3W, 532 nm continuous wave Nd-YAG pump laser (Verdi V6, Coherent). A titanium-sapphire (Ti:Sa) crystal serves as the gain medium for the oscillator. The oscillator generates 78 MHz train of ultrafast pulses, each having an energy of ~ 4 nJ and a pulse duration of ~ 6 fs. The oscillator is shown schematically in Figure 3.1.

Pulses exiting the oscillator are amplified by a chirped pulse amplification (CPA) principle based commercially available FemtopowerTM CompactTM Pro HE amplifier (Figure 3.1). CPA[15] works in three steps: stretching of the ultrashort-pulse, amplification of the stretched pulse, and finally compression of the amplified pulse. Seeded pulses are first stretched up to 25 picoseconds by propagating them through a thick SF57 glass. The peak pulse intensity drops while stretching by several orders of magnitude, which is a prerequisite to avoid optical damage of the optical components during the amplification process. MHz pulse trains then enter the amplification step and pass through a multi-pass crossed-beam Ti:Sa crystal, powered by a Q-switched Nd:YLF pump laser. Following the 4th pass, the pulses are directed to a Pockels cell to reduce the pulse repetition rate from 78 MHz to 3 KHz. The pulse energy is further increased to ~ 1 mJ by another five passes through the amplifier crystal. Pulses after every pass through the gain medium suffer from gain narrowing because the central part of the pulse's spectrum experiences a higher gain compared to its tails. This gain narrowing is compensated by using an acousto-optic, programmable, dispersive filter (Dazzler), which creates a spectral

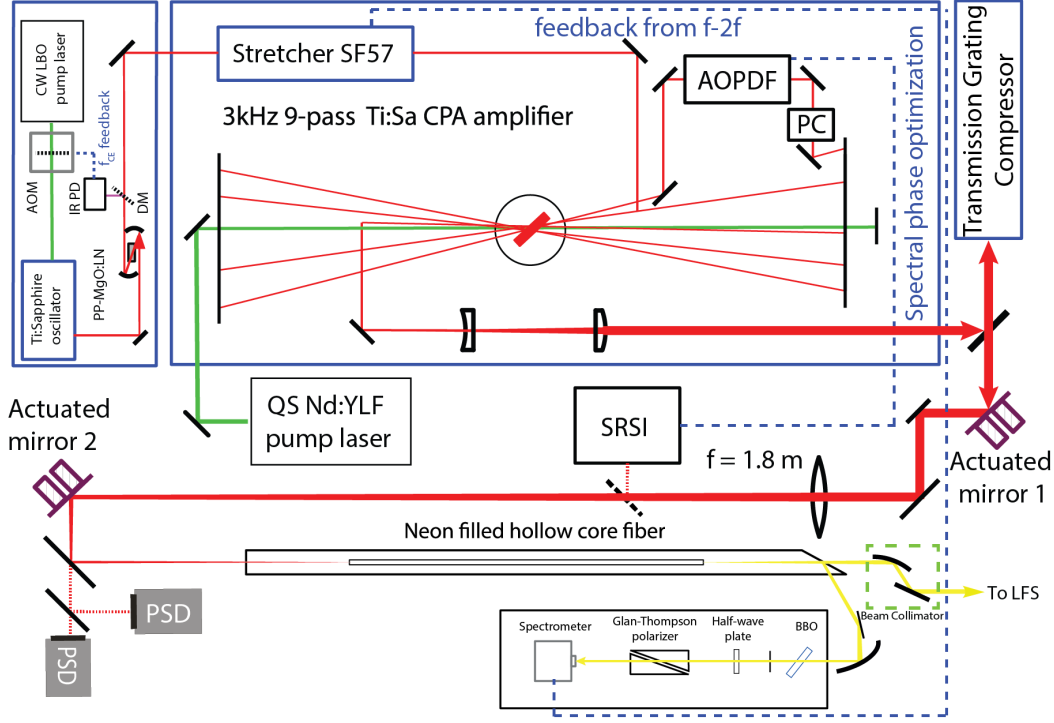


Figure 3.1: **Schematic of the laser system.** A Kerr-lens mode locked, Ti:Sa oscillator supplies ~ 6 fs, 3-4 nJ pulses at a repetition rate of 78 MHz. A dispersive stretcher reduces the peak intensity of the seeded pulses for amplification in a Ti:Sa crystal based gain medium. Pockels cell reduces the pulse repetition rate to 3 KHz after 4th pass and allows the pulse to be further amplified with five more passes in the gain medium. A grating compressor then compress the amplified pulses down to ~ 21 fs. Final amplified pulses with ~ 1 mJ energy are seeded to a Ne gas-filled hollow-core fiber for supercontinuum generation. Figure adapted from ref. [135]

hole in the central region of the spectrum. The working principle of Dazzler is based on the acousto-optic dispersion. Acoustic waves are generated inside a birefringent crystal by radio frequency generators. These waves diffract the seed pulse, with the diffraction efficiency dynamically controlled via a software to produce a quasi-flat-top spectral profile at the end of amplification. The beam size of the pulses is then enlarged to ~ 23 mm to prevent optical damage in the compression stage. The amplified pulses are compressed down to ~ 21 fs using a transmission grating compressor. A Self-Referenced Spectral Interferometry (SRSI) device (Wizzler) measures the temporal properties of the amplified pulses. The final laser pulses produced have an energy of ~ 1 mJ with a central wavelength of 800 nm and a repetition rate of 3 kHz.

3.2 Spectral broadening

In our laboratory, we utilize the nonlinear propagation of the multi-cycle laser pulse through a gas-filled hollow-core fiber (HCF) to broaden its spectral bandwidth. First, amplified

laser pulses are focused at the entrance of the HCF having a core diameter of $250\text{ }\mu\text{m}$ by a bi-convex lens of 1.8 m focal length. A beam stabilization system from *TEM-Messtechnik* containing two mirror actuators and position sensitive diodes ensures stable laser coupling into the fiber, as shown in Figure 3.1. The 1.1 m long HCF is placed inside a tube consisting of an anti reflection coated entrance window and a Brewster window (at an angle $\sim 57^\circ$) at the exit to minimize energy and spectral losses. The tube is filled with Neon (Ne) gas at a pressure of 2.5 bar , allowing the pulses to undergo a third-order nonlinear process of self-phase modulation inside the fiber.

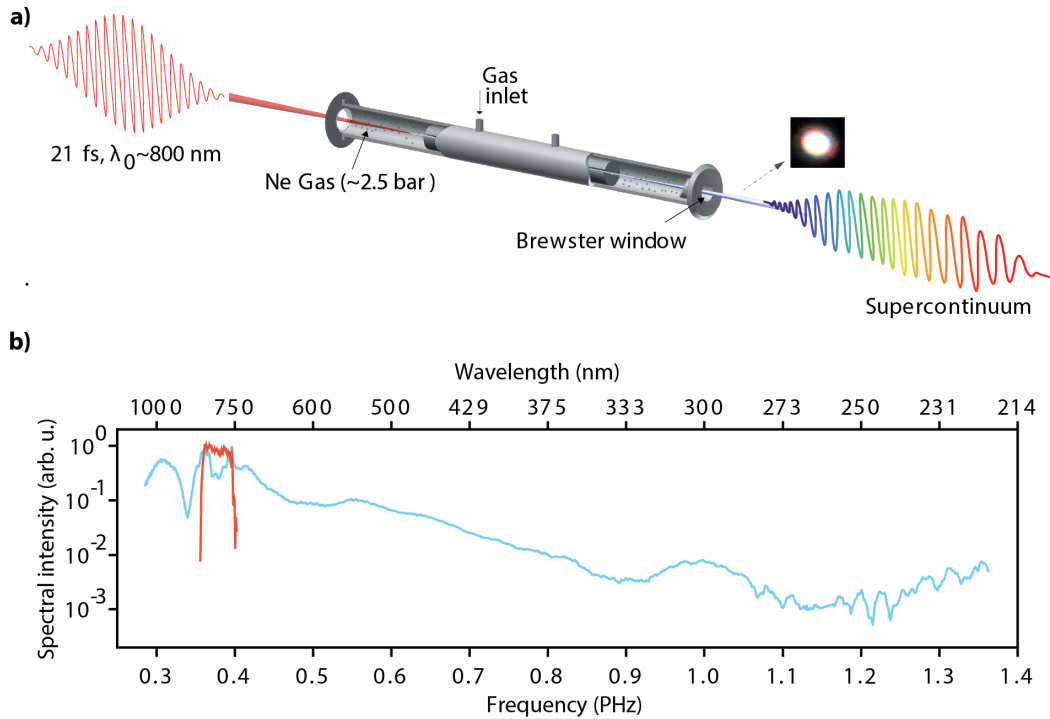


Figure 3.2: **Spectral broadening in a gas-filled hollow-core fiber.** a) Schematic of the intense laser generating supercontinuum in a Ne gas filled hollow-core fiber. b) Multi-octave supercontinuum spectrum (blue), together with the spectrum of the incident laser (red). Figure adapted from ref. [136]

This process broadens the input laser spectrum by generating additional higher and lower spectral components (Figure 3.2). A time varying refractive index, $\eta(t) = \eta_0 + \eta_2 I(t)$ [20], is induced in a medium when it interacts with an ultrashort laser pulse of intensity $I(t) = I_0 \exp(-t^2/\tau^2)$. Here, η_0 is the linear refractive index, while η_2 describes nonlinear refractive index coefficient. Time varying refractive index for the pulse propagation through a medium of length L induces an instantaneous phase shift of the pulse, $\phi(t) = \omega_0 t - \omega_0 L \eta(t)/c$. The instantaneous frequency, thus generated from self-phase modulation, is given by,

$$\omega(t) = \omega_0 - \frac{\omega_0 L}{c} \frac{d\eta(t)}{dt} = \omega_0 \left(1 - \frac{\eta_2 L}{c} \frac{dI(t)}{dt} \right). \quad (3.1)$$

Therefore, new frequency components are generated on both sides of the central frequency, depending on the sign of $I(t)$ vs t slope. The slope is positive at the leading edge of the pulse, where $\omega(t)$ shifts to lower frequencies; but it is negative at the trailing edge of the pulse, where $\omega(t)$ shifts to higher frequencies. The resulting supercontinuum carries an energy of ~ 600 μJ ($\sim 60\%$ transmission) with wavelength spanning from deep ultraviolet (270 nm) to near-infrared (1100 nm). A toroidal mirror with focal length of 75 cm collimates the diverging beam exiting the fiber.

3.3 Carrier-envelope phase (CEP) stabilization

The stabilization of the absolute phase between the carrier and envelope in single-cycle pulses is essential for electric field-sensitive measurements like EUV attosecond streaking [56], as presented in this thesis. Carrier-envelope phase variation is the outcome of the difference between group (v_g) and phase (v_p) velocities of laser pulses inside a laser cavity.

$$\Delta\phi_{CEP} = \frac{2\pi l_c}{T_c} \left(\frac{1}{v_g} - \frac{1}{v_p} \right) \quad (3.2)$$

here, $\Delta\phi_{CEP}$ is the phase offset between consecutive pulses (period T_c) exiting the laser cavity of length l_c . For a train of ultrashort pulses exiting from a laser oscillator, the corresponding spectrum consists of comb of longitudinal laser modes. The CEP shift of consecutive pulses creates a frequency offset of f_0 in the comb line. This offset is known as carrier-envelop offset (CEO). The comb lines have frequencies $f_n = f_0 + n f_{rep}$, where n is an integer and f_{rep} is the repetition rate of the laser. The pulse-to-pulse CEP change is described by,

$$\Delta\phi_{CEP} = 2\pi \frac{f_0}{f_{rep}} \quad (3.3)$$

CEP stabilization of the laser pulses is possible by setting f_0 as the r^{th} fraction of f_{rep} . This allows every r^{th} pulse of the oscillator to have the same phase. In our laser oscillator, stabilization of the CEO is implemented by a self-referencing technique that detects the CEO by difference frequency generation (DFG). The oscillator pulses of wavelengths between 635 nm to 1015 nm are first tightly focused onto a highly nonlinear periodically poled magnesium-oxide-doped lithium niobite (PP-MgO-LN) crystal. Self-phase modulation (SPM) and DFG within the crystal broaden the pulse spectrum up to 1600 nm. DFG between high ($f_0 + n_{high} f_{rep}$) and low ($f_0 + n_{low} f_{rep}$) frequency comb modes generate frequencies at the long wavelength side of the spectrum, which is free of CEO.

$$f_{DFG} = (f_0 + n_{high} f_{rep}) - (f_0 + n_{low} f_{rep}) = (n_{high} - n_{low}) f_{rep} \quad (3.4)$$

Interference between the difference frequency modes $(n_{high} - n_{low}) f_{rep}$ and low frequency wing fundamental modes $f_0 + (n_{high} - n_{low}) f_{rep}$ produces a beating signal containing the

carrier envelope phase of f_0 . Once f_0 is measured by an avalanche photodiode, its value is adjusted closer to $f_{rep}/4$ by tuning the dispersion inside the laser cavity with a piezo-driven glass wedge assembly. The dispersion and f_0 are interrelated as f_0 depends on $\Delta\phi_{CEP}$, $\Delta\phi_{CEP}$ relies on the group velocity v_g , and v_g varies when dispersion changes. In order to lock f_0 , feedback is applied to an acousto-optic modulator (AOM), which modulates the pump laser intensity incident on the oscillator crystal. This intensity control induces a phase shift via the Kerr effect, thereby stabilizing the carrier-envelope phase of every 4th pulse of the oscillator. The Pockels cell then selects these CEP-stabilized pulses for amplification.

A slow loop CEP stabilization is used to correct the phase slippage acquired during amplification and spectral broadening inside the hollow-core fiber. Here a small fraction of the broadband beam is directed to an f-to-2f interferometer [137] and focused into a beta barium borate (BBO) crystal of the interferometer for second harmonic generation. The high frequency part of the fundamental pulse spectrum and the low frequency part of the frequency-doubled spectrum interfere with each other to give a beat note at f_0 .

$$2(f_0 + n_{low}f_{rep}) - (f_0 + n_{high}f_{rep}) = f_0 \quad (3.5)$$

here, $n_{high} = 2n_{low}$. The signature of the beat frequency is imprinted on the interference pattern in the spectral region where the fundamental and frequency-doubled spectra overlap. Any change in CEP is tracked by tracing the variation in the fringe pattern. Depending on the deviation of the phase of these fringes from that of the user-defined reference, an closed-loop feedback with a standard controller algorithm adjusts the distance of a pair of prisms in the amplifier stretcher.

3.4 Light field synthesis

Broadband light pulses generated in the HCF suffer from positive chirp. A state of the art light field synthesizer (LFS) [136, 19] can control this chirp and shape the electric field of the optical pulses. As shown in Figure 3.3.b, dichroic beam splitters (DBS) split the broadband light coming out of the fiber into four different spectral bands (channels): Ch_{NIR} : 1100-700 nm; Ch_{VIS} : 700-500 nm; Ch_{UV-VIS} : 500-350 nm; and Ch_{DUV} : 350-270 nm. Pulses in each channel are compressed to a few-fs duration by reflection off six chirped mirrors. Additionally, a pair of thin glass wedges fine-tunes the dispersion of the pulses in different channels. The duration of the compressed pulses from each channel is then measured by a frequency-resolved optical gating (FROG)[138] apparatus. A set of two mirrors in each channel (except Ch_{VIS}) placed on a piezoelectric stage controls the relative temporal delays among the channels. The compressed light pulses from the four channels are recombined by the same kind of DBS as used for splitting the input broadband spectrum.

Spatial overlap of the beams from different channels is achieved by superimposing the near- and far-field beam profiles of all channels at the same point by adjusting the DBS pairs. Pulses from different channels are temporarily overlapped by adjusting

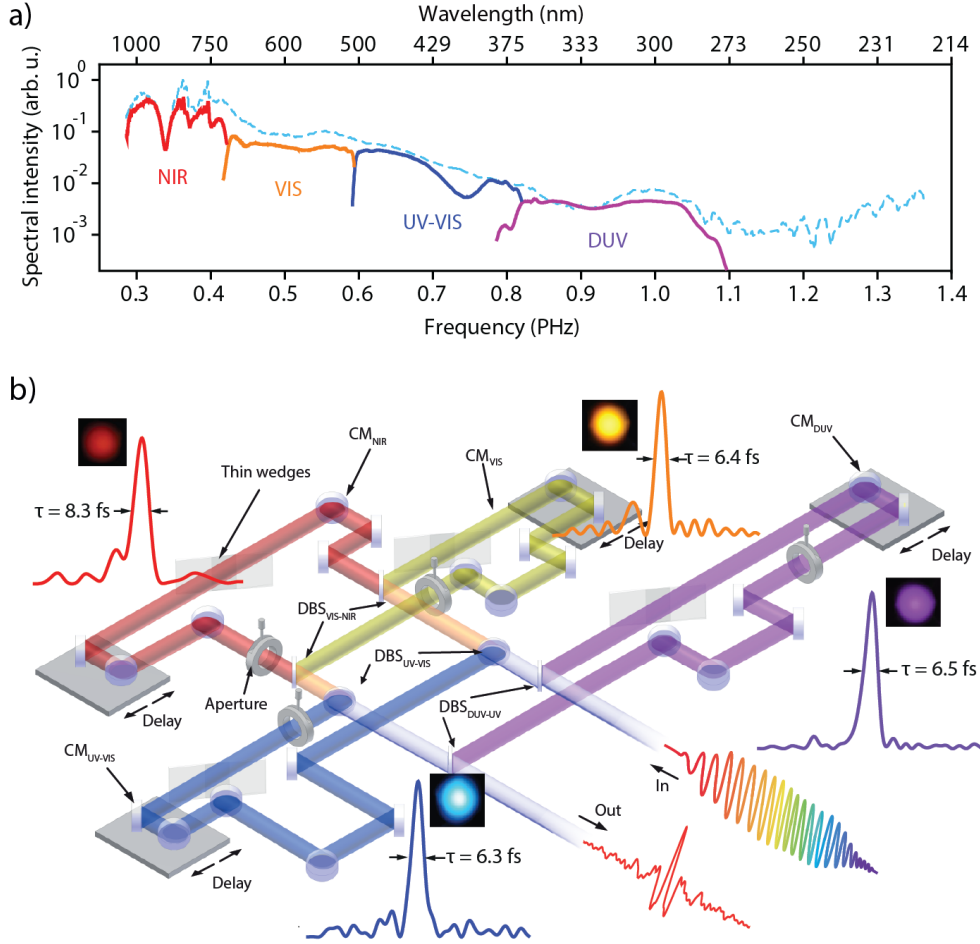


Figure 3.3: **Light field synthesizer** a) Spectral splitting of the broadband supercontinuum coming from the hollow core fiber. b) Dichroic beam splitters split the supercontinuum into four channels, namely, DUV (purple), UV-VIS (blue), VIS (yellow) and NIR (red). Six Chirped mirrors (CM) compress the pulses while apertures and wedges control the amplitude and dispersion of the pulses in each channel. The delay stages control the relative temporal delay between successive channels. Temporal and spatial profile of the pulses of individual channels are shown with their respective color codes. Figure adapted from ref. [136]

the delays among the channels to maximize the high harmonic yields from noble gas. The LFS features both active and passive stabilization, which helps to maintain the relative temporal delay among the channels over an extended period. In order to provide passive stabilization, a water chiller maintains the temperature of the monolithic piece of aluminum on which all the optics are mounted at 20°C. Active stabilization of the temporal slippage is achieved by interferometric path length stabilization. A spectrometer captures a small fraction of the synthesized beam upon reflection from Brewster window of the high harmonic generation chamber. The dispersive optics within the LFS are specifically designed to operate with p-polarized light. Hence, even if the channels of LFS are perfectly

synchronized temporally for p polarization, the tiny contribution from s polarization can remain unsynchronized and can introduce spectral interference between adjacent channels. This interference pattern is used to provide feedback to an active loop that compensates for drift by adjusting the relative delay between adjacent channels. References [136, 19] have more details about the LFS.

3.5 Overview of the experimental section

The experimental section (Figure 3.4) of the AS beamline in our laboratory is capable of using techniques like attosecond streaking [32, 26] measurement, attosecond transient absorption spectroscopy [34, 18], high harmonic (HH) spectroscopy [24, 60], and transient reflection spectroscopy [139]. Among the techniques, EUV attosecond streaking [32] is at the heart of this experimental facility. The setup primarily consists of a HHG chamber connected to the main experimental chamber through two differential pressure reduction chambers. Their pressures are maintained at $\sim 10^{-3}$ and $\sim 10^{-7}$ mBar respectively. Short and intense synthesized pulses from the LFS are delivered and focused into the HHG chamber for high harmonic generation. The focused beam interacts with Neon (Ne) or Argon (Ar) gas from a nickel gas nozzle and generates EUV high harmonics. The EUV beam (blue) collinearly propagates with the optical beam (red) towards the experimental chamber. A free-standing thin aluminum (Al) or zirconium (Zr) filter with the same diameter as the optical beam provides the spectral isolation of the EUV beam from the optical beam. This enables an EUV camera to monitor both the beam profile and the yield of the EUV beam, thus allowing us to optimize the HHG process. The spectra of the EUV pulses can be recorded by substituting the mirror which directs the EUV beam to the EUV camera with a 1200 grooves/mm flat field grating. A filter holder with four slots, mounted on a translation stage provides the required filter on demand at the entrance of the experimental chamber.

The EUV beam can be spectrally and spatially isolated from the optical beam by a thin Zr filter suspended on two 30 μm thick tungsten wires with the same diameter as the EUV beam. The Zr filter passes EUV harmonics with energy > 70 eV. A dual-concave mirror module with a 12.5 cm focal length is used to focus the isolated EUV and optical beams. The inner mirror is a Mo/Si multilayer mirror optimized for a central energy of 85 eV, while the outer mirror is a transparent glass mirror. The inner mirror is mounted on a piezo stage that precisely controls the delay between the reflections from the inner and outer mirrors. An imaging system with a CCD camera is used to image the inner and outer beam focal planes under the time-of-flight (TOF) electron/ion spectrometer. After spatially overlapping the inner and outer mirror foci with the help of this imaging system, the temporal overlap is achieved by checking the interference of optical beams reflected from the inner and outer mirrors. Once the focal spots are spatially and temporally aligned, a Ne/Ar gas nozzle (streaking target) is brought to the focal point under the TOF using a 3D translation stage. The EUV photons with central energy 85 eV ionize the gas atoms, and the TOF spectrometer measures the kinetic energy of the photoelectrons by capturing

the travel time between the trigger and the arrival of photoelectrons on the microchannel

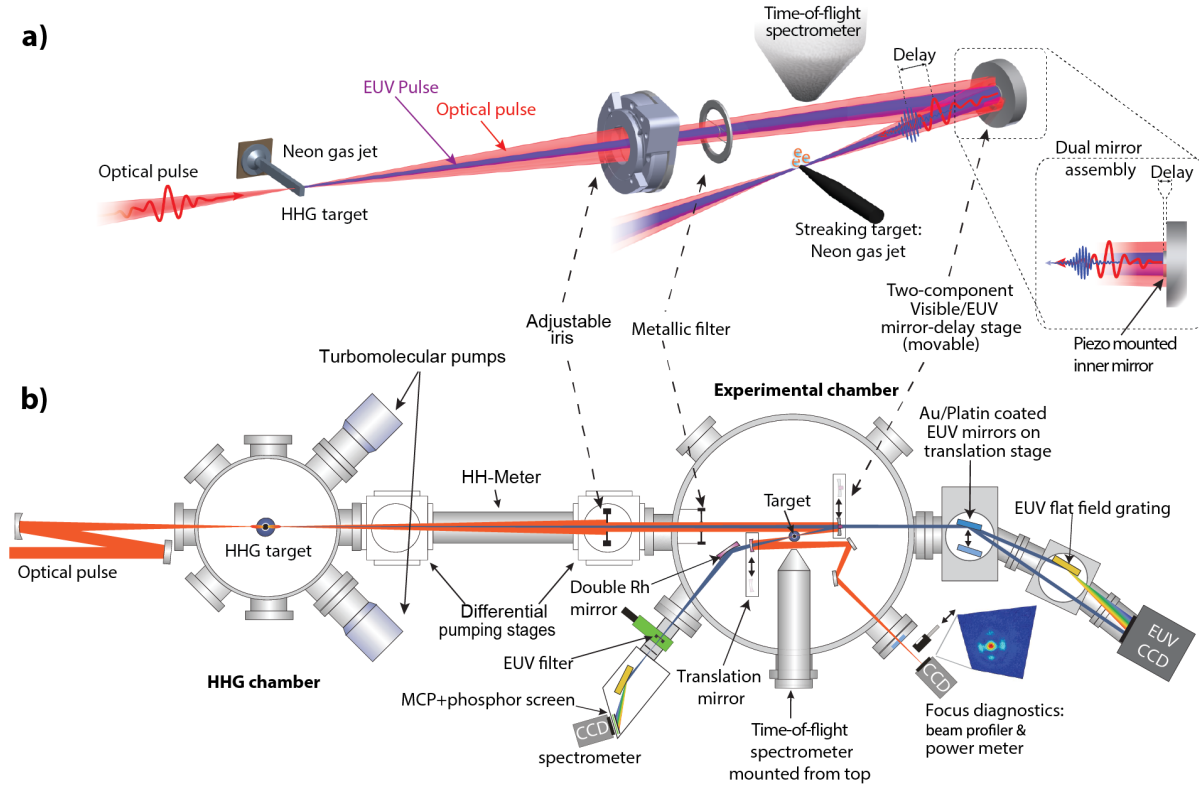


Figure 3.4: **Overview of the AS beamline.** a) Schematic of the EUV-AS streaking set-up. The optical pulses (red) generate EUV (blue) pulses from the Neon gas target. A metallic filter spatially isolates EUV pulses from optical pulses. EUV and optical pulses are delayed and focused on the gas jet by a piezo-driven inner-outer mirror assembly. Finally, the spectrum of the photoelectrons is recorded by the time-of-flight spectrometer. b) Overview of the experimental part with all components. Figure adapted from ref.[140, 141]

plate (MCP) detector of TOF. After the optical field characterization (section 3.6), the streaking target is replaced with solid/gas target of interest for specific experiments. Based on the experiment, an automated replacement of the inner mirror (inner mirror stage assembly) with another mirror having a different reflection bandwidth is possible. A motorized iris diaphragm placed before the experimental chamber controls the optical field intensity. Multiple ports of the experimental chamber allow to install and utilize different measurement instruments, e.g. EUV spectrometers, beam profilers, optical spectrometers, imaging cameras, motorized vacuum stages, etc. More details of this beamline can be found in ref. [140]

3.6 EUV attosecond streaking

Accurate characterization of both temporal profile and amplitude of the electric field is important for the experiments conducted in this thesis. Continuing from the previous section,

once the optical and EUV-AS pulses (central energy 85 eV) are spatially overlapped, they are focused onto the streaking target (Ne gas jet). The EUV pulse reflected off the inner mirror ionizes the gas atoms to yield photoelectrons. The intensity of the optical pulse is kept low so that it does not ionize the gas atoms and acts as a phase gate to modify the momentum of the photoelectrons. The TOF spectrometer positioned above the gas nozzle records photoelectron spectra as a function of the delay between the optical and EUV-AS pulses that results in an attosecond streaking spectrogram.

Classically, we can describe the EUV pulse generated photoelectrons of mass m , accelerated by the low intensity optical field $E_L(t)$ as,

$$m\ddot{x}(t) = -eE_L(t) \quad (3.6)$$

Change in momentum from the ionization time (t_i) to the detection time (t) in TOF is given by,

$$m\dot{x}(t) - m\dot{x}(t_i) = -e \int_{t_i}^t E_L(t) dt \quad (3.7)$$

Photoelectrons are detected in nanosecond (ns) time scale while the optical pulse duration is only a few femtoseconds (fs). Therefore, we can assume $t \sim \infty$ in comparison to t_i . Hence, the momentum gained by the photoelectrons from $E_L(t)$ is,

$$\Delta p(\infty, t_i) = p(\infty) - p(t_i) = m[v(\infty) - v(t_i)] = -eA_L(t_i) \quad (3.8)$$

Where, v is the velocity of the electron and $A_L(t_i) = \int_{t_i}^{\infty} E_L(t) dt$ represents the vector potential. The Kinetic energy of the electrons when detected by the TOF is given by,

$$E_{KE}(\infty, t_i) = \frac{1}{2}mv(\infty)^2 = \frac{1}{2}m \left[v(t_i)^2 + \left(\frac{e}{m} \right)^2 A_L(t_i)^2 - \frac{2e}{m} v(t_i) A_L(t_i) \right] \quad (3.9)$$

As the intensity of the optical pulse is kept very low, A_L^2 term can be neglected. The shift in kinetic energy then becomes,

$$\Delta E_{KE}(\infty, t_i) \approx -ev(t_i)A_L(t_i) \quad (3.10)$$

Therefore, the vector potential of the optical field can be obtained by measuring the spectra of photoelectrons as a function of delay between optical and EUV-AS pulses. The centroid of the streaking spectrogram (Figure 3.5.a) gives a quick evaluation of the vector potential.

Figure 3.5 illustrates the synthesis of single-cycle optical pulses in day-to-day experiments. The synthesis process starts with the measurement of EUV-attosecond streaking spectrogram, as shown in Figure 3.5.a. The Fourier analysis of the electric field (Figure 3.5.e) retrieved from the streaking spectrogram centroid is then used to extract the electric field profile of each channel and their relative delays (Figure 3.5.c). The extraction process utilizes the prior-known spectral bandwidth of individual channel. Next,

ultra-short single-cycle pulses (Figure 3.5.f and 3.5.h) are synthesized by eliminating the relative delays of successive channel.

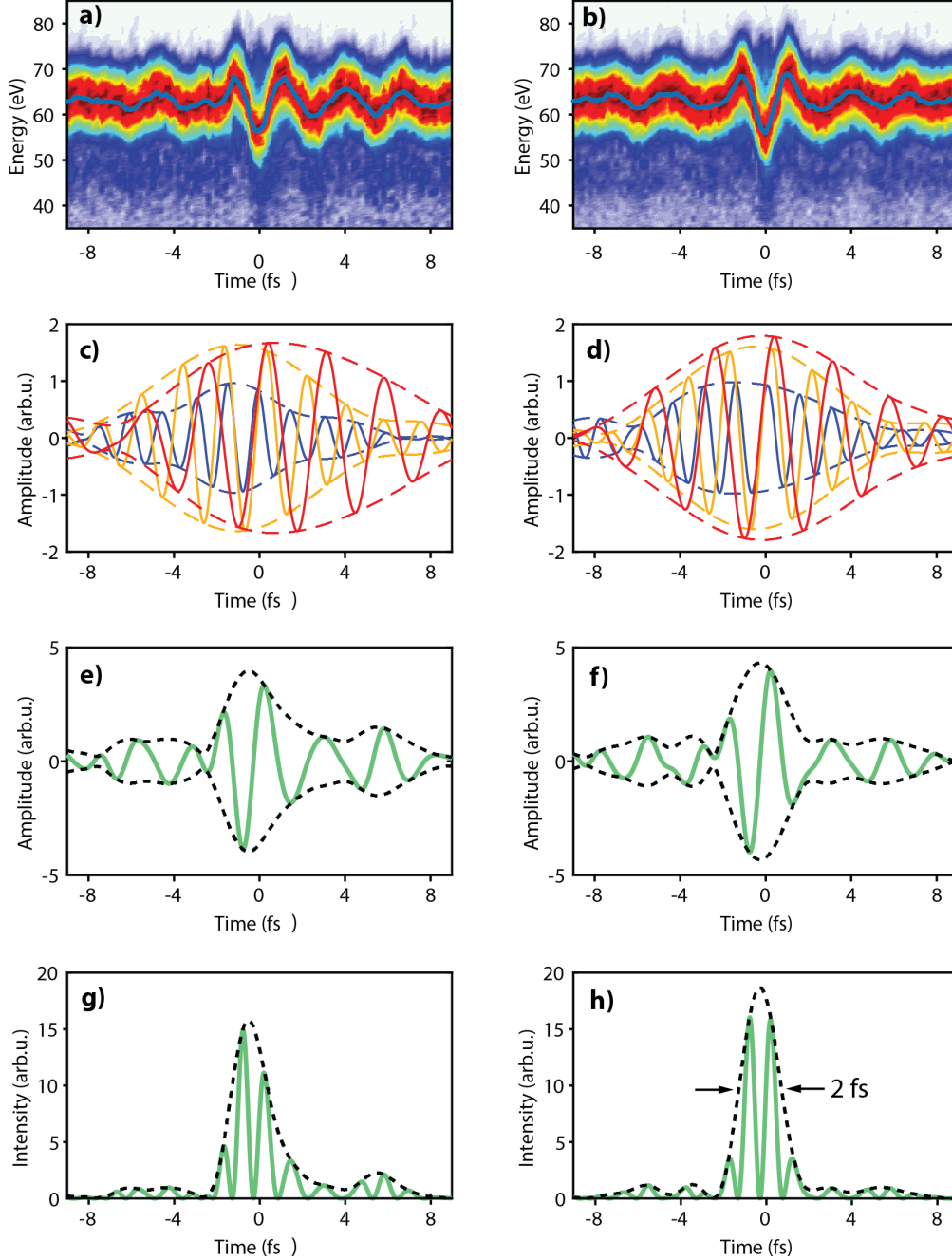


Figure 3.5: **Synthesis and measurement of single-cycle optical pulse.** a), b) Measured streaking spectrograms for delayed (a) and time-overlapped (b) synthesizer channels. c), d) Retrieved waveforms of channels. e), f) Electric fields and g), h) intensity profiles of the extracted optical pulses from the spectrograms a) and b).

Chapter 4

Experimental setup for pump-probe measurements

Pump-probe spectroscopy is a widely used technique to study the ultrafast insulator-to-metal transition in VO_2 [35, 45, 40, 42, 47, 46, 48, 50, 51, 49]. If this technique is combined with broadband probing, the spectral fingerprints of the phase transition can be measured to access the wavelength-dependent optical response of the material [94, 42, 49, 142]. The efforts to uncover the phase transition mechanism of M1- VO_2 during laser-induced excitation led to the upgradation of the pump-probe experimental techniques and quality enhancement of the sample. This chapter presents a detailed overview of the experimental setup and the technical upgrades implemented for the measurement of stable transient reflectivity of M1- VO_2 over a broad spectral region. The ultimate focus is on measuring the transient reflectivity with utmost precision. The combination of EUV attosecond streaking technique together with the advanced pump-probe experimental setup allows for an in-depth analysis of the ultrafast dynamics in the laser induced phase transition of M1- VO_2 . Furthermore, a brief overview of the method used to achieve a high quality polished surface from a rough bulk M1- VO_2 crystal is also presented.

4.1 Experimental setup for transient reflectivity measurements

Light field synthesizer (LFS) (Chapter 3.4) is used as the laser source for the experimental setup illustrated in Figure 4.1. Broadband optical pulses with duration of ~ 2.4 fs are synthesized by spatially and temporally overlapping Ch_{NIR} , Ch_{VIS} and Ch_{UV-VIS} of LFS. These pulses are then characterized in the AS beamline (Figure 4.1.a), where transient reflection experiments are conducted (Figure 4.1.b). The optical pulses are characterized using the EUV attosecond streaking, as described in Chapter 3.6. Here the outer mirror of the dual mirror assembly is a transparent glass mirror and the inner mirror is a Mo/Si mirror.

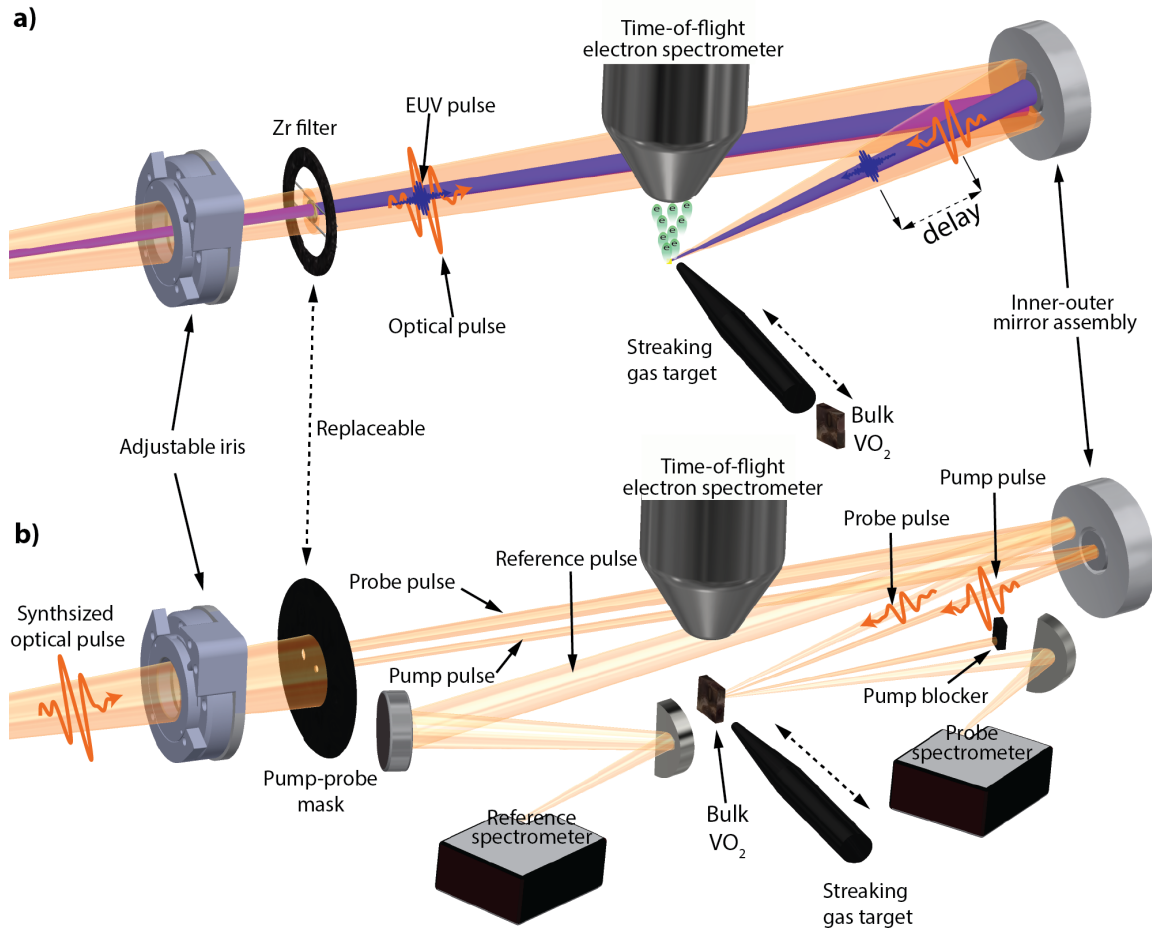


Figure 4.1: **Schematic of the transient reflection spectroscopy setup inside AS beamline.** a) Schematic of the attosecond streaking setup. b) Pump-probe setup to record transient reflectivity. The optical beam from the LFS is spatially separated into pump and probe beam by a metal mask. The pump and probe beams are focused on the VO_2 sample surface by the inner and outer mirrors of the dual mirror assembly respectively. A probe spectrometer records the probe spectrum while a reference spectrometer records the reference pulse spectrum, reflected off the rear side of the transparent outer mirror for spectral intensity fluctuations corrections. Adopted from ref. [139]

After the optical field waveform is characterized, the Ne gas nozzle in the HHG chamber (Figure 3.4) is removed from the beam path using a 3D translation stage and the Zr filter in the experimental chamber 4.1 is replaced by a metal mask containing two circular holes of 1.5 mm and 2.5 mm diameter using a translation stage. This mask spatially divides the optical beam into two parts so that they can be utilized as the pump and probe beams for the transient reflectivity measurements. The holes are separated by a distance of 3.7 mm to provide sufficient spatial isolation between the beams passing through it. The

Mo/Si inner mirror and the streaking Ne gas jet are then replaced by a metallic mirror and a bulk VO₂ sample respectively. The Mo/Si and metal inner mirrors are attached to a 3D piezoelectric translation stage and they can be exchanged on site on demand. Another 3D piezoelectric translation stage controls the replacement of the Ne gas jet and bulk VO₂ sample. All the translation stages discussed above are interfaced with LabVIEW software to automate the replacements.

In the experimental setup, beams passing through the 1.5 mm and 2.5 mm apertures are reflected by the metallic inner mirror and the transparent outer mirrors respectively and serve as the pump and probe beams. We chose this configuration for two reasons. First, the outer mirror reflects only about 4% of the incident power, ensuring that the probe beam has an order of magnitude lower power than the pump beam so that the probe beam does not induce a phase transition at negative pump-probe delay. Second, the probe beam has a smaller spot size at the focal plane compared to the pump beam. As a result, the probe beam assuredly probes the optically excited region of the sample. Upon reflection from the VO₂ sample surface, the focused probe beam is directed to a spectrometer (probe spectrometer) using metal mirrors. A laser blocker is placed to block the pump beam after reflection from the sample surface to eliminate the fringes that can appear from the interference of pump and probe beam in the transient reflectivity signal measured by the probe spectrometer. The reflected beam from the rear surface of the transparent outer mirror is guided to another spectrometer (reference spectrometer) for monitoring the laser spectral intensity fluctuations. A complete description of the fluctuations correction process is presented in the following section. The transient reflectivity data are recorded with an automated LabVIEW software, which interfaces the two spectrometers and the pump-probe delay stage.

4.1.1 Spectral intensity fluctuations compensation

The laser beam travels a long path (few meters) from the amplifier to the experimental chamber in the beamline. During its propagation, airflow, thermal fluctuations, mechanical vibration and the instability of the beam pointing systems can introduce random fluctuations in the spectral intensity of the laser beam. Since the transient reflectivity experiment utilizes spectral intensity as the measurement signal, correcting the spectral intensity fluctuations becomes important to exclude such external influence from the measured data.

Two HR4Pro VIS-NIR spectrometers from *Ocean Optics* with identical specifications are used in the experimental setup. The first spectrometer records the change in reflectivity of the probe beam reflected off the sample, while the second spectrometer captures the random spectral intensity fluctuations of that probe beam. Both spectrometers are synchronized with a 3 kHz trigger originating from the laser system. Two continuously variable metallic neutral density filters control the relative spectral intensities of the beams entering the two spectrometers. The spectral intensity fluctuations are also very sensitive to any vibrations of the two spectrometers. To eliminate this problem, the spectrometers are held firmly by clamping them to the optical table. The spectral intensity fluctuation

as a function of time are adjusted in the following way. Given a probe spectrometer measurement $S_{probe}(\lambda, t)$ at a time t with the corresponding reference spectrometer spectrum $S_{ref}(\lambda, t)$, the fluctuations corrected spectrum $S_{corr}(\lambda, t)$ is given by,

$$S_{corr}(\lambda, t) = \frac{S_{probe}(\lambda, t)}{S_{ref}(\lambda, t)} \times S_{ref}(\lambda, t_0) \quad (4.1)$$

Here, $S_{ref}(\lambda, t_0)$ is the reference spectrometer spectrum at first instance of the experiment at time t_0 .

The correction of the random spectral intensity fluctuations of the probe beam are first standardized in the absence of any sample response, i.e., without a pump beam. The first spectrum recorded by each spectrometer provides the baseline spectrum ($S(\lambda, t_0)$). Then the fluctuations recorded by the probe spectrometer with respect to the baseline spectrum in the following measurement at a time t is $\frac{S_{probe}(\lambda, t) - S_{probe}(\lambda, t_0)}{S_{probe}(\lambda, t_0)}$ and its corresponding fluctuations, which is the correction factor, recorded by the reference spectrometer is $\frac{S_{ref}(\lambda, t) - S_{ref}(\lambda, t_0)}{S_{ref}(\lambda, t_0)}$. Figure 4.2 shows these spectral intensity fluctuations of the probe spectrum (blue) and its corresponding correction (multiplication) factor (magenta) from the reference spectrometer. This result presents a high degree of negative correlation between the two spectrometers. The probe spectral intensity (blue) exhibits a fluctuations of 0%-3.5% across the entire wavelength range. Next, in order to check the stabilization for long-time measurements, 10 spectra at 20 second intervals are measured.

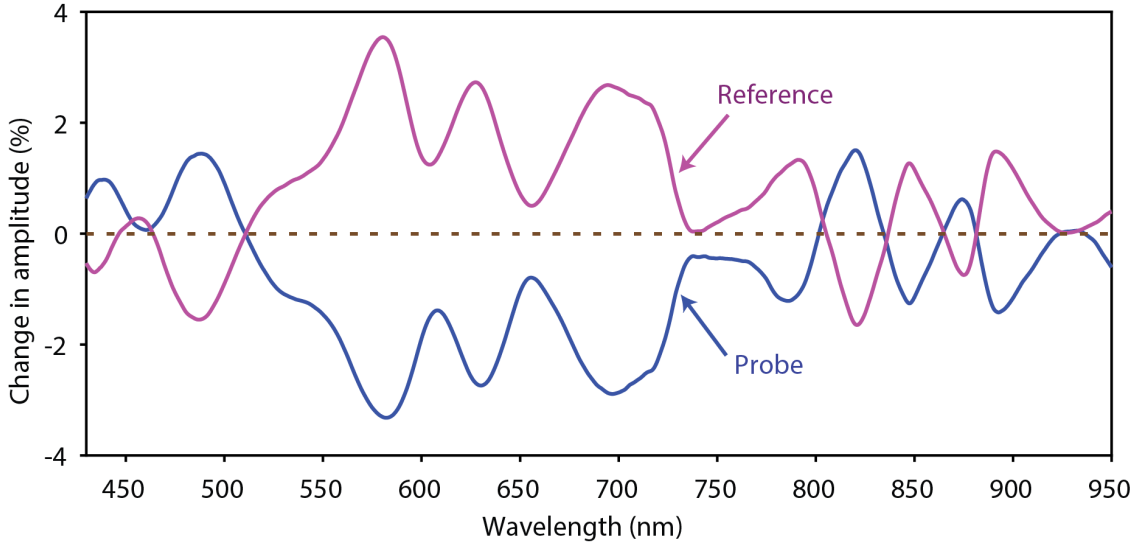


Figure 4.2: **Probe beam spectral intensity fluctuations correction.** Fluctuations of the probe spectral intensity (blue) measured by the probe spectrometer and corresponding correction factor (magenta) from the reference spectrometer in percentage (%).

Figure 4.3 illustrates the standard deviation (SD) of the measured probe signal

fluctuations after correction from the reference spectrum for these ten measurements. The standard deviation of the reference-corrected fluctuations drops to 0.2%-0.3% over the probe spectral range.

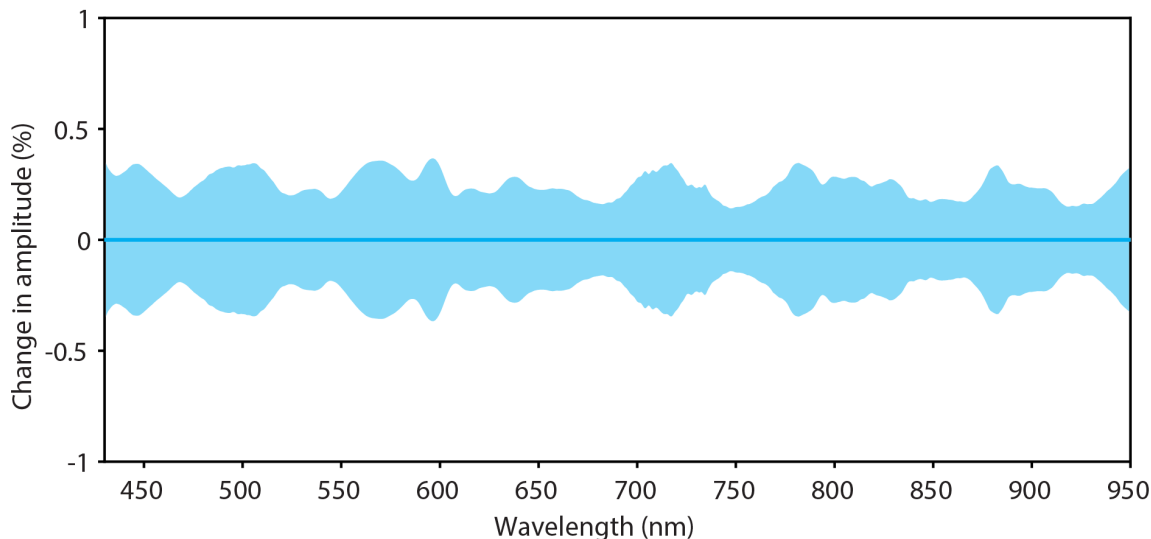


Figure 4.3: **Stabilized spectral intensity of the probe beam.** The standard deviation (light blue) of the laser spectral intensity fluctuations with reference spectrometer correction for 10 measurements.

Hence, with the stabilization system very small changes in spectral signals can be measured without being concerned about actual fluctuations in laser spectral intensity.

4.2 VO₂ sample details

Thin film samples are commonly used in ultrafast VO₂ experiments. However, thin films deposited by sputtering, chemical vapor deposition, or pulsed laser deposition often exhibit interfacial effects, polycrystallinity, defects, and strain due to lattice mismatch between the film and substrate [143, 144, 145, 146]. All these factors affect the characteristics of the pure material. On top of this, the thickness of thin film also influences the optical properties of VO₂ and the insulator-to-metal transition [147, 148]. In contrast, bulk single crystal VO₂ can be utilized to study the inherent material properties without the influence of thickness, substrate-induced strain, and interfacial effects[149]. All experiments related to VO₂ in this thesis are carried out with bulk, single-crystal M1-VO₂. The crystal was grown using liquid-diffusion-limited technique [149] at the group of Prof. Baum in the University of Konstanz.

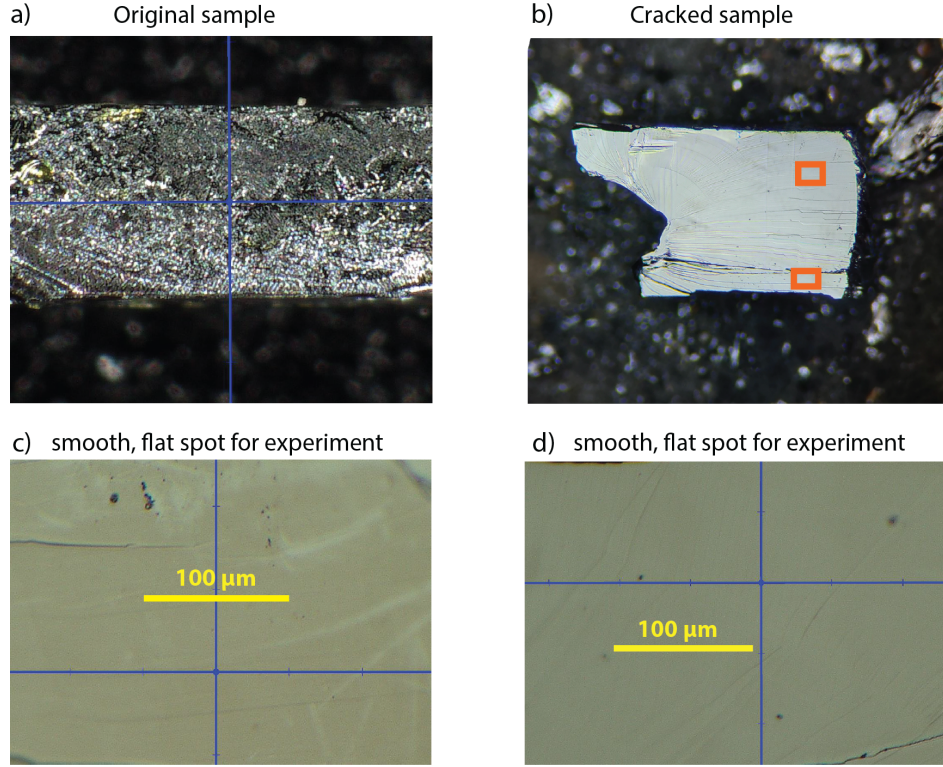


Figure 4.4: **Preparation of smooth, flat spot from the original VO_2 crystal.** a) Original sample as prepared by liquid-diffusion-limited technique. b) Cracked VO_2 crystal surface. c) and d) show two flat, polished exteriors appropriate for optical experiments.

In spite of all the advantages of the bulk single crystal over thin film VO_2 , the only disadvantage is the surface quality of the crystal. The rough surface (Figure 4.4.a) of bulk VO_2 scatters the optical beam and the probe spectrometer can not properly collect the transient signal. Attempt are made to polish the sample with commercial polishing compounds and water. However, Raman and X-ray diffraction (XRD) measurements have showed that the polishing process changes the composition of the monoclinic VO_2 .

Ultimately, a cracking or fracturing technique is followed for obtaining a smooth and polished crystal surface. First, a sharp blade is used to score the sample along a desired fracture line and then, the sample is cracked along the score line by applying force with a fine chisel and a small hammer. Figure 4.4.b shows the surface of the VO_2 as obtained from the fracturing process. A careful inspection of the sample surface under a microscope has allowed to find several smooth and flat spots (Figure 4.4.c and d) appropriate for the pump-probe experiments in reflection geometry. This cracked surface is characterized by XRD and Raman spectroscopy, as illustrated in Figures 4.5.a and .b respectively[‡]. The XRD pattern shows a high quality single crystal monoclinic VO_2 with peaks at (011) and

[‡]Note: Dr. Rostyslav Lesyuk and Annika Bergman have assisted in the collection of the XRD and Raman data respectively.

(022). The Raman spectrum (Figure 4.5.b) exhibits the Raman modes of the monoclinic M1 phase (blue) at room temperature [52], and heating (80°C) the sample above phase transition temperature shows a broad Raman spectrum (red), which was also recognized in other literature [88, 89] as the Raman modes of rutile (Metal) VO₂.

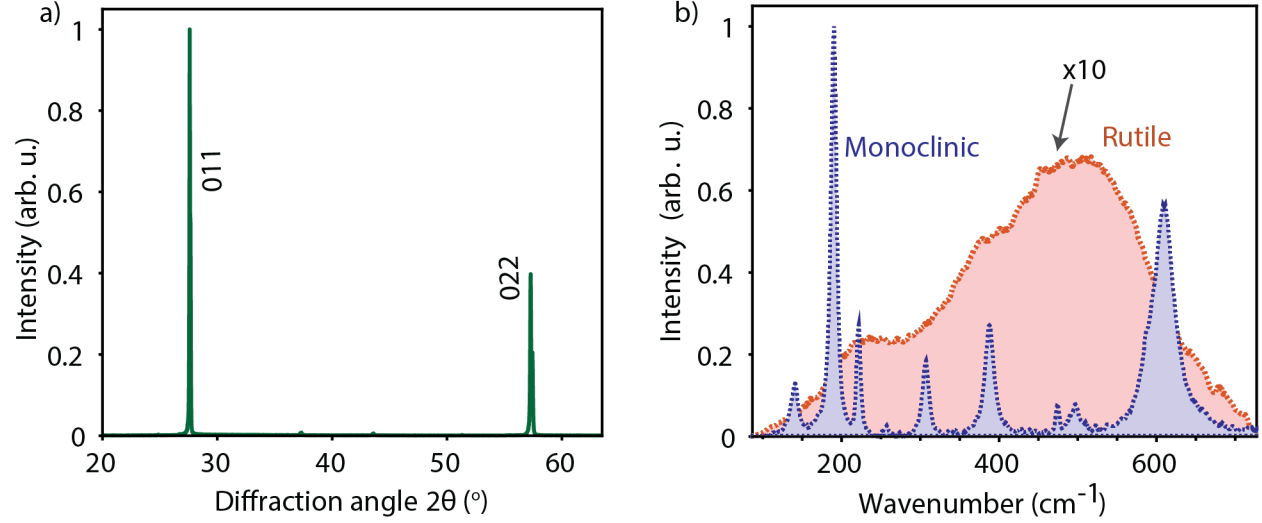


Figure 4.5: **Characterization of the cracked VO₂ sample.** a) Room temperature XRD spectrum of the M1-VO₂ crystal. b) Raman spectra of the crystalline sample at room temperature (blue) and 80°C (red) respectively. Adopted from ref. [139]

Chapter 5

Broadband transient reflectivity measurement in VO₂

Broadband transient reflectivity measurements provide simultaneous access to the temporal and spectral signatures of the phase transition. The use of white light supercontinuum as probe pulse enables access to the material's response in near-ultraviolet, visible and near-infrared wavelengths. This broad spectral coverage facilitates the exploration of transient electronic and structural dynamics, previously inaccessible with narrow-band probing. The present chapter focuses on the single-cycle optical pulse driven broadband probing of the photoinduced phase transition of M1-VO₂ using transient reflectivity measurements. The broadband spectrum of the probe pulse enables simultaneous investigation of multiple dynamics imprinted within it, serving as a phase-specific indicator of the phase transition. The transient reflectivity experiments on M1-VO₂ (at room temperature, 18°C) and R-VO₂ (above phase transition temperature, 80°C) reveal the importance of including the excited rutile phase contribution when retrieving the laser-driven insulating M1-VO₂ population dynamics.

5.1 Ultrafast probing of VO₂ dynamics

A series of pump-probe measurements at room temperature are performed using the experimental setup described in Chapter 4. The broadband optical pulse, with a duration of ~ 2.4 fs, functions as both the pump and probe in the measurements. For the entire set of experiments, pump pulse fluence is set at ~ 21 mJ/cm², which is sufficiently higher than the insulator-to-metal phase transition thresholds [35, 42, 150, 46, 48, 51], but lower than the experimentally determined damage threshold of the bulk VO₂ crystal. Figure 5.1.a shows a spectrogram of the differential reflectivity evaluated from the measured reflectivity changes as a function of pump and probe pulse delay. Differential reflectivity spectrogram is evaluated from the data based on,

$$\frac{\Delta R(\lambda, \tau)}{R_0(\lambda)} = \frac{R(\lambda, \tau) - R_0(\lambda)}{R_0(\lambda)} \quad (5.1)$$

Where $R(\lambda, \tau)$ is the wavelength (λ) dependent reflectivity of the sample at a delay τ between pump and probe pulse. $R_0(\lambda)$ represents the wavelength-dependent reflectivity of the sample in the absence of pump pulse i.e., at far negative delay.

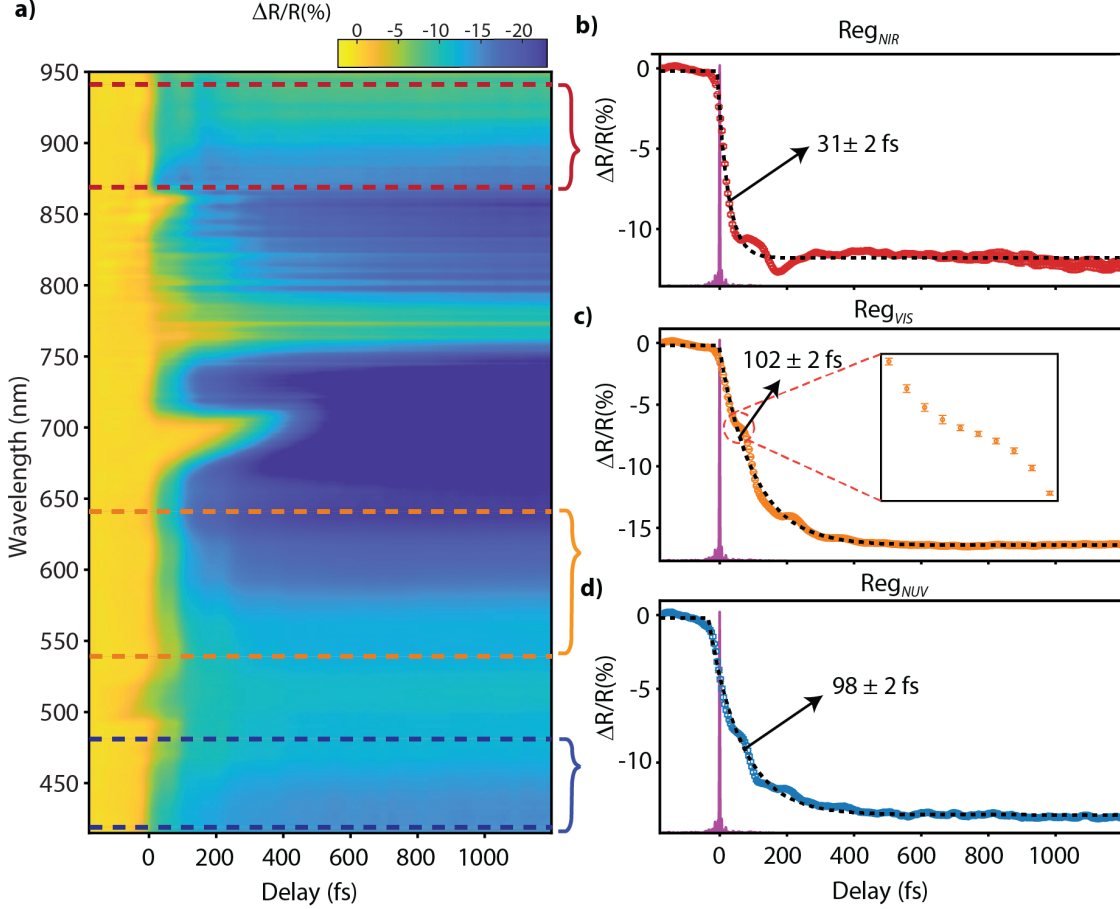


Figure 5.1: **Ultrafast differential reflectivity in VO₂.** a) Broadband spectrogram represents the variation in differential reflectivity across the spectral range of 415 nm – 950 nm. b), c), and d) Spectrally averaged transient differential reflectivity in regions- 870 nm to 940 nm, 540 nm to 640 nm and 420 nm to 480 nm respectively. Exponential fit of the average transient reflectivity (black dashed line) allows evaluation of the decay constants in the three regions. Measured optical pulse intensity waveform (purple curve at zero delay) is presented in all three plots. Adopted from ref. [139]

The transient differential reflectivity spectrogram of the probe signal spans from 415 nm to 950 nm and covers three regions: near-ultraviolet (NUV), visible (VIS), and near-infrared (NIR). A consistent drop in reflectivity is observed over the entire spectral

range for positive delays. This observation agrees with the earlier studies executed over narrower spectral range [45, 42, 43, 48]. The weak pedestal of the laser pulses creates sharp protrusions over narrow areas of the spectrogram. However, these regions with sharp protrusions are not considered for further analysis in this thesis. To demonstrate that the observed protrusions arise solely from the laser pulse pedestal, transient spectral response of the experimental optical pulse characterized by EUV attosecond streaking is simulated in the absence of any sample response in the section 5.3.

The protrusion-free spectral region has been segmented into three parts (marked by the dashed lines): Reg_{NIR} (870 nm to 940 nm), Reg_{VIS} (540 nm to 640 nm) and Reg_{NUV} (420 nm to 480 nm), in order to examine the nature of the wavelength-dependent transient reflectivity decay. Figure 5.1.b, c, and d describe the spectrally averaged transient differential reflectivity at room temperature (18°C) for Reg_{NIR}, Reg_{VIS} and Reg_{NUV} respectively; denoted by $\tilde{R}_{NIR}^{18}$, $\tilde{R}_{VIS}^{18}$ and $\tilde{R}_{NUV}^{18}$. The notable low error bars (inset of 5.1.c) of $\tilde{R}^{18}$ s are the outcomes of the reference spectrometer stabilization correction. The temporal-intensity profile (purple) of the pump pulse measured by EUV attosecond streaking is also presented in all the three plots (Figure 5.1.b, c, and d) to allow evaluation of the time resolution of our experiment. Exponential fitting shown by the black dashed lines of the reflectivity decays $\tilde{R}^{18}$ in the three regions, determines the wavelength-specific decay time constants; $\tilde{R}_{VIS}^{18}$ and $\tilde{R}_{NUV}^{18}$ demonstrate similar decay times, ~ 100 fs, while $\tilde{R}_{NIR}^{18}$ shows almost three times shorter decay time, ~ 30 fs. Therefore, ultrafast broadband probing measures two different decay time scales in a single experiment. These two time scales were previously thought to be the result of electronic and structural contributions in separate experiments [49, 50, 45]. The fast decay time (~ 30 fs) in our experiment agrees well with the fastest transition times measured by Bionta et al. [49] and Jager et al. [50] in the NIR and EUV regions. On the other hand, the slow decay time (~ 100 fs) agrees with the experiment by Cavalleri et al. [45] in the visible spectral range as well as other optical experiments by Cavalleri et al. [35], Kübler et al. [94] and O’Callahan et al. [48].

Thus, the different time scales of the phase transition as reported in previous ultrafast optical studies are now captured by the current experiment, which reveal that the nature of the change in dynamics of transient reflectivity, transient absorption, or transient transmission, depends on the wavelength of the probe pulse. Apart from the fast and slow decay times, another important observation from the current experiment is the step-like drop of the measured reflectivity change across the entire spectral region. As illustrated in the inset of Figure 5.1.c, the experimental error corroborates the observed step-like drop.

5.1.1 Importance of spectral intensity fluctuations correction

The experimental analysis in the previous section has utilized the fluctuations correction module. However, it is essential to point out the importance of this correction. Figure 5.2 describes the same measurement as Figure 5.1 but without considering the fluctuations correction of the probe signal using the reference spectrometer. Once Figure 5.2 is compared

with Figure 5.1, one can find that the absence of laser fluctuations correction leads to random oscillations in the differential reflectivity signal (Figure 5.2.a); and the experimental errors of $\tilde{R}_{NIR}^{18}$, $\tilde{R}_{VIS}^{18}$ and $\tilde{R}_{NUV}^{18}$ (Figure 5.2.b, c, and d) are hitherto elevated.

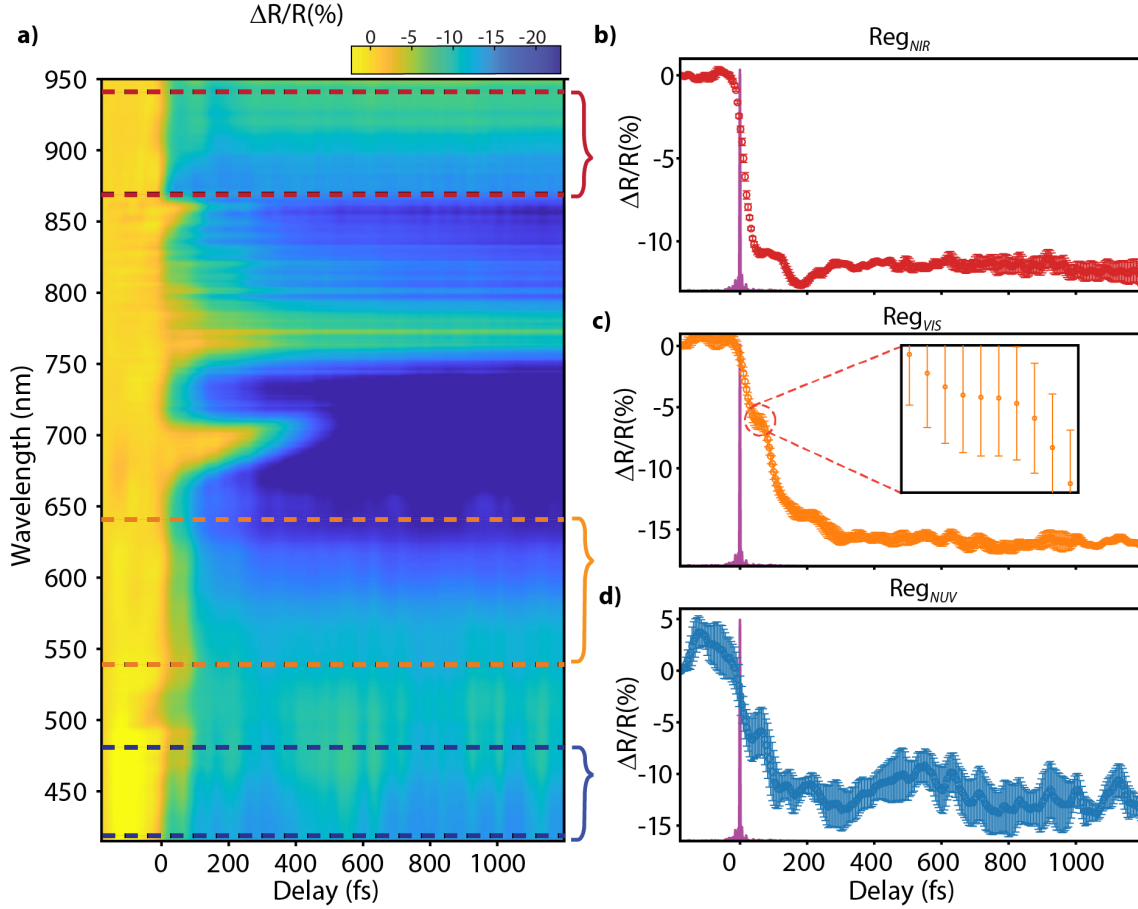


Figure 5.2: **Transient differential reflectivity in the absence of reference spectrometer correction.** a) Variation in differential reflectivity spectra across the broad spectral range. b), c), and d) Spectrally averaged transient differential reflectivity in three regions- $\tilde{R}_{NIR}^{18}$ (b), $\tilde{R}_{VIS}^{18}$ (c), and $\tilde{R}_{NUV}^{18}$ (d).

As a consequence, experimental errors no longer support the step-like reflectivity decay (inset of Figure 5.2.c). Among the three regions, the stability of the NUV part has been affected mostly, probably due to its lower spectral intensity. Therefore, it can be concluded that in order to correctly extract the dynamics during transient reflectivity, transient absorption, or transient transmission measurements, probe spectral intensity fluctuations correction is of utmost importance.

5.1.2 Origin of the step-like decay of transient signals

To explore the nature of the step-like drop, a comparative study of the reflectivity change is performed at low and high fluence laser excitation. The pump fluence is reduced to ~ 3 mJ/cm² and the transient reflectivity of the probe signal from the VO₂ crystal is measured, considering that the fluence is much lower than the IMT threshold in VO₂ [35, 42, 150, 46, 48, 51]. Generally, at excitation fluences below the IMT threshold, the modulation (oscillation) in transient reflectivity is primarily driven by a laser-excited phonon mode of the M1 phase [151, 42, 43]. Here, the goal is to compare the transient differential reflectivity in the visible region for low (~ 3 mJ/cm²) and high fluence (~ 21 mJ/cm²) excitations, such that a direct comparison between the coherent phonon-induced oscillations of the reflectivity and the step-like reflectivity drop is performed.

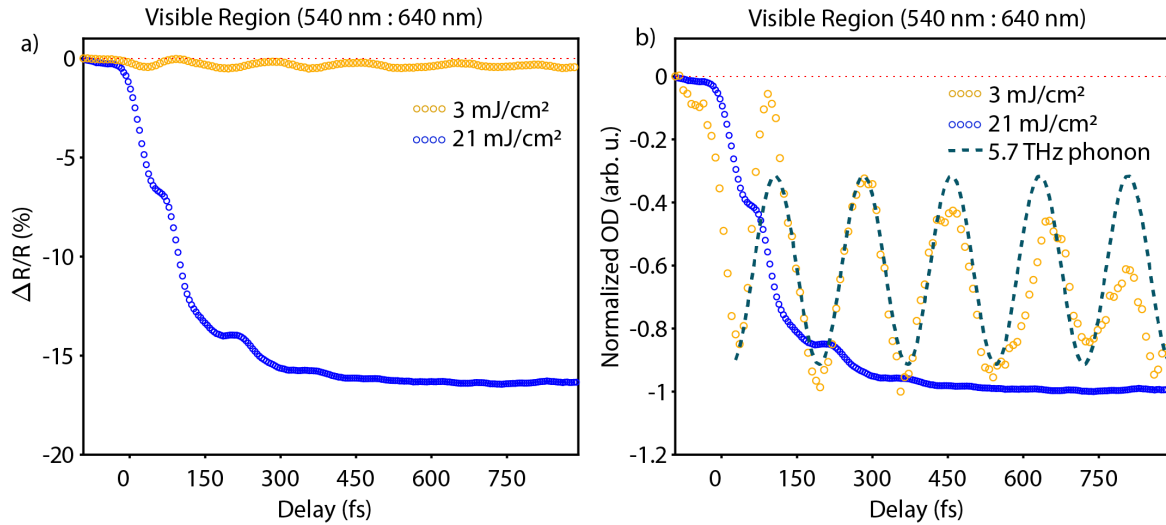


Figure 5.3: **A comparative study of the reflectivity changes stimulated by low (~ 3 mJ/cm²) and high fluence (~ 21 mJ/cm²) pump pulses.** a) Dynamics of spectrally averaged differential reflectivity across the 540 nm – 640 nm spectral range in absolute units for the low (yellow) and high fluence (blue) cases. b) Comparison of the low (yellow) and high fluence (blue) pump-induced transients normalized to -1. The dark green dotted line is guide to the eye for 5.7 THz phonon oscillation of M1-VO₂.

The visible region is chosen for the current analysis owing to the highest modulation of phonon-induced transient reflectivity. Figure 5.3.a shows the variation of the absolute change in $\tilde{R}_{VIS}^{18}$ for low-fluence (yellow) and high-fluence (blue) excitations. The reflectivity change under low-fluence excitation is only ~ 0 – 0.5% compared to $\sim 17\%$ in the high fluence case, indicating that low-fluence pumping does not significantly influence the insulator-to-metal transition. The two transients are then normalized to -1 in Figure 5.3.b for a better comparison of the reflectivity oscillations. Under low fluence pumping, the transient reflectivity shows an oscillating signal with a frequency of 5.7 THz. This oscillation corresponds

to the monoclinic M1 phase phonon and is associated with vanadium-vanadium dimer motion [52]. The Raman spectra (Figure 4.5.b) of the VO₂ sample shows this vibrational mode is present at 190.5 cm⁻¹. A dark green, dotted line in Figure 5.3.b guides to visualize the 5.7 THz oscillation.

The features of low fluence excitation induced reflectivity dynamics (yellow) differ from those of the high fluence excitation (blue) case in (Figure 5.3.b) many ways: 1. Instead of sinusoidal oscillations, a step-like drop is observed in high fluence case. 2. The phonon driven oscillations survives for several hundreds of femtoseconds, whereas the step-like feature disappears after 350-400 fs and reaches a constant value that persists for several picoseconds (observed in our experiment but not presented here). 3. The step-to-step separation (~ 150 fs) in the step-like features does not match the ~ 180 fs periodicity of the oscillations observed under low-fluence excitation. Overall, the step-like features do not appear to result from 5.7 THz coherent phonon oscillations, rather they are more compatible with anharmonic motion of the V-V dimer as predicted by the earlier works [152, 153, 154] on IMT. Chapter 6 will describe more about this.

5.2 Broadband probing above the phase transition temperature (at 80°C)

The monoclinic insulator to rutile metal phase transition in VO₂ is expected to occur over a single time scale, i.e., it should not depend on the spectral region of the probe. But different decay times of $\tilde{R}(\lambda, \tau)$ (Figure 5.1) led to find out the real, wavelength-independent phase transition dynamics in VO₂. One of the possible explanations for the observed variation in decay times can be the superposition of the M1-VO₂→R-VO₂ transition decay and additional hidden dynamics that change the transient susceptibility of the system as well as exhibit wavelength-dependent spectral responses.

When the rutile phase of VO₂ is excited by the pump pulse, the probe response will not reflect the actual characteristics of rutile VO₂; rather, it will present the response of excited rutile (R*-VO₂) state. Similarly, during the M1-VO₂→R-VO₂ transition, one can assume that the hidden dynamics comes from the R*-VO₂ contributions. The best way to verify this assumption is through the experimental response of R-VO₂→R*-VO₂ using the single-cycle pulses. In this spirit, a new set of experiments are conducted: the sample is first heated ($\sim 80^\circ\text{C}$) above the critical temperature ($\sim 67^\circ\text{C}$) of monoclinic to rutile phase transition and pump-probe measurements are then carried out under comparable conditions, as they are in Figure 5.1. Figure 5.4.a presents the differential reflectivity spectra of the excited rutile phase across the 415–950 nm wavelength range. Two distinct regions can be identified based on the sign of the reflectivity change following pump excitation: a positive change is observed in $\frac{\Delta R}{R}$ between 415 nm and 800 nm, while a negative change appears from approximately ~ 850 nm onwards. To highlight the sign reversal in the reflected probe spectrum, the spectrum of the probe beam at a positive delay (white

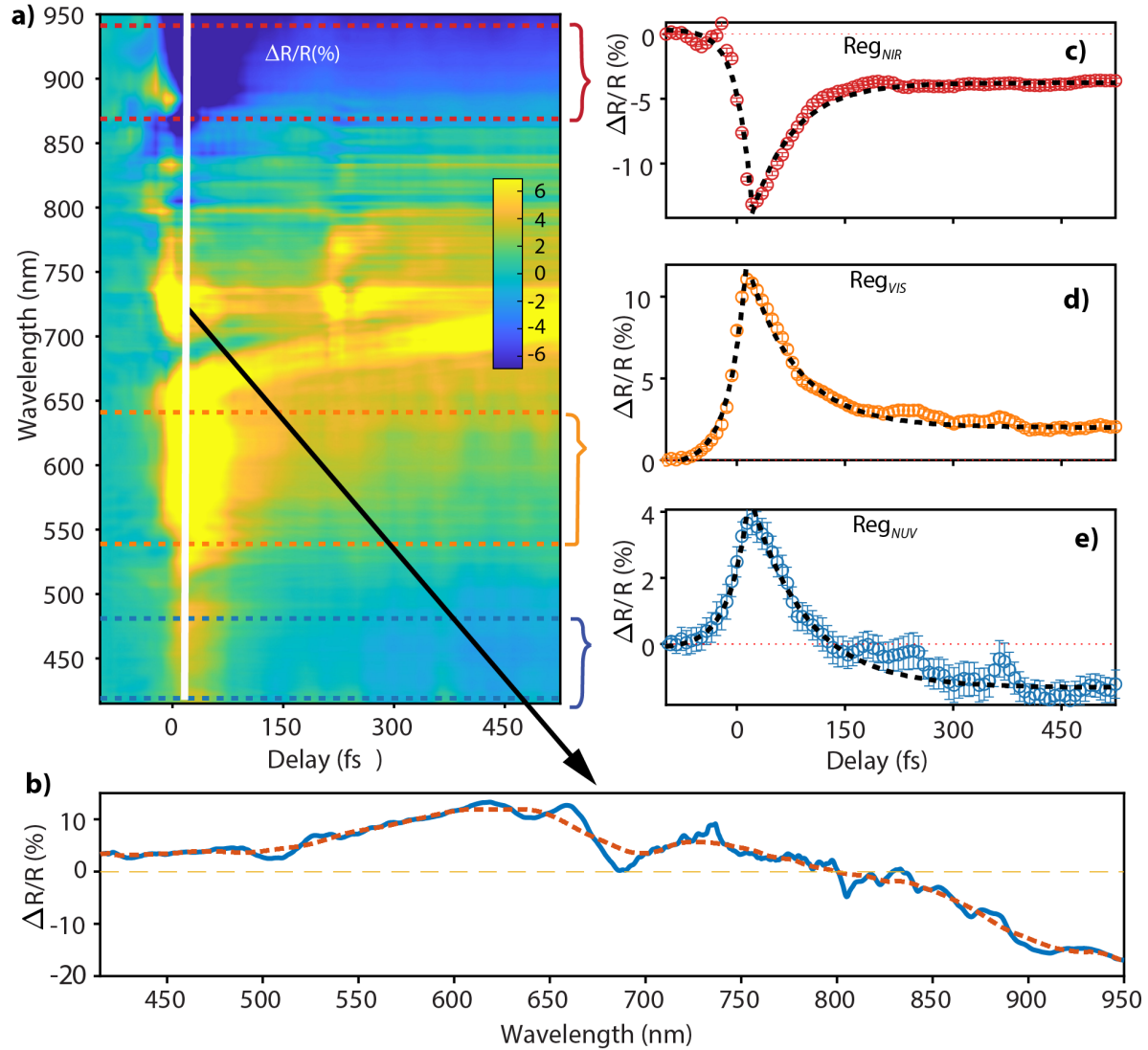


Figure 5.4: **Transient reflectivity dynamics of rutile VO₂** a) Transient differential reflectivity spectra of the VO₂ sample heated above the phase transition temperature. The color scale is tuned in this plot to efficiently illustrate the positive and negative reflectivity change over the full spectral region after the pump excitation. b) The spectrum (blue) of the reflected probe beam from the rutile VO₂ at a positive delay (white line in (a)). The spectrum shows near the plasma frequency of the rutile VO₂, the sign of the reflected probe spectrum changes sign. The dashed red line is a 50 nm moving average of the blue spectrum for better visualization of the sign flip. c), d), and e) represent the spectrally averaged transient reflectivity of heated rutile VO₂ in the three regions of interest: Reg_{NIR} (c), Reg_{VIS} (d), and Reg_{NUV} (e). Adopted from ref. [139]

line in Figure 5.4.a) is separately presented in Figure 5.4.b. The blue line in this plot is the

original spectrum and the dashed red line is the 50 nm moving average of the blue curve that emphasize the sign reversal point. Although the blue curve approaches zero around 680 nm, it is not emphasized here as this wavelength lies within the protrusion region described in Chapter 5.1. The sign reversal of the reflectivity spectra in the pump-probe experiment occurs near the plasma frequency or the plasmon resonance of metals and semiconductors [155, 156]. The pump pulse excitation induces a small shift in the plasma frequency, and a corresponding shift in the spectral reflectivity relative to its original state [155] occurs such that the differential reflectivity changes sign near the plasma frequency [157, 158]. Excited rutile data in Figure 5.4.c, d, and e reveal that the transient dynamics of R*-VO₂(τ) follow the known optical response of an excited metal [159, 160, 161, 162], wherein a fast buildup of the transient signal is followed by a longer decay covering hundreds of femtoseconds. The buildup and decay of the transient signal are typically assigned to the thermalization and relaxation of electrons respectively [159, 160, 161, 162]. An exponential fit (black dashed line) of the buildup (positive or negative slope) times in the three regions shows a fast time range of 21 fs to 27 fs. The decay of each of the three plots after the fast buildup is also fitted (black dashed line) with an exponential to extract the relaxation time of the hot electrons. Three regions possess decay times of ~ 58 fs, ~ 68 fs and ~ 78 fs respectively, which are almost three times longer than their thermalization time counterpart.

By knowing the reasons behind the sign reversal in the rutile pump-probe response and buildup-decay mechanism of the excited metal, the transient reflectivity dynamics of the probe pulse spectrum at 80°C and room temperature (18°C) are then investigated. Since the focus of this work is on the region specific comparison of the transients between the monoclinic and rutile phase experiments, the spectrally averaged differential reflectivity ($\tilde{R}(\lambda, \tau)$) of the three regions (Reg_{NIR}, Reg_{VIS}, and Reg_{NUV}) are juxtaposed for 80°C (orange dots) and 18°C (teal dots) experiments in Figures 5.5.a, b, and c. Three spectrally averaged reflectivities for 80°C data are denoted by $\tilde{R}_{NIR}^{80}$, $\tilde{R}_{VIS}^{80}$ and $\tilde{R}_{NUV}^{80}$. Now, if R*-VO₂ present during the monoclinic to rutile phase transition, or in another words if the transition is occurring from M1-VO₂→R*-VO₂, the transient susceptibility of the system can be influenced because of the long lifetime of R*-VO₂ dynamics. Notably, the dynamics of $\tilde{R}_{NIR}^{80}$ and $\tilde{R}_{VIS}^{80}$ look similar, but are in opposite sign, whereas $\tilde{R}_{NUV}^{80}$ first shows positive response after pump excitation and then changes sign at ~ 150 fs.

The spectrally averaged transient dynamics of M1-VO₂ and R-VO₂ (Figures 5.5.a, b, and c) are now compared to understand the fast and slow decay times of room temperature transient reflectivities. The fast decay time of $\tilde{R}_{NIR}^{18}$ can be explained by the presence of R*-VO₂ dynamics in the background (Figure 5.5.a) of $\tilde{R}_{NIR}^{18}$, since the negative reflectivity response of R*-VO₂ in NIR region will accelerate the real M1-VO₂→R-VO₂ decay process. However, in a similar logic, the positive buildup response of R*-VO₂ will elongate the real M1-VO₂→R-VO₂ transition dynamics in the visible range (Figure 5.5.b). Figure 5.4.c also supports the presence of R*-VO₂ during the M1-VO₂→R-VO₂ transition in the following way: the decay time of $\tilde{R}_{NUV}^{18}$ is expected to be elongated like in the visible region due to the positive response of $\tilde{R}_{NUV}^{80}$, but as $\tilde{R}_{NUV}^{80}$ has a negative contribution at longer delays, the $\tilde{R}_{NUV}^{18}$ dynamics would be slightly faster than that in the visible region,

which is confirmed by the experimental result in the *NUV* region of Figure 5.1.d.

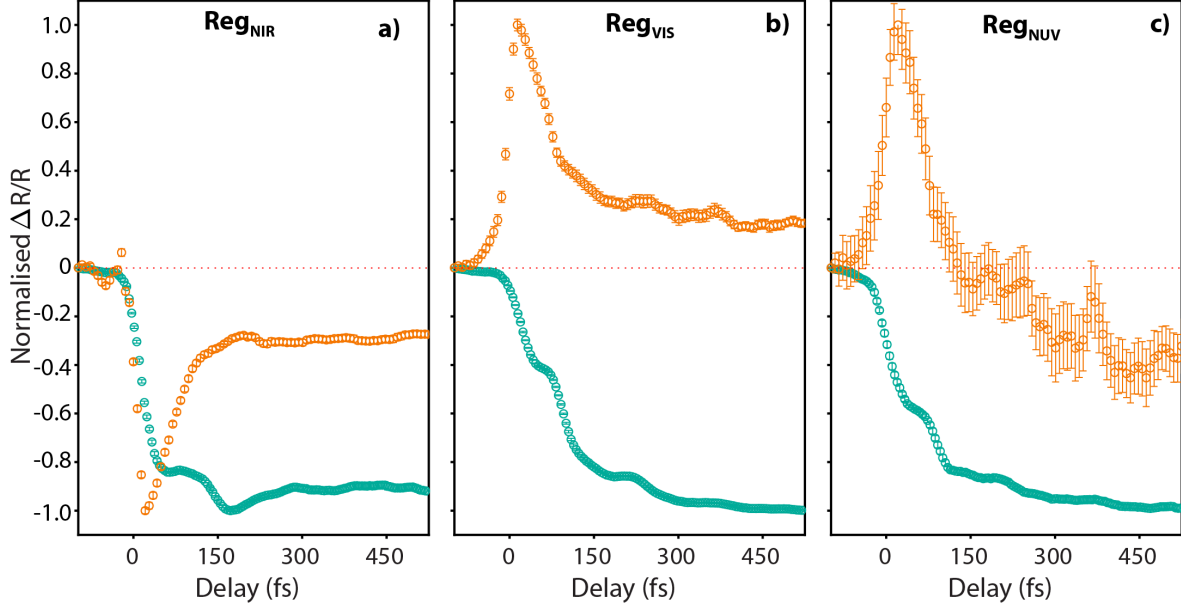


Figure 5.5: **Comparison of transient reflectivity change dynamics of VO_2 at room temperature and 80°C (monoclinic and rutile phase's respectively).** a) , b) and c) compare the spectrally averaged transient reflectivity of room temperature (teal points) and 80°C heated (orange points) VO_2 in the three regions: Reg_{NIR} (a), Reg_{VIS} (b), and Reg_{NUV} (c). The plots are normalized for better comparison between the two temperature datasets. Adopted from ref. [139]

Therefore, our experiments have suggested that in laser excited $\text{M1-VO}_2 \rightarrow \text{R-VO}_2$ transition, the excited rutile ($\text{R}^*\text{-VO}_2$) response is present over the full spectrum of the probe pulse; as well as depending on the spectral responses of $\text{R}^*\text{-VO}_2$, fast and slow dynamics of transient reflectivity changes are observed over NIR and visible regions of the probe spectrum. Hence, in the room temperature time-resolved experiment, the phase transition occurs from monoclinic VO_2 to excited rutile VO_2 ($\text{M1-VO}_2 \rightarrow \text{R}^*\text{-VO}_2$), followed by system's electron thermalization and relaxation. Thanks to the ultrabroad bandwidth of our laser pulse, the transient signal serves as a spectroscopic marker for the identification of the feature of $\text{R}^*\text{-VO}_2$.

5.3 Transient spectral response of the optical pulse

This section models the effect of optical laser pulse on a reflectivity spectrogram. This is accomplished by considering the reflectivity ($R(t)$) at a given instant t that results from accumulated reflectivity changes $\Delta R(t_0, t)$ at all prior times stimulated by the instantaneous

field intensity $I(t_0)$.

$$R(t) = R_0 + c \int_{-\infty}^t \Delta R(t_0, t) dt_0 \quad (5.2)$$

Here, c is a scaling constant and the reflectivity of the unexcited state is R_0 . By assuming that the reflectivity change linearly scales with the instantaneous laser intensity and drops exponentially with a time constant δ , the reflectivity change at time t can be written as,

$$\Delta R(t_0, t) = cI(t_0) \left[e^{-\frac{t-t_0}{\delta}} - 1 \right] \quad (5.3)$$

Thus equation 5.2 can be written as,

$$R(t) = R_0 + c \int_{-\infty}^t I(t_0) \left[e^{-\frac{t-t_0}{\delta}} - 1 \right] dt_0 \quad (5.4)$$

In the limit $\delta \rightarrow 0$, i.e. for instantaneous transition, equation 5.4 simplifies to a time integration of the intensity envelope,

$$R(t) = R_0 - c \int_{-\infty}^t I(t_0) dt_0 \quad (5.5)$$

Now, the spectrogram probed by a weak replica of the pump pulse can be written as a function of delay τ and spectral frequency ω as,

$$\begin{aligned} S(\tau, \omega) &= \left| \int_{-\infty}^{\infty} \sqrt{R(t)} E(t + \tau) e^{i\omega t} dt \right|^2 \\ &= \left| \int_{-\infty}^{\infty} E(t + \tau) e^{i\omega t} \left[R_0 + c \int_{-\infty}^t I(t_0) \left[e^{-\frac{t-t_0}{\delta}} - 1 \right] dt_0 \right]^{\frac{1}{2}} dt \right|^2 \end{aligned} \quad (5.6)$$

Here, $E(t)$ is the electric field of the optical pulse. Equation 5.6 can be used to simulate the spectral response in differential reflective spectrogram originating solely from the waveform of optical pulse. To do so the field waveform of the optical laser pulse is recorded using EUV attosecond streaking [32] for a time window of 540 fs. The use of a long waveform is important for the calculation of the spectrogram, as it enables the accurate representation of long-range protrusions. Figure 5.6.a and b represent the measured optical field waveform for -270 fs to 270 fs and -10 fs to 10 fs respectively.

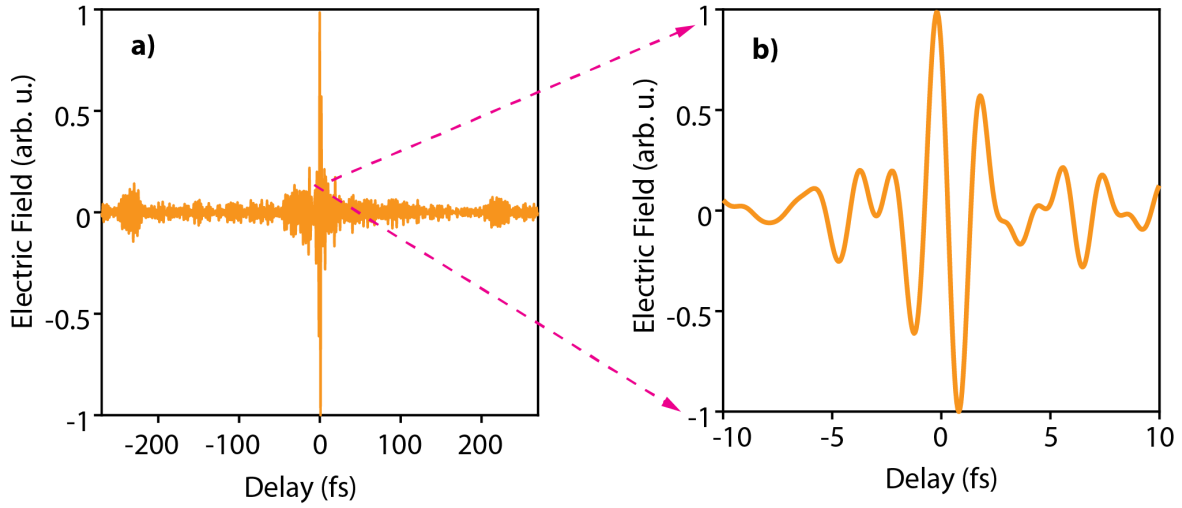


Figure 5.6: **Optical field waveform recorded by long-range attosecond streaking measurement.** a) Optical field waveform from attosecond streaking measurement for a time range of -270 fs to 270 fs. b) The measured waveform in -10 fs to 10 fs. Adopted from ref. [139]

This measured electric field is utilized to simulate the transient reflectivity in the limit $\delta \rightarrow 0$, which is shown in Figure 5.7.a. This simulations of the transient reflectivity change using long-range optical pulse waveform confirm that the observed protrusions in the transient reflectivity signal of VO_2 indeed arise from the laser pedestals. In order to facilitate a better visualization, the spectrogram is segmented into five regions: Figure 5.7.b 870 nm : 940 nm, 5.7.c 650 nm : 870 nm, 5.7.d 540 nm : 640 nm, 5.7.e 490 nm : 530 nm and 5.7.f 420 nm : 480 nm. Since the second and fourth regions (5.7.c and 5.7.e) show long-range protrusions are purely coming from the waveform of the driving pulse, not related to transition dynamics, they are not included in this thesis for any analyses. Whereas the other three regions i.e. Reg_{NIR} (870 nm to 940 nm), Reg_{VIS} (540 nm to 640 nm) and Reg_{NUV} (420 nm to 480 nm) are used for all the analyses, as presented before.

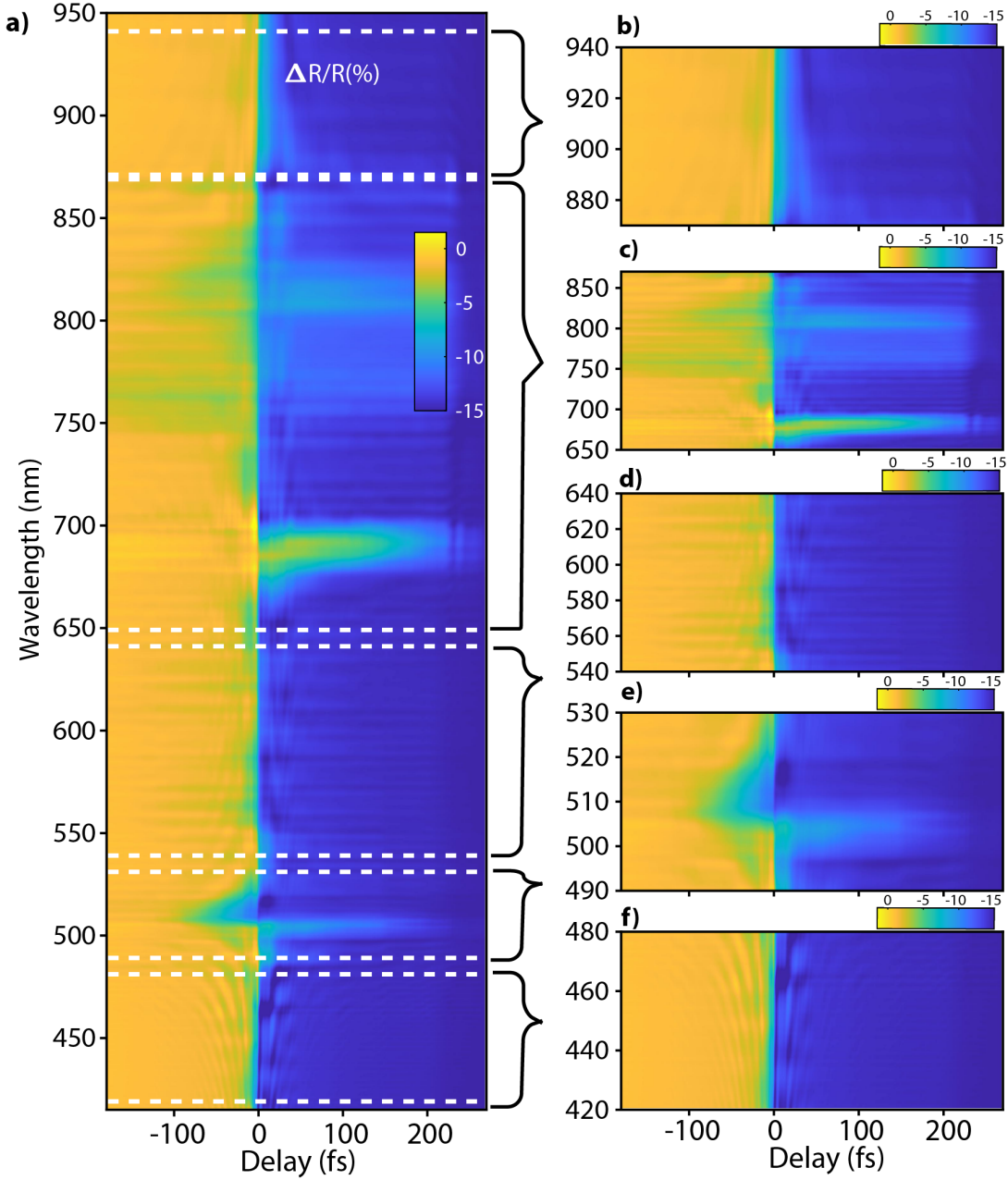


Figure 5.7: **Inherent pulse dynamics.** a) Simulated transient spectral response due to the optical laser pulse. b), c), d), e) and f) Separated regions from (a) marked by the white dashed-lines and black brackets. The corresponding spectral ranges are as follows: 870-940 nm (b), 650-870 nm (c), 540-640 nm (d), 490-530 nm (e) and 420-480 nm (f). Adopted from ref. [139]

Chapter 6

Disentanglement of the hidden dynamics in photoinduced phase transition of VO₂

The previous chapter has demonstrated that during the room temperature photoinduced phase transition of M1-VO₂, the electronic response of excited rutile phase (R*-VO₂) overlaps with the M1-VO₂→R-VO₂ dynamics. This chapter proposes a model to disentangle the population dynamics of the M1-VO₂ (and R-VO₂) phase and the excited rutile phase (R*-VO₂) contribution. The derived population dynamics are then utilized to extract the vanadium-vanadium bond length alternation [74] dynamics occurring in the M1-VO₂→R-VO₂ phase transition.

6.1 Mathematical formulation of the problem

Here a theoretical model has been proposed to disentangle the population dynamics of M1-VO₂ and R-VO₂ from the M1-VO₂→R*-VO₂ phase transition dynamics at room temperature, assuming the reflectivity and populations are directly proportional. This model further incorporates the thermalization-relaxation response of R*-VO₂ during the phase transition. In this scenario, the time-dependent total reflectivity of the M1-VO₂ ($R_{M1}(\lambda, t)$) and R-VO₂ ($R_R(\lambda, t)$) system in terms of the normalized population dynamics of M1-VO₂ ($N_{M1}(t)$) and R-VO₂ ($N_R(t)$) phases is described by,

$$R(\lambda, t) = R_{M1}(\lambda, t) + R_R(\lambda, t) = R_{M1}^0(\lambda)N_{M1}(t) + R_R^0(\lambda)N_R(t) \quad (6.1)$$

Where, $R_{M1}^0(\lambda)$ and $R_R^0(\lambda)$ are the proportionality constants which denote the reflectivity of the pure M1-VO₂ and R-VO₂ phases respectively. Since the total populations of M1-VO₂

and R-VO₂ phases are conserved at any instant,

$$N_{M1}(t) + N_R(t) = 1 \quad (6.2)$$

The absolute transient reflectivity signal for the M1-VO₂→R*-VO₂ phase transition can now be expressed as the sum of two parts: a signal proportional to the M1-VO₂ population dynamics and a contribution from the R*-VO₂ thermalization-relaxation response. To account for the underlying R*-VO₂ response during M1-VO₂→R*-VO₂, the thermalization-relaxation response can be modeled at a given instance in time as the cumulative response of R-VO₂→R*-VO₂ reflectivity from all instances before the given instant and at each instant weighted by the instantaneous rate of growth of the R-VO₂ population, $\frac{dN_R}{dt}$. Hence, the total reflectivity of the system during the M1-VO₂→R*-VO₂ phase transition can be presented as

$$R(\lambda, t) = R_{M1}^0(\lambda)N_{M1}(t) + \int_{-\infty}^t \frac{dN_R(t')}{dt'} R_R^*(\lambda, t - t') dt' \quad (6.3)$$

where, $R_R^*(\lambda, t)$ is the wavelength-dependent absolute dynamic reflectivity variation which can be extracted from the R-VO₂→R*-VO₂ differential reflectivity spectrogram ($S_R(\lambda, t)$) (Figure 5.4.a).

$$S_R(\lambda, t) = \frac{R_R^*(\lambda, t) - R_R^0(\lambda)}{R_R^0(\lambda)} = \frac{R_R^*(\lambda, t)}{R_R^0(\lambda)} - 1 \quad (6.4)$$

Here, R_R^0 is the reflectivity of pure rutile.

$$R_R^*(\lambda, t) = R_R^0(\lambda)[S_R(\lambda, t) + 1] \quad (6.5)$$

Equation 6.3 can be rewritten as,

$$\begin{aligned} R(\lambda, t) &= R_{M1}^0(\lambda)N_{M1}(t) + \int_{-\infty}^t \frac{dN_R(t')}{dt'} R_R^0(\lambda)[S_R(\lambda, t - t') + 1] dt' \\ &= R_{M1}^0(\lambda)N_{M1}(t) + R_R^0(\lambda) \int_{-\infty}^t \frac{dN_R(t')}{dt'} S_R(\lambda, t - t') dt' + R_R^0(\lambda) \int_{-\infty}^t \frac{dN_R(t')}{dt'} dt' \\ &= R_{M1}^0(\lambda)N_{M1}(t) + R_R^0(\lambda) \int_{-\infty}^t \frac{dN_R(t')}{dt'} S_R(\lambda, t - t') dt' + R_R^0 N_R(t) \end{aligned} \quad (6.6)$$

From the absolute reflectivity $R(\lambda, t)$ the differential reflectivity spectrogram ($S_{M1}(\lambda, t)$) for M1-VO₂→R*-VO₂ is derived by using equation 6.2 and 6.6 as follows:

$$\begin{aligned}
S_{M1}(\lambda, t) &= \frac{R(\lambda, t) - R_{M1}^0(\lambda)}{R_{M1}^0(\lambda)} \\
&= N_{M1}(t) + \frac{R_R^0(\lambda)}{R_{M1}^0(\lambda)} N_R(t) + \frac{R_R^0(\lambda)}{R_{M1}^0(\lambda)} \int_{-\infty}^t \frac{dN_R(t')}{dt'} S_R(\lambda, t - t') dt' - 1 \\
&= -1[1 - N_{M1}(t)] + \frac{R_R^0(\lambda)}{R_{M1}^0(\lambda)} N_R(t) + \frac{R_R^0(\lambda)}{R_{M1}^0(\lambda)} \int_{-\infty}^t \frac{dN_R(t')}{dt'} S_R(\lambda, t - t') dt' \\
&= \left[\frac{R_R^0(\lambda)}{R_{M1}^0(\lambda)} - 1 \right] N_R(t) + \frac{R_R^0(\lambda)}{R_{M1}^0(\lambda)} \int_{-\infty}^t \frac{dN_R(t')}{dt'} S_R(\lambda, t - t') dt'
\end{aligned} \tag{6.7}$$

Equation 6.7 can be further simplified as,

$$S_{M1}(\lambda, t) = [a(\lambda) - 1] N_R(t) + a(\lambda) \int_{-\infty}^t \frac{dN_R(t')}{dt'} S_R(\lambda, t - t') dt' \tag{6.8}$$

Here, $a(\lambda) = \frac{R_R^0(\lambda)}{R_{M1}^0(\lambda)}$ is the wavelength-dependent sensitivity coefficient, signifying the reflectivity ratio between the R-VO₂ and M1-VO₂ phases.

6.2 Reconstruction of the differential reflectivity spectrogram $S_{M1}(\lambda, t)$

Equation 6.8 describes how the population dynamics $N_R(t)$ is imprinted in the differential reflectivity spectrogram $S_{M1}(\lambda, t)$. It is accessible by performing a spectrogram reconstruction. In the initial stage of the spectrogram reconstruction, equation 6.8 is parameterized using constants based on the following two conditions:

(i) As the exact experimental magnitude of the thermalization-relaxation effect from the R*-VO₂ phase in $S_{M1}(\lambda, t)$ is unknown, a scaling parameter C is introduced for the second term on the right-hand side of equation 6.8. This parameter adjusts the relative magnitude of the second term in equation 6.8 relative to the first term and is assumed to be independent of both wavelength λ and time t . Thus equation 6.8 becomes

$$S_{M1}(\lambda, t) = [a(\lambda) - 1] N_R(t) + Ca(\lambda) \int_{-\infty}^t \frac{dN_R(t')}{dt'} S_R(\lambda, t - t') dt' \tag{6.9}$$

(ii) The comparison of experimental spectrograms $S_{M1}(\lambda, t)$ and $S_R(\lambda, t)$ from Figure 5.1 and Figure 5.4 highlight a saturation behavior at delays beyond 500 fs (far delays). Therefore at far delays, the population of R-VO₂, $N_R(t)$, is also inferred to be

saturated, leading to its rate of change to be localized in time. This allows to set boundary condition $N_R^b = N_R(t \rightarrow \infty)$ and compute the values of $a(\lambda)$ from the spectrogram $S_{M1}(\lambda, t \rightarrow \infty)$ with the parameters N_R^b and C .

$$a(\lambda) = \frac{S_{M1}(\lambda, \infty) + N_R^b}{N_R^b [1 + CS_R(\lambda, \infty)]} \quad (6.10)$$

A MATLAB code solves the differential equation 6.9 for each wavelength in the spectrogram for three region of interests Reg_{NIR} , Reg_{VIS} and Reg_{NUV} ; and yields a set of $N_R(t)$ for a given set of parameters N_R^b and C . To extract a representative $N_R(t)$ profile from this set of $N_R(t)$ for the three spectral regions, singular value decomposition (SVD) is applied and the principal component is selected. The spectrogram reconstruction problem is then reduced to an optimization problem of minimizing the error between the experimental and reconstructed spectrograms against the parameters N_R^b and C . The optimal solution corresponds to the minimum error in the N_R^b – C parameter space. Thus the ultimate solution is achieved by minimizing the experimental and reconstructed spectrogram error in the N_R^b – C space (Figure 6.1.a) and the principle solution of $N_R(t)$ is correspondingly retrieved (Figure 6.1.b). Figure 6.2 compares the experimental and reconstructed spectrogram obtained from the above method.

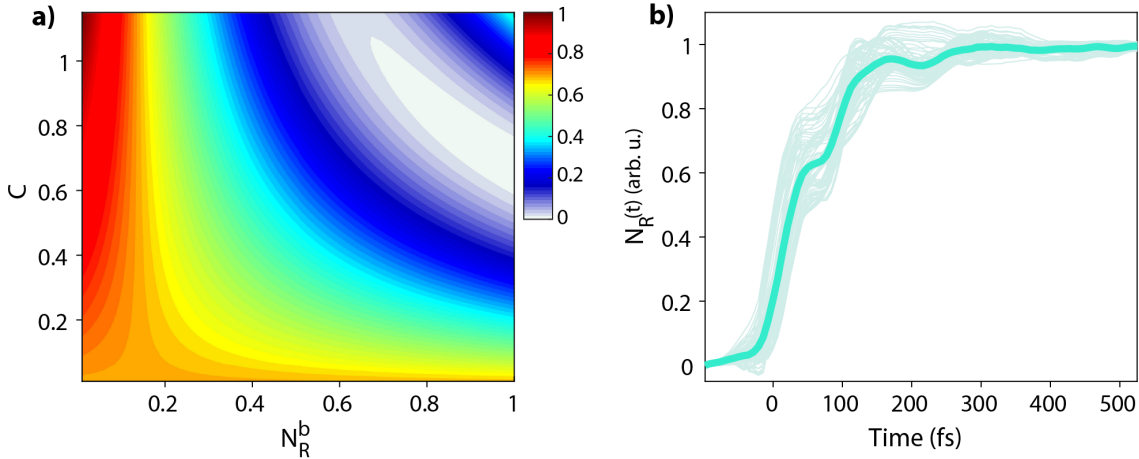


Figure 6.1: **Extracted rutile population dynamics.** a) Error between experimental and reconstructed spectrograms as a function of N_R^b and C . The error is normalized with respect to its maximum value. b) Rutile population dynamics $N_R(t)$ (thin transparent cyan curves) retrieved at each wavelength components in the three regions of the spectrogram. Principal $N_R(t)$ is presented by the thick cyan curve. Adopted from ref. [139]

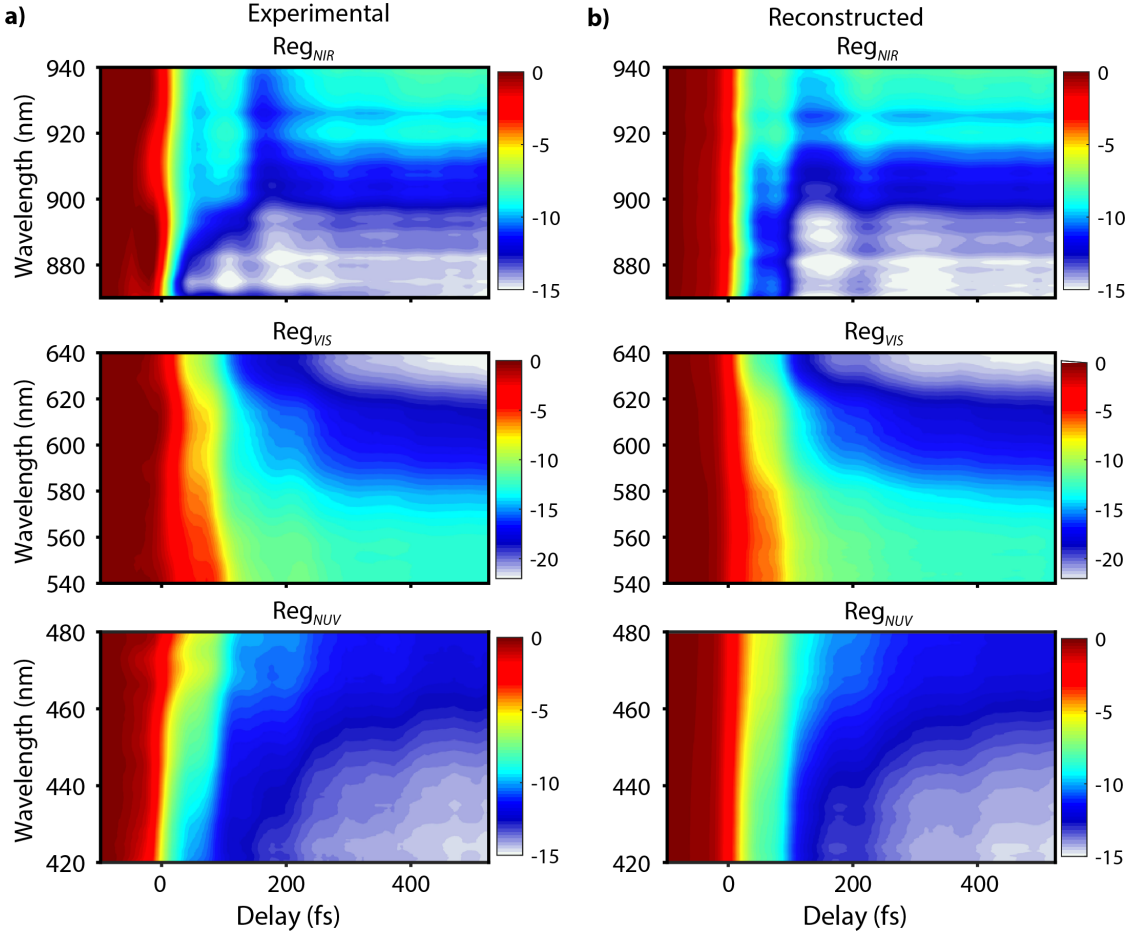


Figure 6.2: **Comparison of the experimental and reconstructed differential reflectivity spectrogram from the model.** a) Experimentally recorded differential reflectivity spectrograms in the three regions of interest: Reg_{NIR} , Reg_{VIS} , and Reg_{NUV} . b) Reconstructed differential reflectivity spectrograms in the corresponding regions. Note: Color scales are in %. Adopted from ref. [139]

Figure 6.3.a shows the population dynamics of the monoclinic phase $N_{M1}(t) = 1 - N_R(t)$, which exhibits a stepwise drop after pump excitation. Since the population dynamics do not show a simple exponential drop, the population change of the monoclinic phase is expressed via the transition rate ($\frac{dN_{M1}(t)}{dt}$), rather than a simple exponential fit. The transition rate thus evaluated in Figure 6.3.b reveals that the transformation from the M1-VO₂ insulating phase to the R-VO₂ metallic phase occurs in steps: $\sim 60\%$ of the photoexcited M1-VO₂ population transforms to R-VO₂ in first 49 fs and the remaining $\sim 40\%$ completes in weaker steps.

The stepwise transition may appear surprising at first sight, but it helps in the understanding of the background electron dynamics of the excited rutile phase. The underlying electron dynamics (thermalization-relaxation) of the R*-VO₂ retrieved for a

representative wavelength of 580 nm (Figure 6.3.c) exhibits two main temporal bursts. This corresponds well with the rate dynamics of Figure 6.3.b, which also show two main bursts. These observations suggest that electron thermalization and relaxation effects occurs when a significant amount of R*-VO₂ population is created.

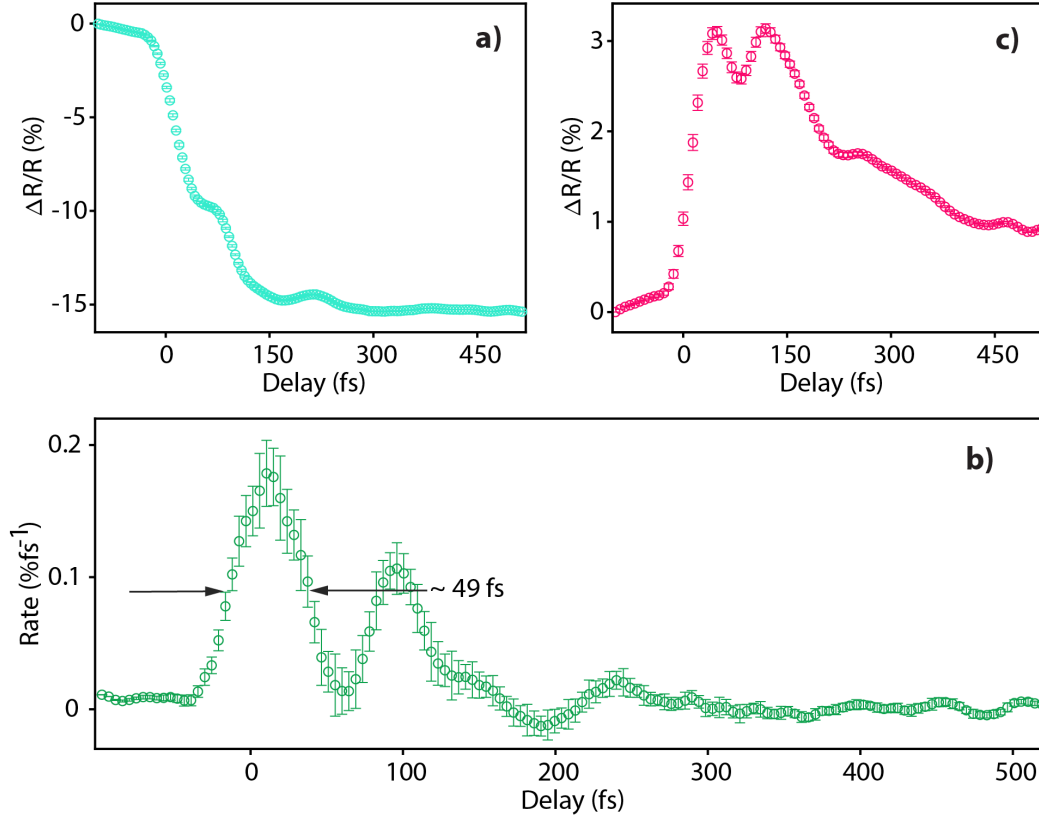


Figure 6.3: **Disentanglement of the population dynamics $N_M(t)$ and the electronic response of R*-VO₂.** a) Population dynamics of M1-VO₂ during phase transition. b) Transition rate evaluated by taking the derivative of population dynamics (a) with respect to time. c) Disentangled thermalization-relaxation response of the R*-VO₂ at a representative wavelength of 580 nm during the photoinduced phase transition at room temperature. Adopted from ref. [139]

6.3 Extraction of bond length alternation from the population dynamics

Having derived the time-dependent populations $N_{M1}(t)$ and $N_R(t)$, it is now the time to explore their connection to the quantum dynamics of the system. The experimental results do not support instantaneous Mott-like mechanism, since the time duration of population change is much slower compared to the temporal resolution of the experiments; rather the step-like drop in the population, together with its associated time scale suggests a series of rapid and quasi-periodic rearrangements of atoms during the phase transition.

Vanadium atoms form alternate short (d_{V-V}^{short}) and long (d_{V-V}^{long}) vanadium-vanadium bonds (Figure 6.4.a) along the crystallographic axis (c) of the monoclinic (M1) structure. The short and long V-V bonds become equal in the rutile (R) phase (Figure 6.4.b) because the V atoms align in an equispaced configuration. The vanadium-vanadium bond length alternation (d) describes how the V-V bonds are arranged in a specific structure of VO_2 and can be defined as [74],

$$d = |d_{V-V}^{long} - d_{V-V}^{short}| \quad (6.11)$$

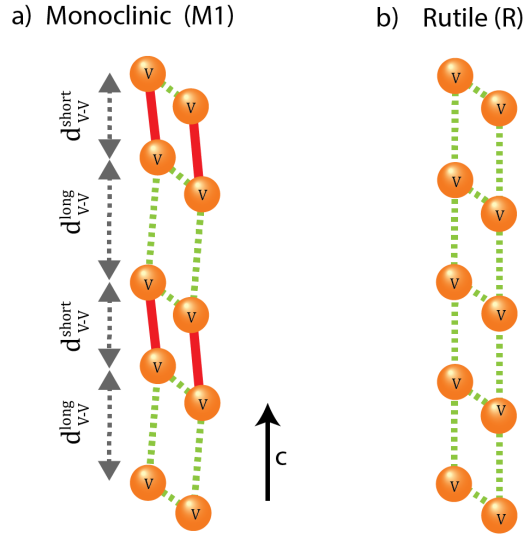


Figure 6.4: **Schematic of the arrangement of V atoms in monoclinic and rutile phases.** a) Short and long V-V bonds in the monoclinic structure. b) Uniformly spaced V-V bonds in the rutile structure.

According to equation 6.11, the bond alternation value vanishes for the rutile phase and takes a specific value for the monoclinic phase. Therefore, the experimental values of the time-dependent V-V bond length alternation $d(t)$ can describe the photoinduced phase transition dynamics associated with its structure. This section will elaborate on the extraction process of time-dependent bond length alternation using the population dynamics of the M1- VO_2 during the phase transition. To this end, the monoclinic to rutile phase transition is modeled such that the populations of M1- VO_2 ($N_{M1}(t)$) and R- VO_2 ($N_R(t)$) at any instant determine the rate of transition at that given instant. $N_{M1}(t)$ and $N_R(t)$ satisfy population conservation and their master equation [163] takes the form

$$\frac{dN_{M1}(t)}{dt} = -\Gamma_a(t)N_{M1}(t) + \Gamma_d(t)N_R(t) \quad (6.12)$$

Here, $\Gamma_a(t)$ and $\Gamma_d(t)$ denote the *association* and *dissociation* probability rates of the M1- $\text{VO}_2 \leftrightarrow$ R- VO_2 phase transition. *Association* and *dissociation* characterize the correspondence of V-V bond length alternation with the R- VO_2 and M1- VO_2 phase respectively.

$\Gamma_a(t)$ and $\Gamma_d(t)$ can be modeled as a function of $d(t)$, assuming the probability for alternating bond lengths to have exponential dependence in stable equilibrium [164, 165, 166].

$$\Gamma_a(t) = \beta_a [e^{-\alpha_a\{d(t)-d_{M1}\}} - 1] \quad (6.13)$$

$$\Gamma_d(t) = \beta_d [e^{\alpha_d\{d(t)-d_R\}} - 1] \quad (6.14)$$

Here, β_a and β_d represent the intrinsic *association* and *dissociation* rates of the phase transition; α_a and α_d signify the inertia for changing the proportions of alternate bond lengths during *association* and *dissociation*; and d_{M1} and d_R describe the limits of bond length alternation, where $d_R \leq d(t) \leq d_{M1}$. The values of d_{M1} and d_R for M1-VO₂ and R-VO₂ phases are approximated to 0.64 Å and 0.0 Å respectively [74, 167, 81, 46, 51, 153].

Using equations 6.13 and 6.14, equation 6.12 can be rewritten as,

$$\frac{dN_{M1}(t)}{dt} + \beta_a [e^{-\alpha_a\{d(t)-d_{M1}\}} - 1] N_{M1}(t) - \beta_d [e^{\alpha_d\{d(t)-d_R\}} - 1] N_R(t) = 0; \quad (6.15)$$

It is possible to determine $d(t)$ by solving equation 6.15 with conditions $N_{M1}(t) + N_R(t) = 1$. The solution process minimizes the left hand side of equation 6.15 using the Levenberg-Marquardt method in MATLAB.

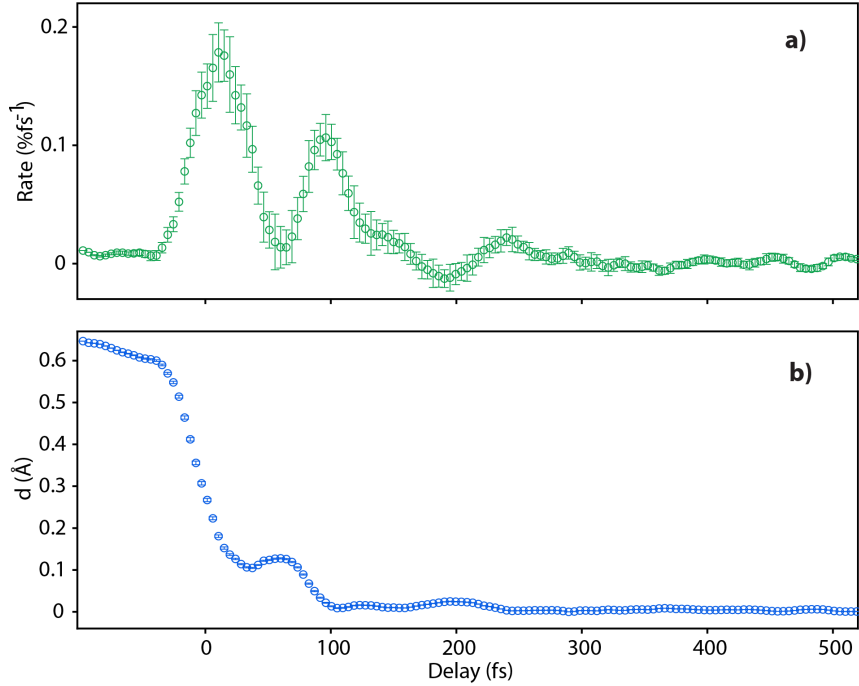


Figure 6.5: **Experimentally determined bond length alternation dynamics.** a) Transition rate as presented in Figure 6.3.b. b) Variation of the V-V bond alternation amplitude with time, as obtained by solving equation 6.15. Adopted from ref. [139]

Figure 6.5.b illustrates the extracted bond length alternation dynamics. As expected during the negative delays, i.e., in the absence of pump pulse, $d(t)$ values (~ 0.64 Å) represent M1-VO₂ phase. Meanwhile, when the pump pulse interacts with the material, the $d(t)$ values drop from M1-VO₂ phase value to R-VO₂ phase value (~ 0 Å) with few small oscillations. Now, when comparing Figure 6.5.b with 6.5.a, it is clear that the bond alternation follows the transition rate. The peaks of the transition rate at specific delays signify the most efficient conversion from M1-VO₂ $\rightarrow$ R-VO₂. With the increase in delay, the transition rate reaches zero and the bond length alternation value corresponds to the rutile phase.

6.4 Bond length alternation from real-time time -dependent density functional theory

The V-V bond length alternation dynamics extracted from the experiment are not compatible with light-driven phonon modes of V-V oscillation; rather they are more compatible with the works that describe IMT as the result of the anharmonic motion of the V-V dimers [152, 153, 154]. To validate our experimental findings, real-time time-dependent density functional theory (rt-TDDFT) simulations were conducted on M1-VO₂ using conditions very similar to our experiment, including the driving field waveform as obtained via EUV attosecond streaking measurement.

The Sheng Meng group from the Chinese Academy of Sciences has conducted the simulations. The rt-TDDFT simulations are performed in Quantum Espresso [168] using projector augmented-waves (PAW) [169] method and Perdew-Burke-Ernzerhof (PBE) [170] exchange-correlation functional. The photoinduced structural dynamics of M1-VO₂ are simulated within the TDDFT+U protocols [153], where the Hubbard U value is chosen to be 3.5 eV [171, 172] for V_{3d} states so that the band gap value became ~ 0.7 eV, close to the experimental value of 0.6 eV [78]. With the lattice constant of $a=5.60$ Å, $b=4.61$ Å and $c=5.45$ Å, and $\beta=121.70^\circ$ [153], a 2 x 2 x 2 supercell of M1-VO₂ is used in experimental laser pulse driven photoexcited simulations. The atomic configuration was first equilibrated for 3 ps at 300 K in NVT ensemble.

Figure 6.6.a shows the dynamics of the V-V pair lengths for both the short (d_{V-V}^{short}) (transparent brown curves) and long (d_{V-V}^{long}) (transparent green curves) bonds. The dark brown and dark green curves represent the average trajectory of the short and long bond lengths respectively. The transparent magenta curves in Figure 6.6.b are the difference between long and short bond length trajectories, while the dark magenta curve is the average of their differences. A clear similarity is observed when comparing the simulated bond length difference (dark magenta) with the experimental bond length alternation (dashed cyan), where a rapid initial anharmonic distortion of the bond alteration is followed by non-periodic oscillations in both cases. The small difference between the simulated and experimental bond length alternation after 100 fs is probably due to (i) the standard deviation of the simulated bond length differences, or (ii) the fact that the simulation doesn't consider the relaxation responses of R*-VO₂, or (iii) both.

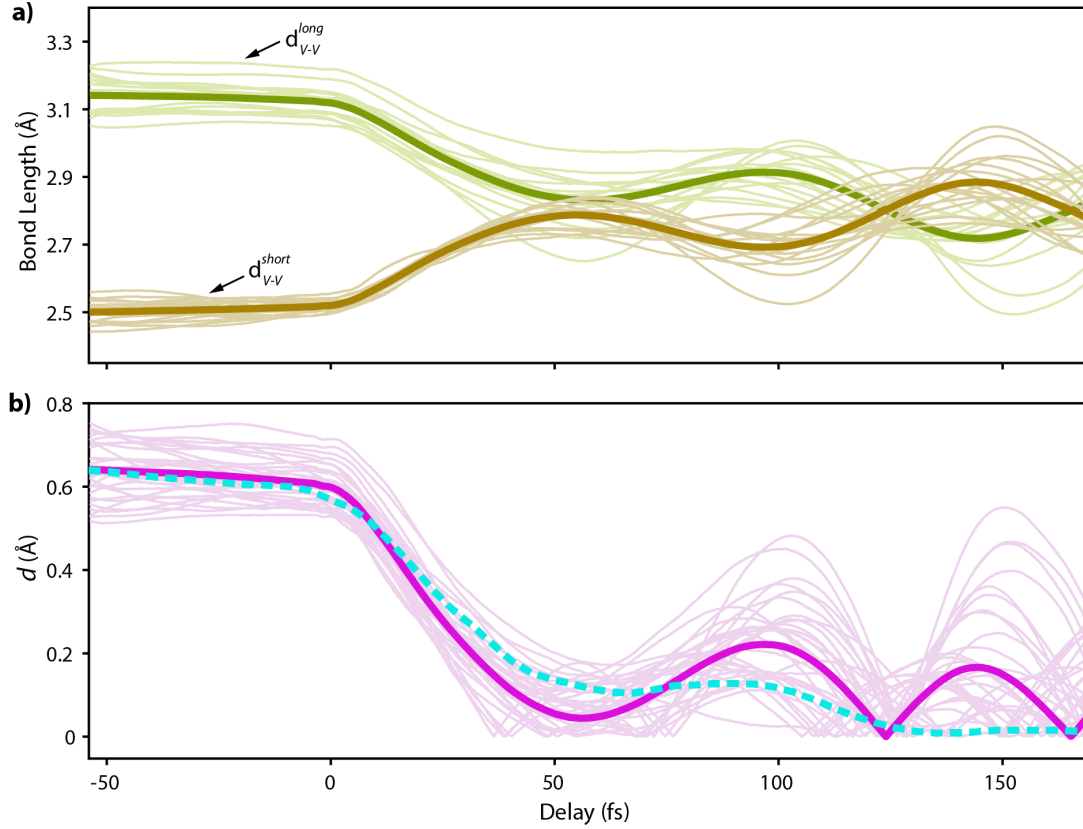


Figure 6.6: **Simulated bond length alternation dynamic.** a) Simulated dynamics of short (transparent brown curves) and long (transparent green curves) V-V bonds after photoexcitation using rt-TDDFT method. The dark brown curve and dark green curve represent the average trajectory of the short and long V-V bond dynamics respectively. b) The absolute difference (transparent magenta curves) between the long and short V-V bonds evaluated from (a). Dark magenta line is the average of the difference curves. Cyan dashed line is the experimentally retrieved bond length dynamics from Figure 6.5.b. Here time zero point is defined at the time when electronic excitation greatly increases. Adopted from ref. [139]

This section concludes that the light-induced phase transition of M1-VO₂ indeed results from the anharmonic motion of V-V dimers. Furthermore, the use of ultrashort pulses reveals that there is no instantaneous Mott-like mechanism taking place in the M1 phase as the time-scale in which the population dynamics changes is at least an order of magnitude higher than the temporal resolution of the experiment.

Chapter 7

Development of a state of the art solid-state high harmonic spectroscopy apparatus

Since the first discovery of high harmonic generation in bulk solids [23], there has been growing interest in studying the electronic structure of solids using HHG spectroscopy. Mid-infrared laser-driven HHs were used to reconstruct the momentum-dependent bandgap [173]; and optical laser-induced extreme ultraviolet HHG was used to investigate the energy dispersion of the conduction band and trace the laser-induced intraband electron dynamics [24, 60]. The orientation-dependent HH yields have been linked to the spatial arrangement of ions in the crystal lattice [62, 174]. A recent study has described HHG as the scattering of strong laser-driven quasi-free electron motion on the periodic potential of the crystal lattice [61] to reconstruct two-dimensional valence potential and electron density of crystals from the laser field strength-dependent yields in three crystal directions from the lowest to the highest measurable harmonics. This concept could be extended to picture the valence electron density of a crystal in two dimensions or even three dimensions by measuring 360° orientation-dependent high harmonic yields, provided the orientation-dependent yields of all the harmonics are nearly symmetric. Additionally, the determination of the onset field for perturbative to nonperturbative transition requires simultaneous measurement of all harmonics and an accurate measurement of the electric field responsible for the HHG. Therefore, the broad application of solid high harmonic spectroscopy requires not only harmonics in the EUV region but also simultaneous information about the lower-order harmonics, as well as precise knowledge of the driving laser field strength.

In this chapter, the development of an advanced experimental apparatus for HH generation and spectroscopy in solids is presented, which has the following properties: (i) it can measure nearly symmetric orientation-dependent HHs of crystalline solids, (ii) it possess absolute electric field calibration, and (iii) it can simultaneously measure all the harmonics for two driving lasers with different carrier energies 2.0 eV and 1.5 eV.

7.1 Overview of the experimental apparatus

Figure 7.1.a illustrates the schematic of the high harmonic generation and spectroscopy apparatus. The apparatus uses the visible (Ch_{VIS} with photon energy 2.0 eV) and near-infrared (Ch_{NIR} with photon energy 1.5 eV) channels of the light field synthesizer (LFS) [136, 19] as the laser source. The apparatus is divided into three main chambers: HHG chamber, imaging chamber and UV-EUV dual spectrometer chamber. One roughing pump (*Edward Vacuum*) and two turbomolecular pumps (*Pfeiffer Vacuum*) maintain a pressure of $\sim 10^{-6}$ mbar inside the apparatus, while an additional turbomolecular pump (*Pfeiffer Vacuum*) keeps the UV spectrometer (*Macpherson*) at a pressure of $\sim 10^{-5}$ mbar.

At first, a set of chirped mirrors in a pulse compressor negatively chirp the optical pulses from the LFS to compensate the positive chirp introduced by a laser power controlling continuously variable neutral density (ND) filter in the later stage (Section 7.2). A motorized shutter then allows the beam to pass when the camera records the high harmonic yields at the end of the setup. Next, the beam travels through the ND filter and a pick-up mirror guides the beam to a custom-built transient-grating frequency-resolved optical gating (TG FROG) [138] setup (Section 7.2) for analyzing the temporal profile of the pulse. In order to track the laser power fluctuations during experiments, a small fraction of the light is continuously monitored by a photodiode.

Owing to the geometry of the experimental setup and grating orientation, a periscope is used before the HHG chamber so that the p-polarized optical pulses exiting from the laser power controller are converted to s-polarized pulses. The beam enters the HHG chamber through a 500 μm fused silica window (mounted at Brewster's angle), which removes any remaining p-polarized components from the s-polarized pulses and guarantees high transmission of the s-polarized components. The pulses are in turn focused onto the sample inside the HHG chamber by a concave silver mirror of focal length 37.5 cm. The sample is mounted on a home-built multi-axis goniometer that can not only rotate the sample about three mutually orthogonal axes (Section 7.3) but also can displace it in two dimensions. An imaging camera has been installed at the rear side of HHG chamber for two purposes: to select the best spot on the sample surface for laser irradiation and to track the focal plane.

The diverging optical beam exiting from the sample, along with the HHs generated from it is focused again by an aluminum toroidal mirror onto a ceramic pinhole hosted on a 3D translation stage assembly. The pinhole at the focal plane of the toroidal mirror blocks the HH signal having a larger spatial diameter than that of the pinhole, if required. The optical beam can then be picked up by a glass wedge (placed behind the pinhole) and diverted outside the vacuum chamber through a glass window with the help of two additional wedges (used also to reduce the laser power). Outside the vacuum chamber, a biconvex lens focuses the optical beam onto a beam profiler, which images the sample plane at one-to-two magnification (Section 7.3). In the absence of the pickup wedge, the optical beam and the UV-EUV high harmonics enter the custom-built UV-EUV dual-spectrometer

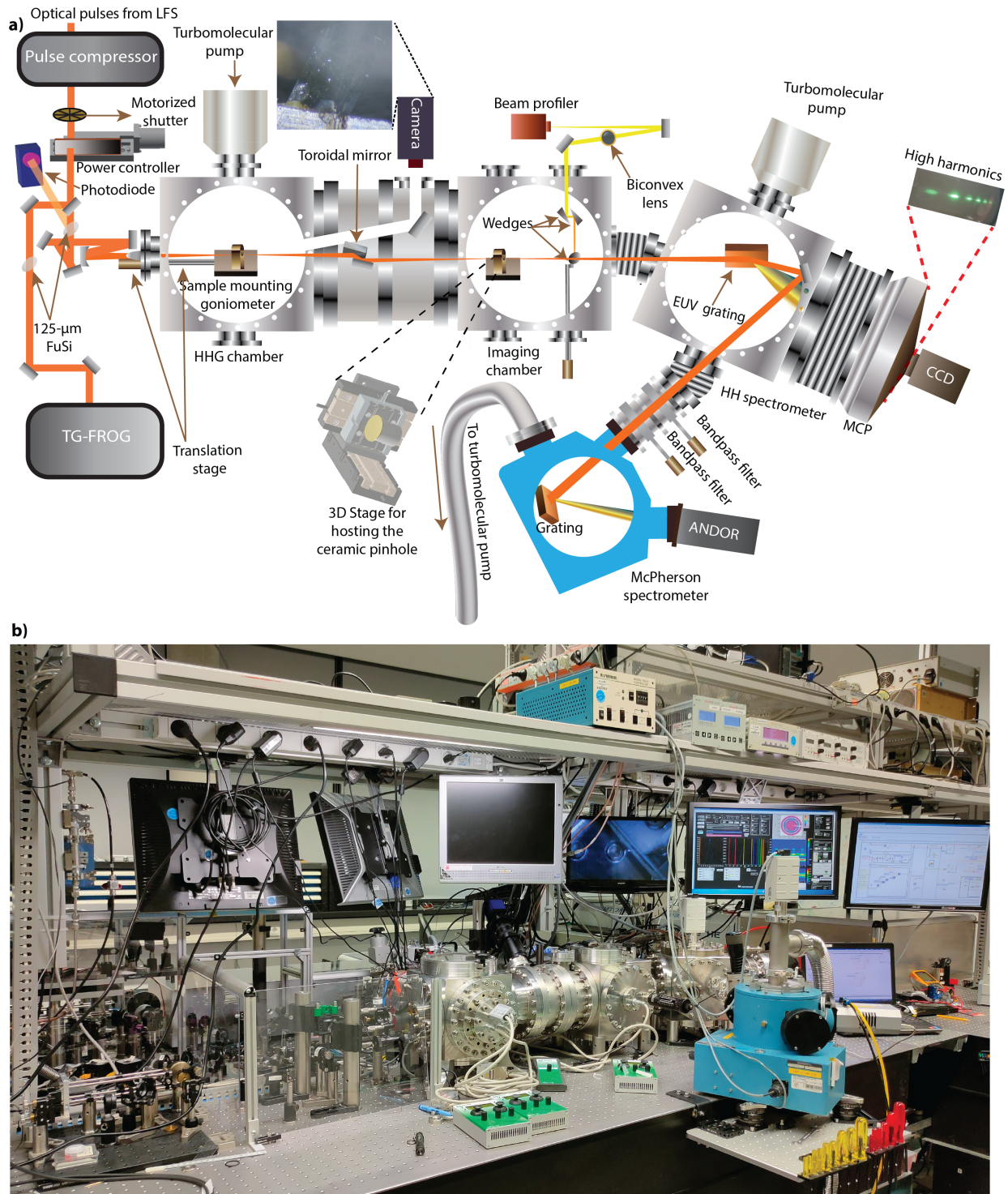


Figure 7.1: **Schematic of the HHG and spectroscopy apparatus.** a) From left, laser beam from the LFS is negatively compressed by the pulse compressor and focused onto the sample chamber for HHG. The HH signal and the driving laser proceed to the HH spectrometer, where a McPherson spectrometer together with the home-made EUV spectrometer records all the harmonics. b) Photograph of the developed HHG apparatus.

(Section 7.4), where a Macpherson spectrometer records a part of the spectrum (3^{rd} harmonic), and a 3-stage microchannel plate (MCP) detector-based spectrometer records the higher-order EUV harmonics.

7.2 Laser power control and pulse compression

Efficient high harmonic generation in crystalline solids requires extremely thin samples of thickness few micrometers to hundreds of nanometers to minimize the dispersion of optical driving pulse and laser-induced heating. However, due to the challenges encountered during sample preparation, such thin samples are often imperfectly polished, resulting in surface roughness and scratches. As a result, the laser-driven HHs becomes sensitive to the position of the focused laser spot on the sample surface. By utilizing a variable ND filter in transmission geometry as a laser power controller or laser electric field amplitude controller, the laser spot can be stabilized on the sample surface while maintaining a fixed focal spot size during laser intensity scans, a significant advantage over a laser power controller like a spatial iris aperture [175, 176]. The laser spot size remain stable because the laser propagation direction is not affected in transmission geometry. One problem with the ND filter is that, when short pulses pass through it, the glass substrate introduces positive dispersion (chirp).

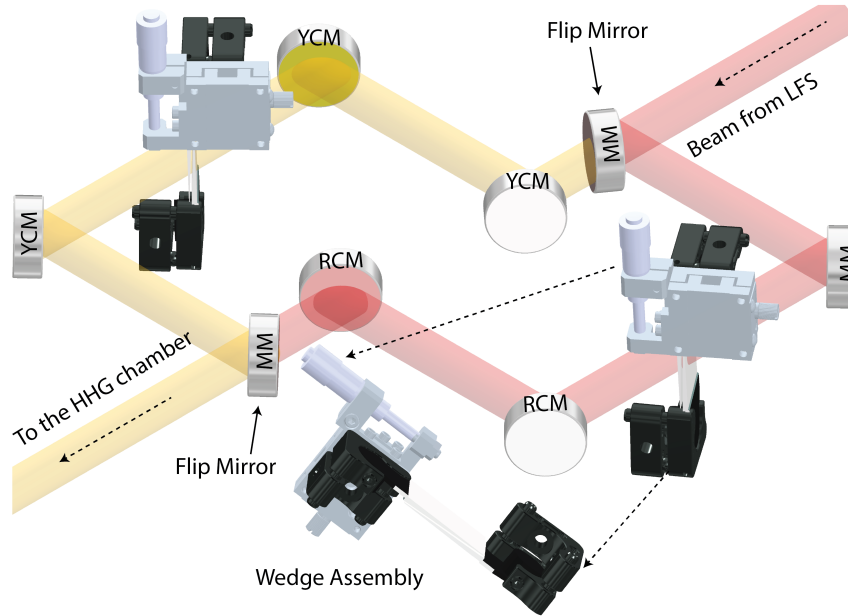


Figure 7.2: **Post-pulse compression.** Schematic of visible (yellow) and NIR (red) pulse compressor. Pulses from LFS are compressed by chirped mirrors and a pair of wedges in individual channel. YCM = Yellow chirped mirror, RCM = Red chirped mirror, MM = Metallic mirror.

In the current apparatus, a pulse compressor is designed to negatively chirp the pulses before they pass through the ND filter. It (Figure 7.2) has two paths: visible

($Path_{VIS}$: 500 nm - 700 nm), and NIR ($Path_{NIR}$: 700 nm - 1100 nm). Each path has four mirrors (placed at 45°) and one pair of thin rectangular wedges (placed at Brewster's angle). $Path_{NIR}$ has two chirped mirrors, and $Path_{VIS}$ has three chirped mirrors, each of the chirp mirror can compensate approximately -70 fs^2 chirp. After being compressed by the chirped mirrors, the dispersion of the constituent pulses are fine-tuned by the rectangular wedges with the help of a micrometer translation stage. Depending on the experiment, pulses from Ch_{VIS} or Ch_{NIR} are selected from the LFS, and a flip mirror (in Figure 7.2) then sends the pulses to the corresponding path of the post-pulse compressor. In the apparatus, a ~ 2.2 mm thick rectangular (25 mm x 10 mm) continuously variable ND filter (power controller) is used to control the power of the transmitted laser. A motorized translation stage, on which the filter is mounted, varies the position of the ND filter so that the transmitted beam power can change accordingly. To mitigate the spatial gradient effect produced by the ND filter, the diameter of the laser beam is reduced to sufficiently small size (3.5 mm) in comparison with the gradient of the filter, with the help of an iris.

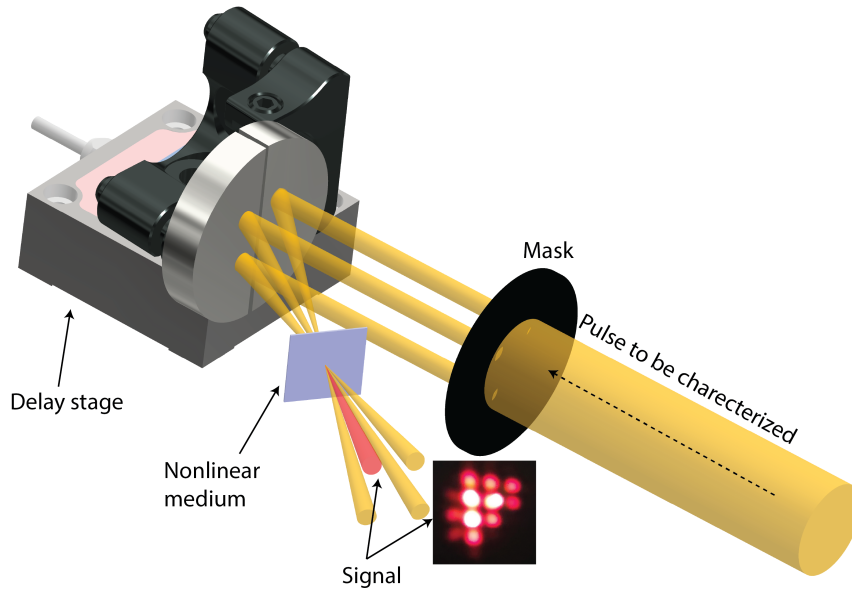


Figure 7.3: **Schematic of the TG-FROG setup.** Pulses to be characterized are split into three replicas and then focused onto a nonlinear medium for generating a nonlinear signal (red beam).

Figure 7.3 shows the schematic of the TG-FROG [138] setup, developed and used during this project for the temporal characterization of pulses. The TG-FROG setup comprises of spatial mask, two 10 cm focal length D-shaped mirrors, a piezo-controlled translation stage and an optical spectrometer. The spatial mask splits the incoming beam into three replicas. Two of them are focused by one of the D-shaped mirrors onto a nonlinear medium (fused silica) to create a refractive index grating, while the third beam reflected by the second D-mirror is diffracted by this grating. The second D-mirror is mounted on the piezo-controlled translation stage to delay the two mirror with nanometer precision. The resulting nonlinear signal (red beam) is spatially separated and directed

into the spectrometer for spectral analysis. Figures 7.4.a and b present the FROG traces of pulses from visible and near-infrared paths (measured after the ND filter) when the pulses are not compressed. Figures 7.4.c and d show the corresponding results after the dispersion compensation. The retrieved temporal intensity (blue) and temporal phase (red) of the pulses from $Path_{VIS}$ and $Path_{NIR}$ are shown in Figures 7.4.e and f respectively, where the pulse durations (FWHM) are $\tau \approx 6.9$ fs and $\tau \approx 8.6$ fs.

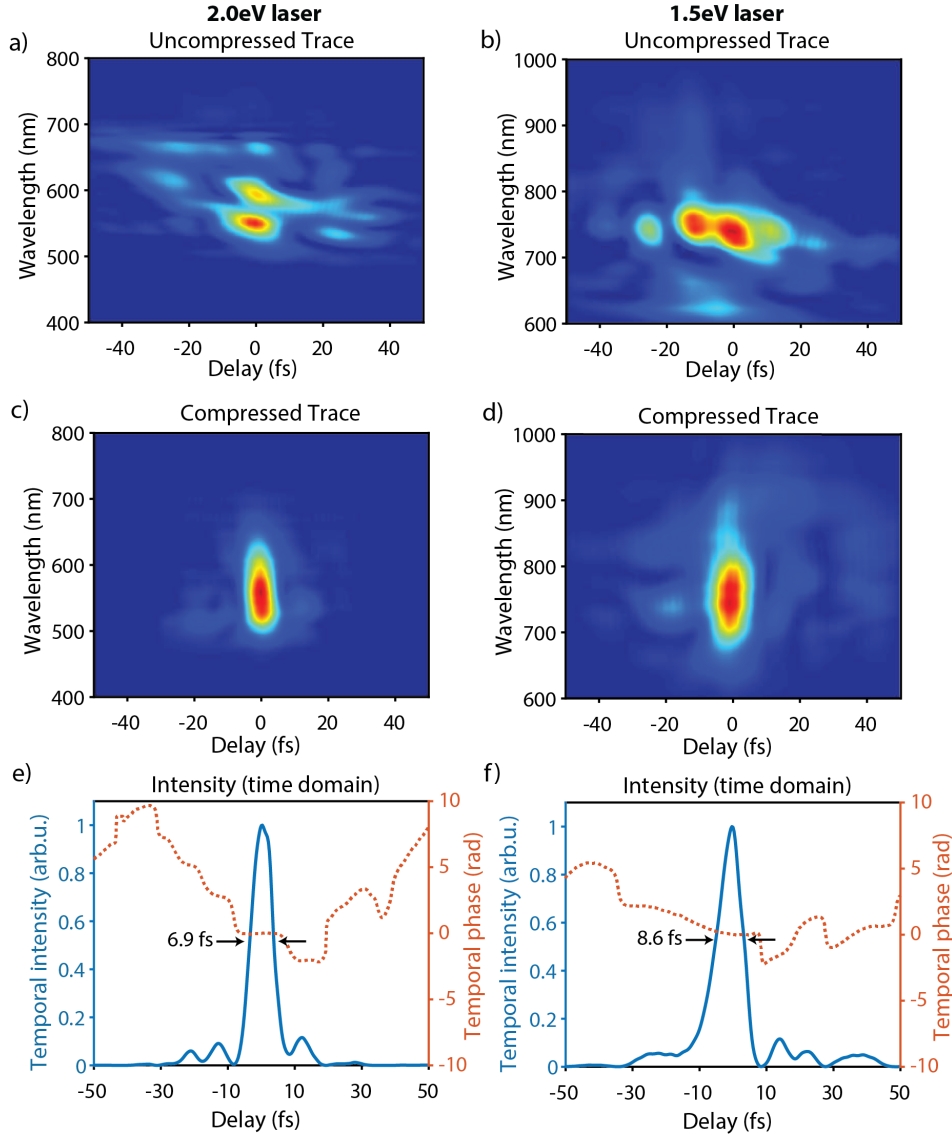


Figure 7.4: **Few-cycle pulse characterization with TG-FROG setup** (left $Path_{VIS}$, right $Path_{NIR}$). a), b) Measured TG-FROG traces of the uncompressed pulses passing through the laser power controller. c), d) Recorded traces of the compressed pulses. e), f) Reconstructed temporal intensity profile (blue) and its corresponding temporal phase (red). The retrieved pulses have a duration (FWHM) of $\tau_{VIS} \approx 6.9$ fs and $\tau_{NIR} \approx 8.6$ fs.

7.3 Home-built multi-axis goniometer

As discussed in the previous section, the quality (roughness and scratches) of thin crystal influences the HH yields. Therefore, if the focused laser position moves on the sample surface during orientation (rotation) dependent HHG measurement, then instead of only the symmetry of the crystal the HHs will also experience the effect of roughness of the sample. Generally, this sample surface roughness can cause asymmetric HH yields in an orientation-dependent HH measurement. One of the techniques to perform an orientation-dependent scan is to rotate the crystal relative to the laser polarization. To do so, the rotation axis of the sample and the Poynting vector of the laser beam must coincide. Otherwise, the focused beam spot moves on the sample surface. To correct for this movement, a crosshair is introduced at the focus (on the sample holder) to provide a reference to align the laser with the rotation axis of the sample. This section will first discuss about the goniometer and the function of its constituent parts, and then describe how the imaging of a crosshair mounted on the goniometer stage allows the focused beam position to remain static during rotational scans.

For the rotation and translation of the solid sample, an advanced multi-axis goniometer (Figure 7.5.b) has been designed, which integrates three rotational and two translation piezo-driven stages. Any commercial X-ray goniometer can not be used because the sample has to be displaced in case of damage or bad spot without affecting its orientation with respect to the laser propagation axis. To achieve this, the goniometer is designed in a way that two translation stages are mounted orthogonally on the rotation stages, and the sample holder (Figure 7.5.c) is affixed on the topmost translation stage. The rotational stage 1 rotates the assembly of two rotational and two translation stages with respect to the laser polarization. A heavy weight (copper) counterbalances the torque generated during this rotation. The remaining rotational stages (stage 2 and stage 3) can rotate the sample in the other two dimensions as well as align the crystal surface (plane) perpendicular to the laser propagation direction. This adjustment compensates for any tilting in the sample surface that may occur when mounting on the holder. Since the translation stages have 12 mm travel range, they simultaneously allow the replacement of more than six samples in the XY plane with micrometer precision. The overall goniometer design enables the transition between samples without any adjustments to the rotational axis. A linear translation stage moves the whole goniometer along the laser propagation axis to find laser focal plane by maximizing the high harmonic yield. An imaging camera magnifies the sample by ~ 50 times and helps to select a polished and a scratch-free spot for efficient HHG.

The layout of the one-to-two imaging system, which magnifies the focused beam profile on the sample plane is presented in Figure 7.5.a. The basic components of the imaging system are one toroidal mirror, three glass wedges, one biconvex lens, and one *DATARAY* beam profiling camera (4.6 μm resolution). The imaging system functions in the following way: The toroidal mirror magnifies the focused beam profile of the sample plane by a factor of two, and the biconvex lens placed outside the vacuum chamber images

the focused beam profile of the toroidal mirror with one-to-one magnification. The inset in Figure 7.5.a shows the beam profile at the sample plane which is a Gaussian profile with $\sim 75 \mu\text{m}$ FWHM.

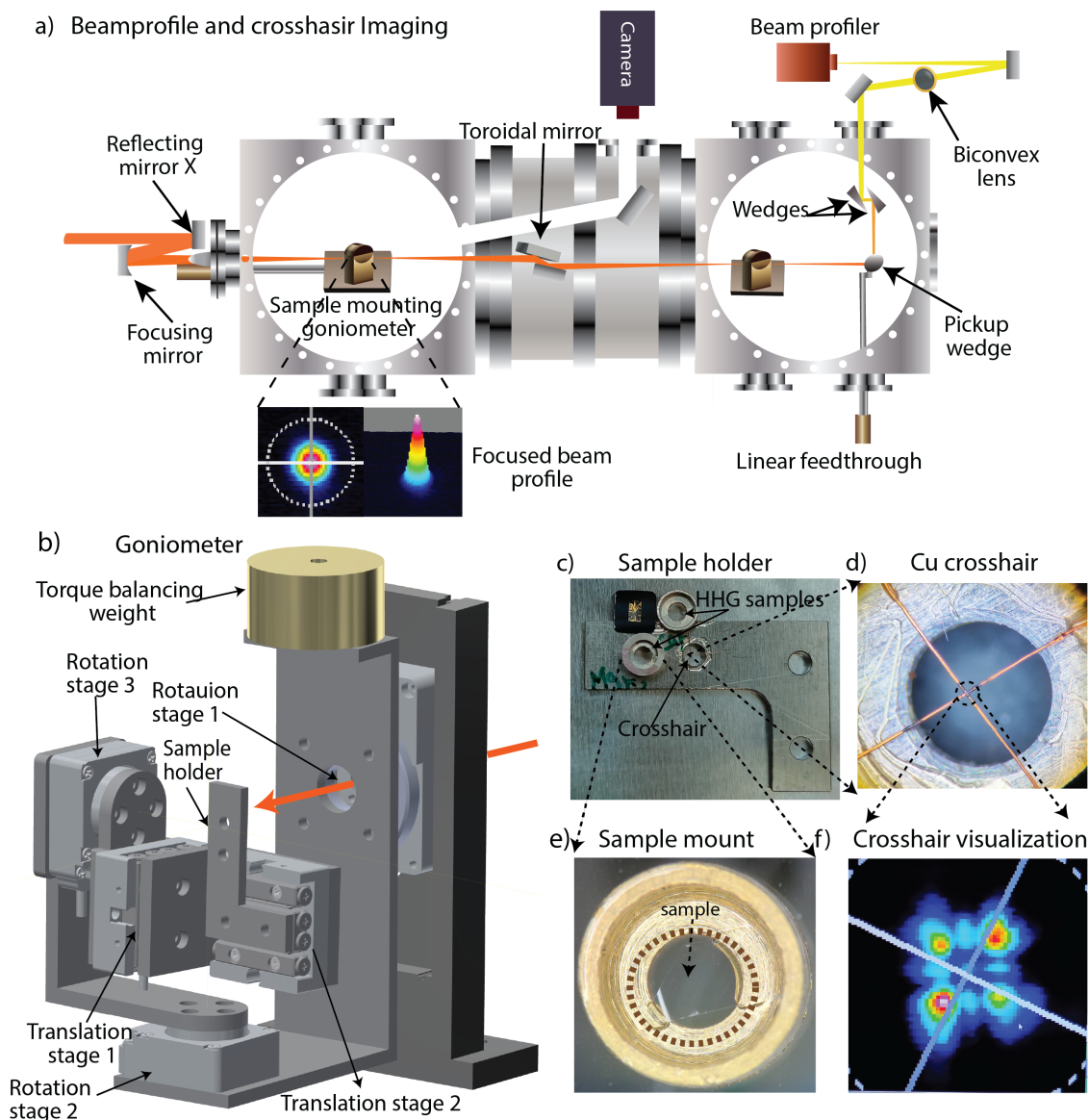


Figure 7.5: **Home-built multi-axis goniometer and crosshair imaging** a) Layout of the one-to-two imaging system used for aligning the rotation axis of the crystal sample. b) Three-axis rotation and XY-translation goniometer with sample holder. c) Photograph of the sample holder with three mounted samples and a crosshair. d), e) Photograph of the Cu crosshair and HHG sample respectively. f) Imaged crosshair with the beam-profiler-based imaging system.

Each custom designed sample holder (Figure 7.5.c) contains a $40 \mu\text{m}$ thick

crosshair that has been suspended on to the circular aperture (Figure 7.5.d). The beam profiler images the laser-illuminated crosshair (Figure 7.5.f) in order to track the relative changes in the sample rotation axis with respect to the laser propagation axis. If these two axes do not overlap, then the mounts of the reflecting mirror X and the focusing mirror (Figure 7.5.a) are fine-tuned to coincide the laser beam with the sample rotation axis. This step is repeated until the sample rotation axis and the laser propagation axis become coaxial. After the alignment of the beam with respect to the rotational axis, the sample (Figure 7.5.e) is translated to the beam path with the translation stages.

7.4 Dual spectrometer design

The EUV spectrometer uses a Hitachi aberration-corrected concave grating. The spectrometer chamber is positioned at an angle of 72.5° relative to the HHG chamber so that the optical beam together with the high harmonics impinge on the grating surface at a grazing angle of 5° . An adjustable vacuum expansion bellow positions a 3-stage microchannel plate (MCP) detector at a distance of 17 cm from the grating center. This arrangement enables the utilization of the full MCP surface for high harmonic detection [177, 178] for both driving laser pulses (energy 2 eV and 1.5 eV), as shown in Figure 7.6. Because of the large MCP surface (6.8 cm), the EUV spectrometer can resolve well defined HH peaks with energy spacing of 3.0 eV or 4.0 eV in the energy range of 7 eV to 35 eV. A 200 μm thick magnesium fluoride (MgF_2) window (Figure 7.6) is placed before the MCP by a manual translation stage to absorb the second-order diffracted HHs. Since the MgF_2 window absorbs signals with energies greater than 10 eV, the manual translation stage adjusts the MgF_2 window position within the diffracted beam path to prevent absorption of first order harmonics with energies higher than 10 eV. One CCD camera from Point Grey records the HH signal detected by the MCP.

The MCP detector has poor sensitivity for photon energies below 7 eV. As the 3rd harmonic of both the driving lasers are below 7 eV, a separate commercial McPherson spectrometer is used for capturing the harmonic in this UV energy range. The zeroth order beam from the Hitachi grating is picked up by a bare aluminum mirror and is directed to the McPherson spectrometer (Figure 7.1.a). Vacuum compatible bandpass filters are placed at the entrance of the McPherson spectrometer to filter out the optical beam from entering the spectrometer. With the help of vacuum valves, it is easy to insert or remove the bandpass filters whenever required. The central energies and full width at half maximum (FWHM) of the bandpass filters are: 4.8 eV with 0.5 eV FWHM and 6.4 eV with 0.8 eV FWHM. The detector of the McPherson spectrometer consists of a fiber-coupled multi-channel plate/phosphor screen and a camera (Andor) cooled to -40°C in order to reduce its dark current and enhance the signal-to-noise ratio. This UV spectrometer can measure the third harmonics (central energies of 4.5 eV and 6.0 eV) of both the driving lasers with high sensitivity. Therefore, the combination of the UV and EUV spectrometers can measure all the harmonics (lowest to the highest order) concurrently.

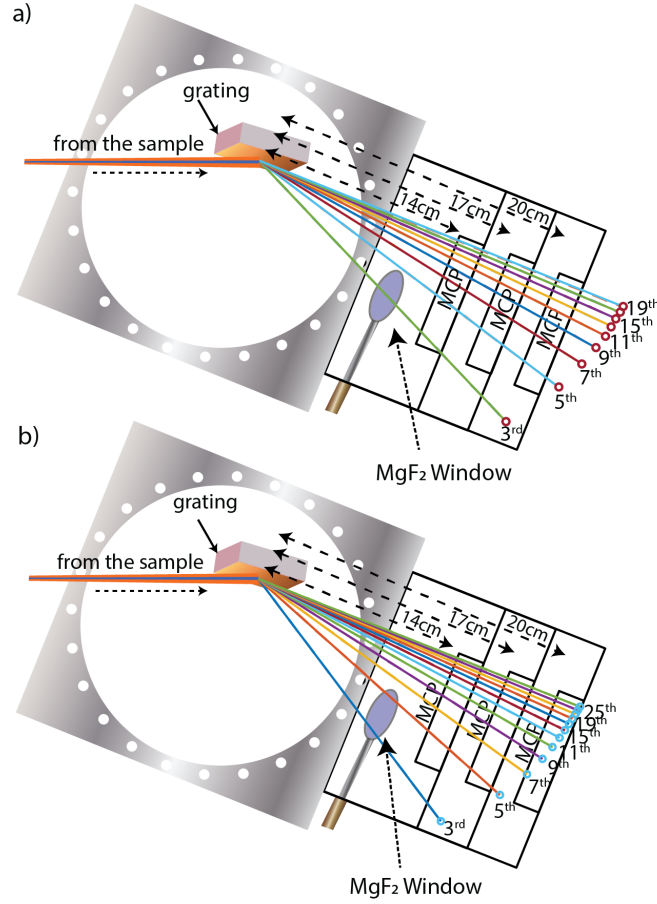


Figure 7.6: **VUV spectrometer design.** a), b) Design of the VUV spectrometer for capturing HHs of visible (a) and NIR (b) pulses respectively. The optimal arrangement for two channels is achieved when the MCP is positioned at a distance of 17 cm from the grating. Harmonics order are denoted by numbers such as 3rd, 5th, 7th and so on.

7.5 Data acquisition

A complete electric field- or orientation-dependent HH measurements require extended acquisition times, due to both stage movement (which controls the change in electric field amplitude or crystal orientation) and integration time at each step of the measurement. During such long exposures, the laser-induced damage restrict the access of higher-order harmonics for the complete scan. The laser-induced damage threshold of a solid drops with the increase in the number of laser shots (or exposure time) on the solid material [179, 180, 181, 182, 183]. Therefore, minimizing exposure times improves access to higher-order harmonics. This solution is executed in the following way: a motorized shutter is placed before the HHG chamber, which allows the laser beam to pass through the sample only when the dual spectrometer cameras record the HH yields. Thus, although the total

EF- or orientation-dependent scan takes a long time (few minutes), the solid is irradiated only for the short time (few seconds) of the HH measurements. A home-made LabVIEW-based software interfaces the translation stage of the laser power controller, rotational and translation stages of the goniometer, CCD cameras of the dual spectrometer, photodiode (that measures laser stability) and the mechanical shutter. This software controls the components interfaced with it to acquire HH spectra for different crystal orientations and optical field strengths.

7.6 Electric field calibration

Due to the compactness of the HHG apparatus and the presence of multi-axis goniometer, measurement of the absolute electric field of the laser pulse is not possible. This leads to the utilization of the attosecond beamline [137] in our lab for the calibration of the absolute electric field (EF) of the pulse in the current apparatus. For this calibration, EUV gas attosecond streaking [32, 56] first measures the exact peak EF amplitude of the laser pulse, and HHs in solid are then generated by replacing the streaking gas nozzle with a 150 nm thin fused silica sample. A pair of rhodium mirrors guide the HHs into the HH spectrometer for measurement, as illustrated in Figure 7.7a. Figure 7.7.b shows the EF-dependent HHs of fused silica measured in the attosecond beamline. An identical fused silica sample is attached to the sample holder (Figure 7.5.c) inside the HHG chamber of the current HHG apparatus. First, a similar laser power-dependent high harmonic yields are measured from the fused silica in this apparatus, then the electric field is calibrated by comparing the onset of the highest harmonic measured in this current setup with that of the attosecond beamline's electric field-dependent HH yields. Figure 7.7.b and 7.7.c illustrate this comparison (after the calibration of the electric field) between electric field-dependent HH yields generated by NIR laser pulses in the two setups. After EF calibration the fused silica is replaced with a new crystal sample for high harmonic generation using goniometer translation stage.

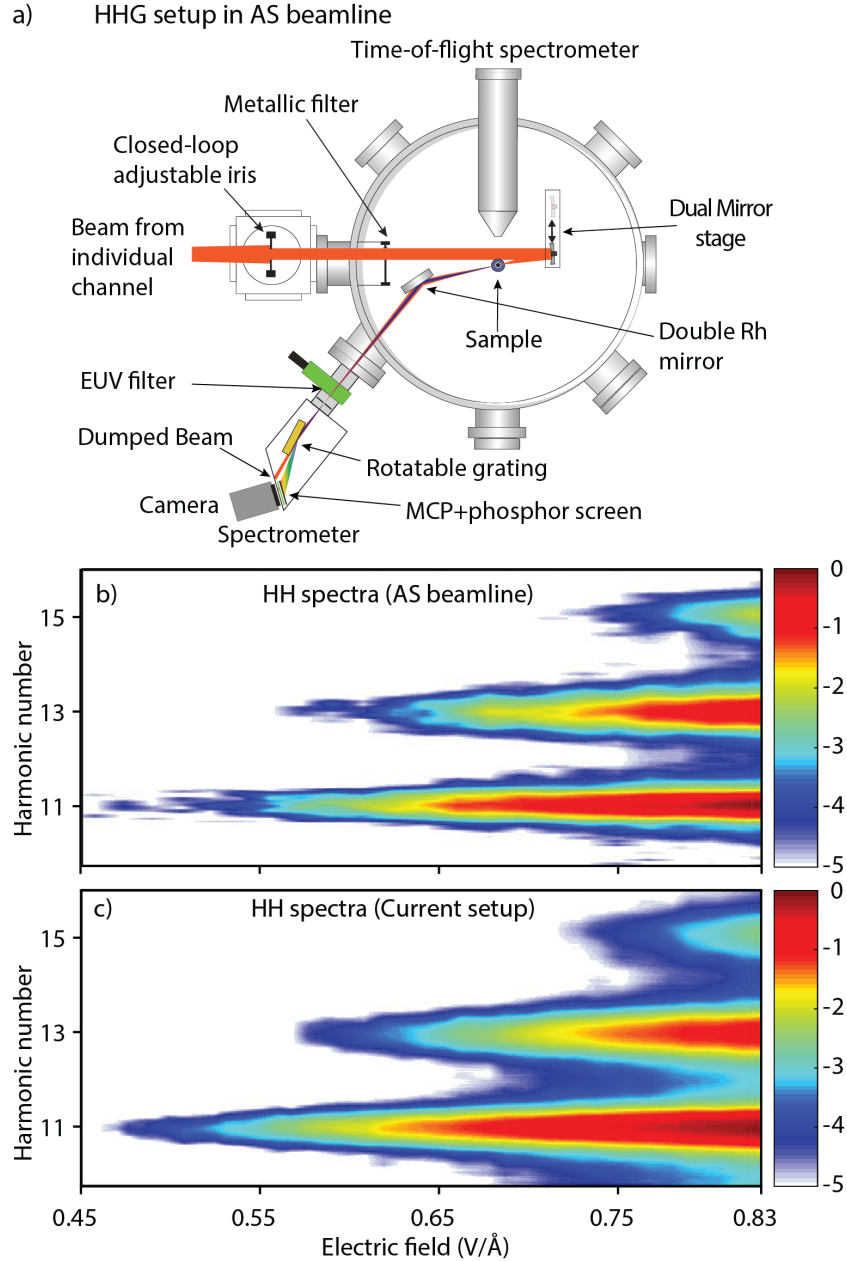


Figure 7.7: **Absolute field calibration using AS beamline.** a) Schematic of the AS beamline used for electric field-dependent HH generation in fused silica sample. b) Recorded HH yield of NIR pulses with its corresponding electric field measured from EUV AS streaking. c) Calibrated absolute EF dependent HHs from the new HHG apparatus.

7.7 Results

7.7.1 Broadband high harmonic yields

As a first experimental measurement, a free-standing, amorphous, 150 nm thick fused silica sample is shone by linearly polarized few-cycle visible laser pulses of carrier photon energy 2.0 eV. Figure 7.8.a shows the harmonic spectra in linear scale for a driving field strength of 0.83 V/Å, where the HHs span from 3rd to 15th order. All the HHs are measured simultaneously by the home-made spectrometer. A field strength-dependent measurement in Figure 7.8.b shows that the highest-order harmonic varies from 7th to 15th order when the field strength increases from 0.48 V/Å to 0.83 V/Å.

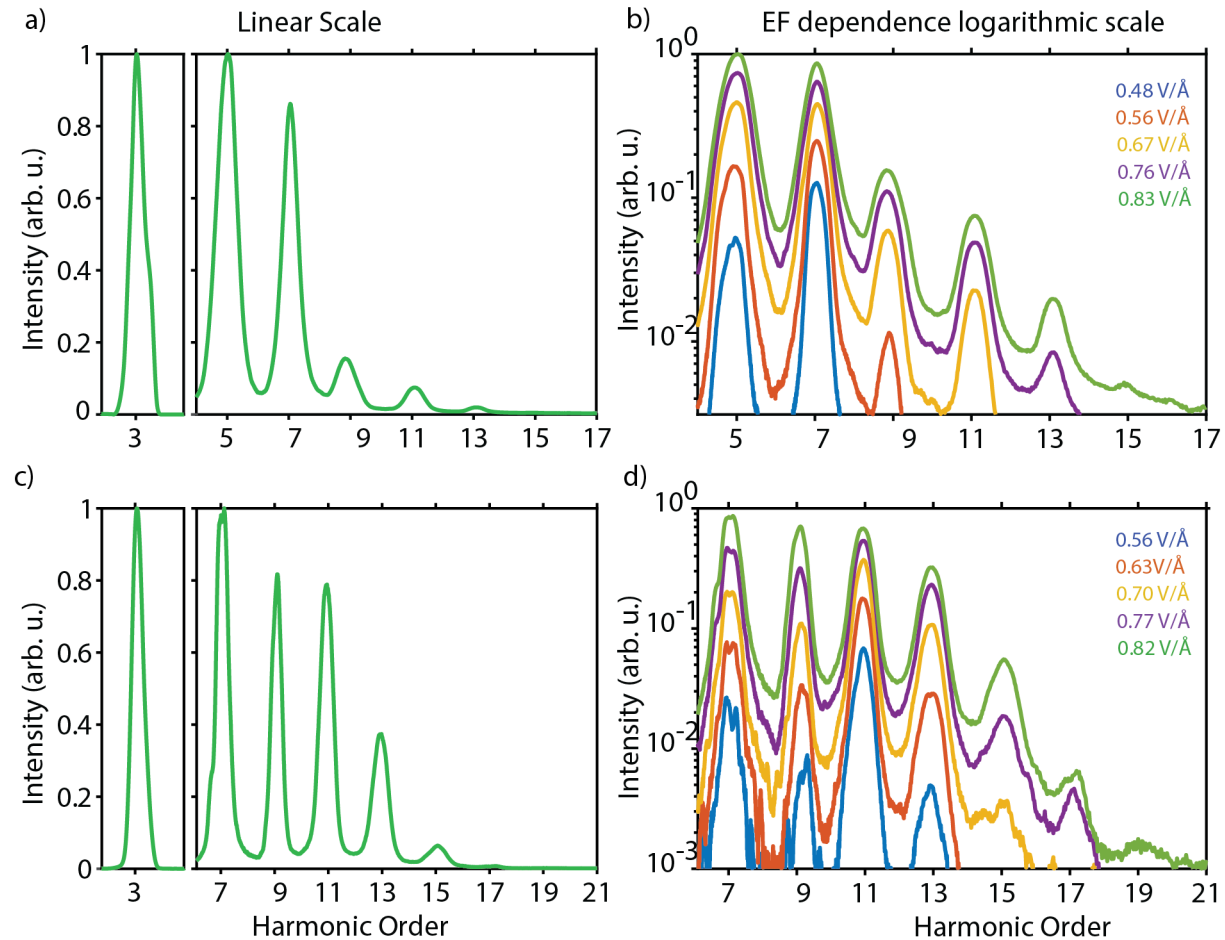


Figure 7.8: **Harmonic spectra in fused silica.** a), c) visible (a) and NIR (c) laser driven harmonics measured from 150 nm thick fused silica. b), d) Electric field-dependent high harmonics in logarithmic scale for the visible and NIR laser pulses respectively. The legend shows the driving EF strength of the corresponding measurements with the same color code.

Next, the HHs from the same fused silica sample are measured using NIR laser pulses. The harmonic spectrum as presented in Figure 7.8.c corresponds to a field strength of 0.82 V/Å. Figure 7.8.d shows higher-order harmonics up to 19th order appear with the increase of driving laser field strength.

7.7.2 Orientation-dependent high harmonic yields

In order to check the capability of the apparatus to record orientation-dependent HHs in a single crystal, a c-cut magnesium oxide (MgO) crystal is illuminated with few-cycle pulses of carrier photon energy 2.0 eV. Laser polarization- or crystal orientation-dependent HHs are generated by rotating the crystal axis with respect to the linearly polarized laser. Figure 7.9 shows the recorded harmonic yields for a complete 360° rotation of the crystal with 5° step size.

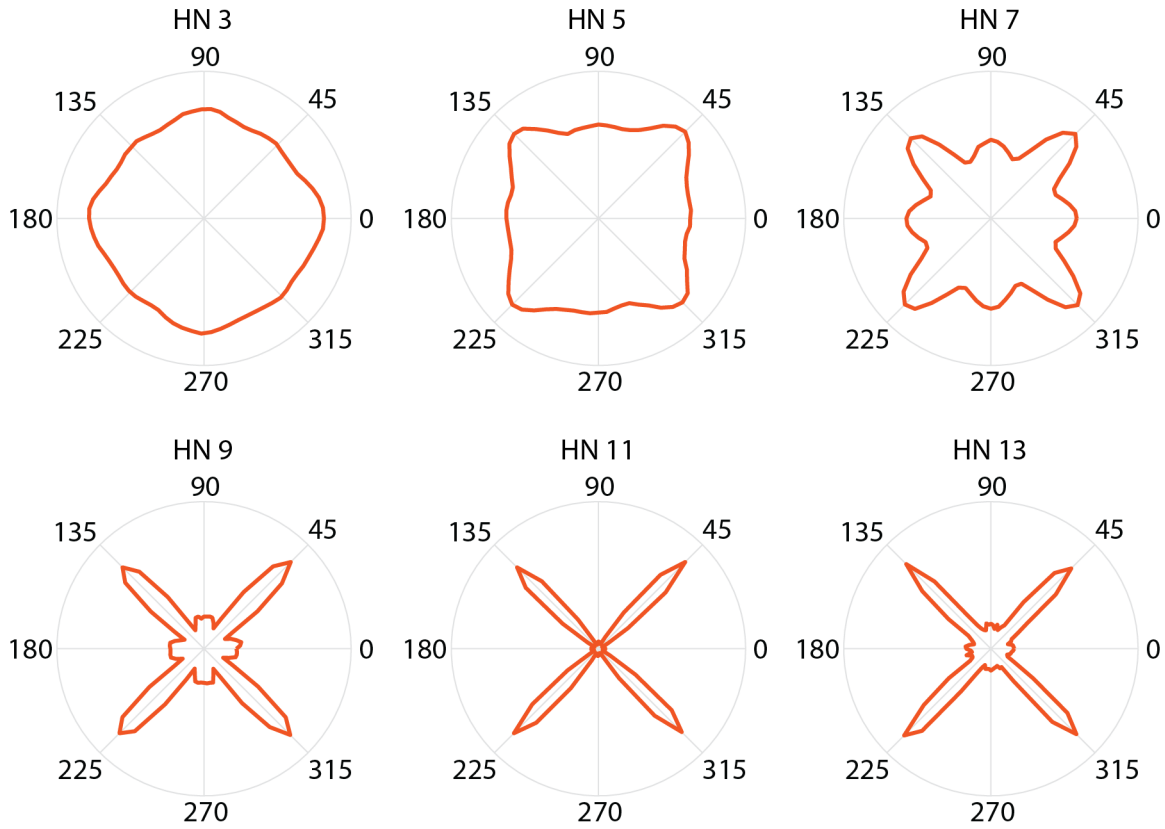


Figure 7.9: **Crystal orientation-dependent HH yields of MgO crystal.** Each panel depicts the intensity yield of the emitted odd harmonics (3rd to 13th order) as a function of crystal direction for driving pulses with 2 eV photon energy. The emitted harmonics' intensity is represented by the radial direction, whereas the azimuthal direction indicates the angle of rotation for the crystal. HN denotes Harmonic Number.

All the emitted harmonics intensities show a 90° periodicity of the MgO crystal

structure. One can evaluate the capability of the experimental setup in capturing the symmetric HH yields by observing the excellent symmetric harmonic yields extended up to 26 eV i.e., from 3rd harmonic to 13th harmonic.

Examining the orientation-dependent high harmonic yields across varying field strengths would further validate the apparatus's ability to record symmetric harmonic yields with different amplitudes. Figure 7.10 presents the emitted HH yields from MgO as a function of the crystal angle for five driving field strengths (0.40, 0.47, 0.54, 0.60 and 0.67 V/Å).

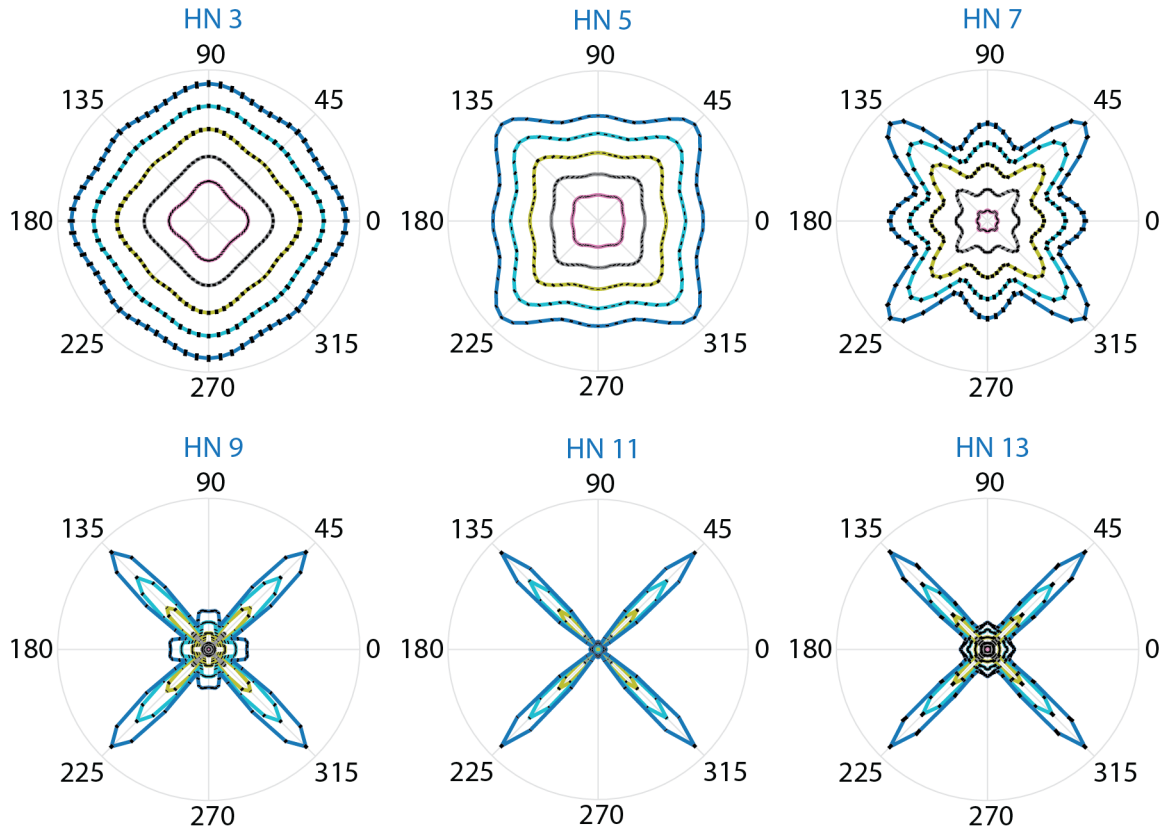


Figure 7.10: **Electric field dependent HH yields in MgO as a function of crystal rotation angle.** The high harmonics are captured for five representative field strengths of 0.40, 0.47, 0.54, 0.60 and 0.67 V/Å. The solid lines are HH yields and the black lines are errors. The yield of each harmonic is normalized with its maximum field amplitude yield.

The angular HH plot for a system with n -fold symmetry shows the mean of n symmetric segments from the full 360° scan, each segment displacing an angle of $360^\circ/n$ at the radial center. The black error bars in Figure 7.10 are the cumulative standard errors arising from the n symmetric segments and from the number of measurements. This error is negligible with respect to the level of HH yields at all driving field strengths of Figure 7.10.

Chapter 8

Extreme nonlinearity in bulk solids

One of the notable features of high harmonic generation is the transition from perturbative to nonperturbative regime with the increase in laser field strength [65]. Perturbative to nonperturbative transition (PNT) shifts the physics of harmonic generation from multiphoton absorption to tunnel ionization [184]. Although the electric field of the driving laser pulse in the perturbative region is strong enough to affect the electronic structure of the crystal and induce a nonlinear response, it remains weak compared to the internal binding forces on electrons within the lattice. The nonlinear phenomena that arise from this interaction can be explained within the framework of perturbation theory [20]. The harmonics generated in the perturbative regime follow a predictable scaling (E^{2N}) of the harmonic (N) yield with the laser field strength (E) [71, 185, 186]. This picture however breaks down when the field strength rises — the energy delivered by the field becomes sufficient to drive electrons across the bandgap, and the system moves into the nonperturbative regime. Generally, the nonperturbative regime is characterized by the emergence of high-order harmonics and breakdown of the perturbative scaling [64, 23].

The onset of extreme nonlinearity or extreme photonics of a system is marked by the transition from perturbative to nonperturbative regime [70]. Thus, deviation from the multiphoton or perturbative nonlinearity indicates the onset of extreme or nonperturbative nonlinear optics. In HHG, it is identified when the N^{th} -order harmonic yield stops following the I^N scaling with laser intensity (I) [65, 71, 186], known as power law. The onset of strong-field effects in gaseous medium is usually determined by the Keldysh parameter γ of the gas [73]. Conversely, the PNT for solids has not been experimentally validated for a wide range of materials using any parameter.

8.1 Nonlinearity of experimental harmonic yields

In this work high harmonics have been generated in five bulk crystalline materials, diamond (C), magnesium oxide (MgO), magnesium fluoride (MgF₂), calcium fluoride (CaF₂), and lithium fluoride (LiF), with the aim to study the onset of extreme nonlinearity in bulk

solids. Figure 8.1 illustrates the structure of the crystalline materials. Two experimental aspects are important in identifying this onset using the nonlinearity of the harmonic yields: first is the correct knowledge of the electric field amplitude and the second is excellent statistics of the measured HH yields. Excellent statistics minimize the errors in laser field-dependent measurements of HH yields ensuring an accurate determination of the deviation of the harmonic yield nonlinearity with the power law. The experimental measurements presented in this chapter fulfill both requirements: electric field calibration with EUV attosecond streaking provides the correct knowledge of the absolute field amplitude, while the state of the art experimental setup (Chapter 7) allows high fidelity measurements of the harmonic yields.

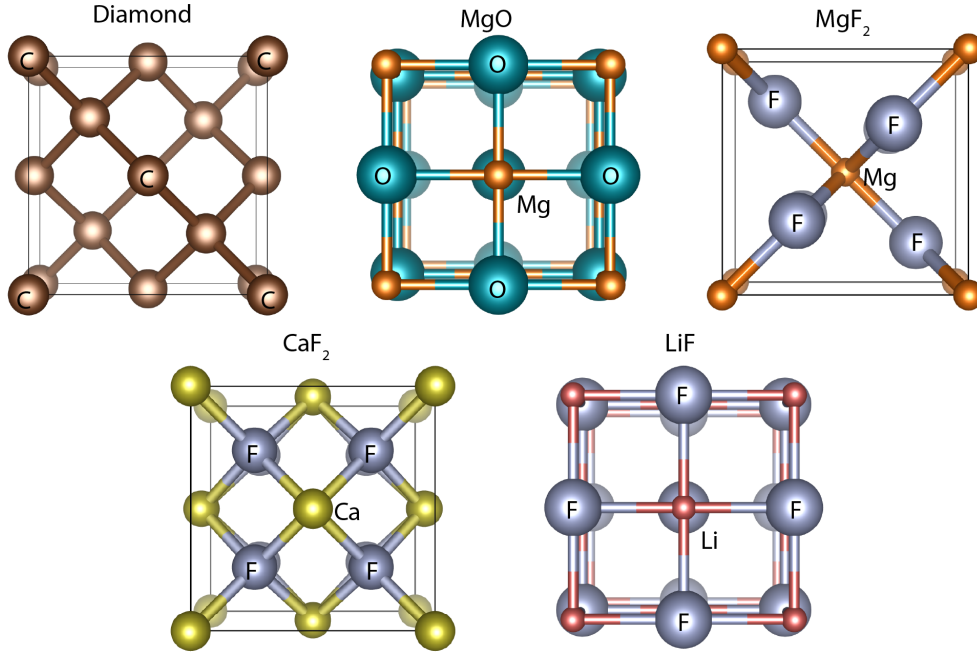


Figure 8.1: Unit cells of the five crystals used for high harmonic generation.

8.2 Nonlinearity of the harmonic yields of MgF_2 crystal

As a first material of the study, a c-cut MgF_2 crystal has been chosen. The crystal is illuminated along the $[100]$ direction with linearly polarized, few-cycle laser pulses of photon energy 2 eV. Figure 8.2.a illustrates the spectrum of the measured harmonics from the two spectrometers. The harmonics span from the 3rd to the 11th order. The peak laser field amplitude is varied from 0.3 V/Å to 0.8 V/Å to record the driving field strength-dependent 3rd harmonic yield, which is presented in Figure 8.2.b. The yield increases

smoothly with the increase in driving field amplitude. The maximum laser field strength in this measurements is kept below the damage threshold of the material, which is identified prior to the laser field strength-dependent experiment.

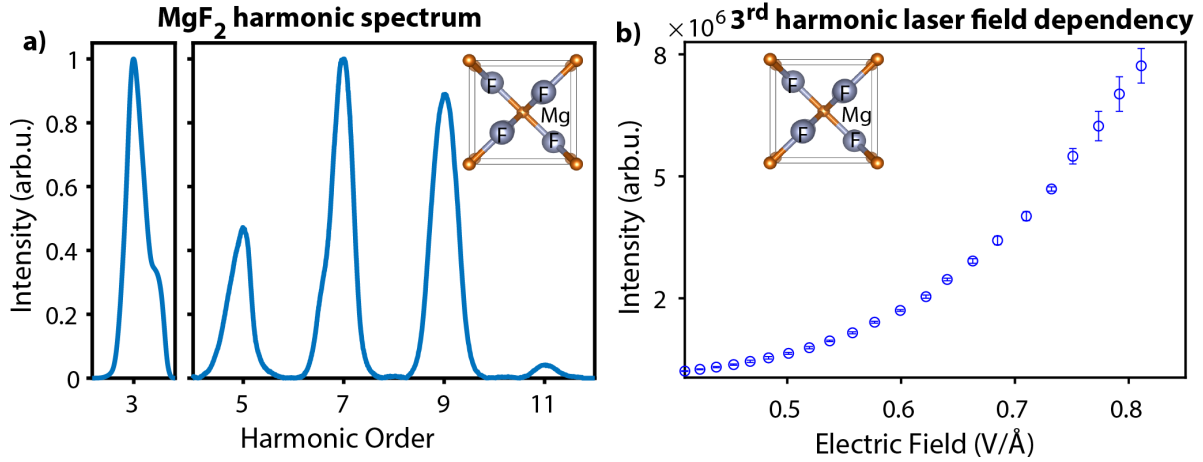


Figure 8.2: **HH spectrum in MgF_2 .** a) Measured HH spectra of MgF_2 extended up to 11th order. b) Intensity yields (blue dots with error bars) of the emitted 3rd harmonics versus driving field strength.

Once the driving field-dependent harmonic yields are measured, their nonlinearities with the driving field strength are evaluated. Figure 8.3.a, b, c, d depict the nonlinearity of 3rd, 7th, 9th and 11th order harmonics respectively. In this study, the nonlinearity of the lowest-order harmonic yield has been analyzed among all measured harmonics to identify the onset of the extreme nonlinear regime. The reasons for using the lowest-order harmonic over higher-order harmonics are following: (i) lowest-order harmonic is generated at a lower field strength than the higher-order harmonics, and a transition from perturbative to nonperturbative regime is more clearly observable in the lowest-order harmonic. On the other hand, the nature of higher-order harmonics can be nonperturbative at any field measured. (ii) The lowest-order harmonic yield is generally perturbative in nature. Therefore a transition of the lowest-order harmonic yield from perturbative to nonperturbative nonlinearity suggests the PNT for higher-order harmonics too (or they are already nonperturbative at that field).

To illustrate the nonlinearity of the 3rd harmonic yield, the field strength-dependent 3rd harmonic yield has been presented on logarithmic scale (blue circles) together with the 3rd power (red line) of the laser intensity (I) of the corresponding field strength (Figure 8.3.a). While the nonlinearity of 3rd harmonic follows power law at lower field strengths, it deviates from the power law when the field amplitude exceeds a specific value. Due to the small experimental error it is possible to define the onset field at a point (marked by the dashed magenta lines in Figure 8.3.a) where the nonlinearity of the harmonic yield deviates from the power law within experimental error. Under the above consideration,

the amplitude of the onset fields in MgF_2 is determined to be $0.47 \text{ V/\AA}$.

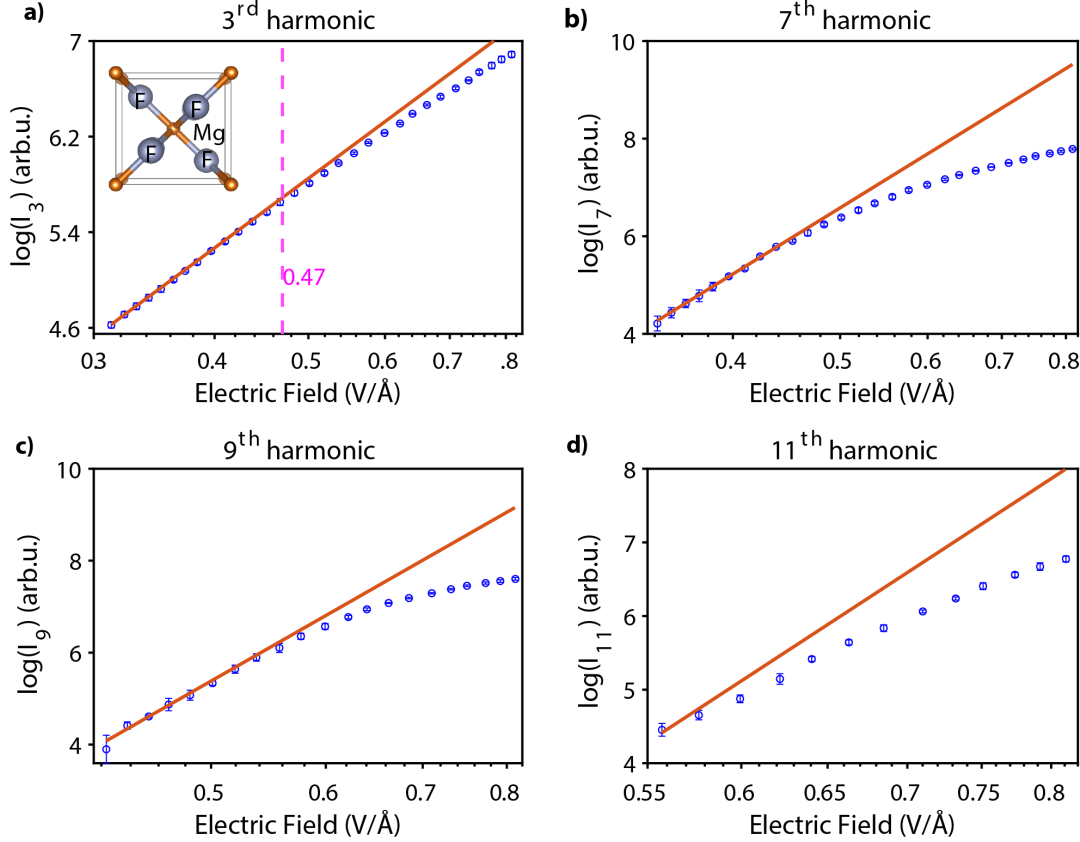


Figure 8.3: **Nonlinearity of the harmonic yields in MgF_2 .** a) 3rd harmonic intensity yield (blue dots with error bars) as a function of laser fields strength in logarithmic scale. The red line is the perturbative scaling of the field intensity (I^3) in logarithmic scale. b), c) and d) represent the same plot as (a) for higher-order harmonics 7th, 9th and 11th.

Even though the nonlinearity of the 3rd harmonic yield captures the onset field, the nonlinearity of the higher-order harmonics' yields also needs to be examined to verify if the PNT is the overall system's response or only a 3rd harmonic-dependent phenomenon. To this end, Figure 8.3.b-d present the nonlinearity of the higher-order harmonic yields (blue dots), and they show a PNT at a field strength very similar to the 3rd harmonic case. Similar to Figure 8.3.a, the red lines in Figure 8.3.b, c and d represent the N^{th} power of the laser intensity. Therefore, it can be concluded that the system undergoes a perturbative to nonperturbative transition within the experimental field range, as nonperturbative nonlinearity is observed in all the harmonics.

8.3 Nonlinearity of the harmonic yields in diamond, MgO, CaF₂, and LiF crystals

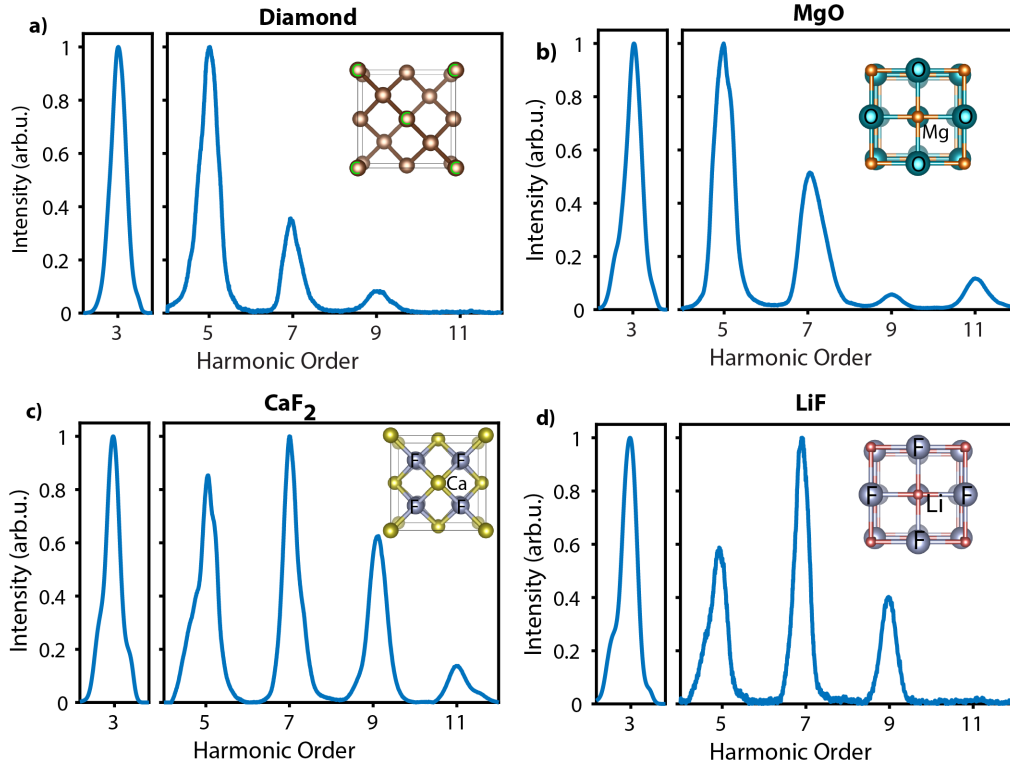


Figure 8.4: **HH spectra of four materials.** a), b), c) and d) Measured HH spectra of diamond, MgO, CaF₂ and LiF. All four materials show harmonics up to the 11th order except diamond. Inset shows the structure (unit cell) of corresponding material.

Thereafter, similar experiments are extended in diamond, MgO, CaF₂, and LiF to investigate if the nonlinearity behavior observed in the HHs of crystalline MgF₂ is maintained in other crystalline materials too. The crystals are exposed along the [100] direction with the same few-cycle laser field as in the MgF₂ case, and the corresponding HH spectra are presented in Figure 8.4 for diamond (a), MgO (b), CaF₂ (c) and LiF (d) respectively. Next, by varying the laser field amplitude, field strength-dependent HHs are measured in all four materials. First, the nonlinearity of the 3rd harmonics are plotted as a function of driving field strength in Figure 8.5 to identify the onset field strengths. For this purpose, the driving-laser field strength-dependent 3rd harmonic yields are presented on logarithmic scale (blue circles) together with the 3rd power (red lines) of the laser intensity (I) of the corresponding field strength.

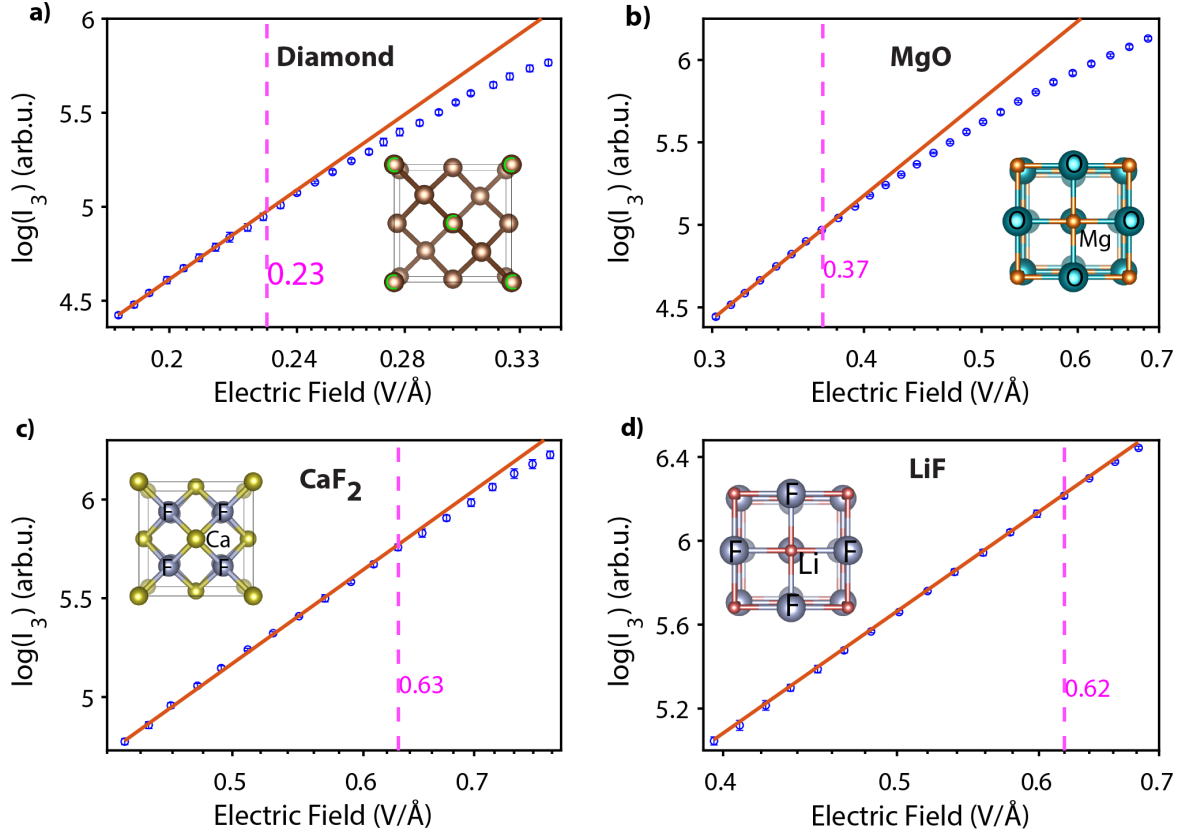


Figure 8.5: **Nonlinearity of the 3rd harmonic intensity yields.** a), b), c), and d) describe the nonlinearity of 3rd harmonics with driving field strength of Diamond (a), MgO (b), CaF₂ (c) and LiF (d) respectively. The logarithm of the HH yield is denoted by the blue dots, whereas the red line shows the perturbative scaling of the field intensity (I^3) in logarithmic scale. Onset fields are marked by the magenta dashed lines.

Similar as MgF₂ at lower field strengths, the nonlinearities of 3rd harmonics of all four materials follow power law dependence, and when the field amplitude exceeds a particular value, they deviate from the power law. The amplitudes of the onset fields thus captured are- Diamond : 0.23 V/Å, MgO : 0.37 V/Å, CaF₂ : 0.63 V/Å, and LiF : 0.62 V/Å. These onset fields indicate that larger bandgap materials require stronger fields to transition from the perturbative to nonperturbative regime.

Figure 8.6 describes the nonlinearity of the higher-order harmonic yields for these crystalline materials; the three plots in each row correspond to the higher-order harmonics of a particular crystal. The higher-order harmonic yields of all materials show nonperturbative nonlinearity; where some of them make perturbative to nonperturbative transition, while the others are nonperturbative at any field measured. The onset field for PNT in all the harmonics from these four materials shows similar field strength as deduced from the third harmonics of the corresponding materials. Therefore, each material performs

a perturbative to nonperturbative transition within the experimental field range around a particular field strength.

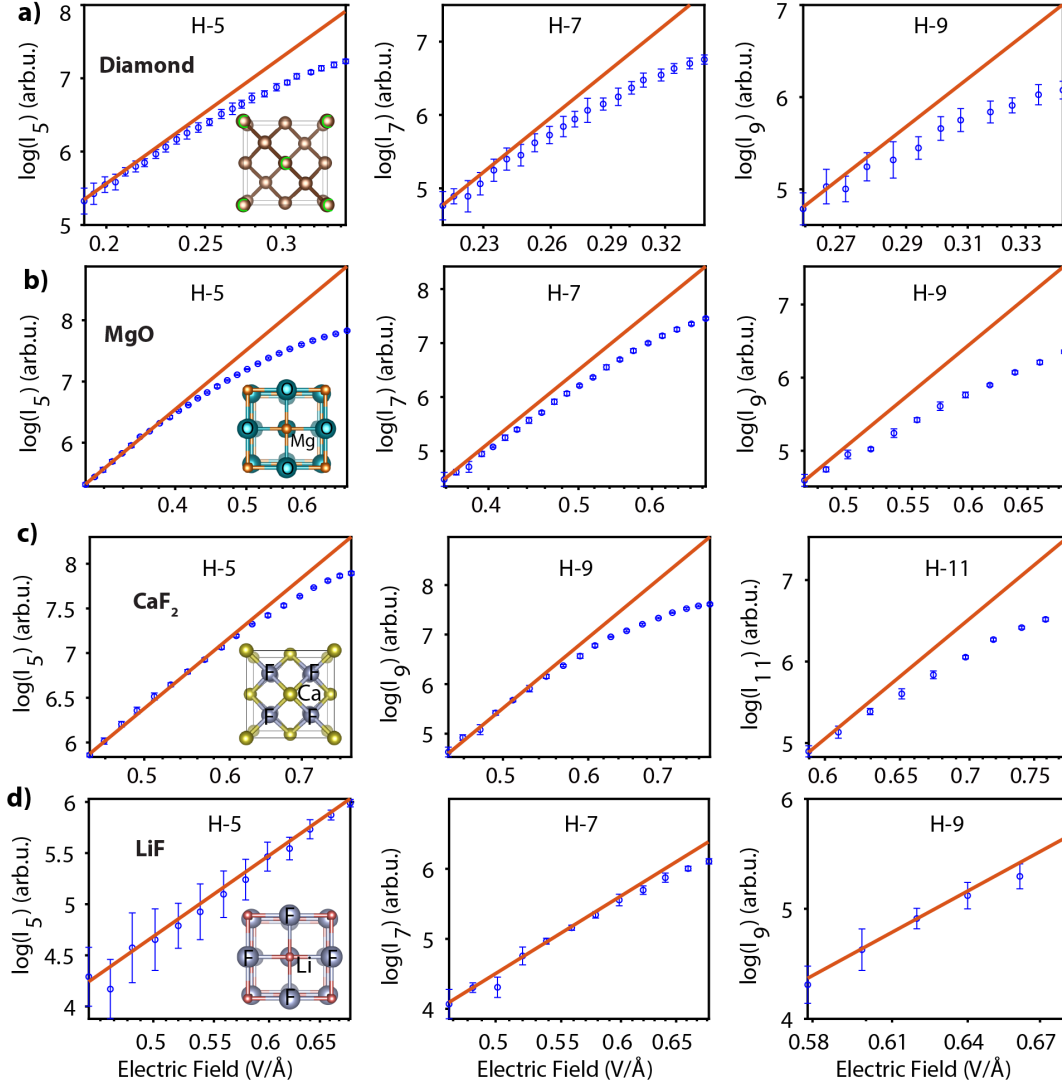


Figure 8.6: **Nonlinearity of the higher-order harmonic intensity yields.** a), b), c), and d) describe the nonlinearity of higher-order harmonics with driving field strength for Diamond (a), MgO (b), CaF₂ (c) and LiF (d) respectively. The blue dots with errors denote the logarithm of the HH yield, and the red lines illustrate the perturbative scaling of the field intensity (I^N) in the logarithmic scale. H-N stands for harmonic order (N).

This section confirms that all five materials discussed in this chapter, including MgF₂, possess a specific onset field characteristics. Hence, our experiments have successfully determined the onset fields for a range of materials with their bandgaps varying from 7.1 eV to 14.1 eV using driving laser of carrier photon energy 2 eV. After the successful determination of experimental onset fields for extreme nonlinearity across five materials,

the subsequent task is to predict them theoretically. In the following section, the applicability of the Keldysh parameter (γ) in solids for predicting these experimental onset fields will be examined.

8.4 Keldysh ionization rates

The process of HHG starts with the strong laser field-driven ionization of the electrons. The Keldysh theory has been widely used for understanding the strong-field ionization process [73]. In 1965, Leonid Keldysh formulated the so called Keldysh ionization rates, that describe the probabilities or rates of electron ionization in material under the influence of a strong electromagnetic field, like a laser. While this theory describes ionization in gases as the ionization of individual atoms, this process in solids is modeled as the transitions of electron from the valence band to the conduction band. The photoionization rate R_{PI} for solids as calculated in this article [73] is given by,

$$R_{PI} = \frac{2w}{9\pi} \left(\frac{\sqrt{1+\gamma^2} mw}{\gamma \hbar} \right)^{3/2} Q \left(\gamma, \frac{\tilde{\Delta}}{\hbar w} \right) \exp \left[-\pi \left\langle \frac{\tilde{\Delta}}{\hbar w} + 1 \right\rangle \times \left\{ K \left(\frac{\gamma}{\sqrt{1+\gamma^2}} \right) - D \left(\frac{\gamma}{\sqrt{1+\gamma^2}} \right) \right\} / D \left(\frac{1}{\sqrt{1+\gamma^2}} \right) \right] \quad (8.1)$$

Here,

$$\tilde{\Delta} = \frac{2}{\pi} \Delta \frac{\sqrt{1+\gamma^2}}{\gamma} D \left(\frac{1}{\sqrt{1+\gamma^2}} \right)$$

$\langle y \rangle$ represents the integer part of the number y , and the functions K and D are complete elliptic integrals of the first and second kind. Also Q is given by,

$$Q \left(\gamma, \frac{\tilde{\Delta}}{\hbar w} \right) = \left[\pi / 2K \left(\frac{1}{\sqrt{1+\gamma^2}} \right) \right]^{1/2} \times \sum_{n=0}^{\infty} \exp \left[-\pi \left\{ K \left(\frac{\gamma}{\sqrt{1+\gamma^2}} \right) - D \left(\frac{\gamma}{\sqrt{1+\gamma^2}} \right) \right\} n \right] / D \left(\frac{1}{\sqrt{1+\gamma^2}} \right) \times \phi \left[\left\{ \pi^2 \left(2 \left\langle \frac{\tilde{\Delta}}{\hbar w} + 1 \right\rangle - 2 \frac{\tilde{\Delta}}{\hbar w} + n \right) \right\} / 2K \left(\frac{1}{\sqrt{1+\gamma^2}} \right) \times D \left(\frac{1}{\sqrt{1+\gamma^2}} \right) \right]^{1/2} \quad (8.2)$$

The function $\phi(z)$ is defined as, $\phi(z) = \int_0^{(y^2-z^2)} dy$. Keldysh theory helps to describe ionization in terms of multiphoton and tunnel process based on the frequency (ω) and

strength of the applied field (E). The Keldysh parameter γ separates the multiphoton and tunnel regimes.

$$\gamma = \frac{\omega\sqrt{m^*\Delta}}{eE} \quad (8.3)$$

Here, m^* is the reduced mass of electron and hole, e is the charge of electron and Δ is the bandgap energy of the material.

8.4.1 Multiphoton regime

For $\gamma \gg 1$, the photoionization rate reduces to the multiphoton ionization rate, R_{MPI} .

$$R_{MPI} = \frac{2}{9\pi} w \left(\frac{mw}{\hbar} \right)^{3/2} \phi \left[\left(2 \left\langle \frac{\tilde{\Delta}}{\hbar w} + 1 \right\rangle - \frac{2\tilde{\Delta}}{\hbar w} \right)^{1/2} \right] \times \exp \left\{ 2 \left\langle \frac{\tilde{\Delta}}{\hbar w} + 1 \right\rangle \right. \\ \left. \times \left(1 - \frac{e^2 E^2}{4mw^2 \Delta} \right) \right\} \left(\frac{e^2 E^2}{16mw^2 \Delta} \right)^{\langle \tilde{\Delta}/\hbar w + 1 \rangle} \quad (8.4)$$

and here,

$$\tilde{\Delta} = \Delta + \frac{e^2 E^2}{4mw^2}$$

This regime is described by low laser intensity and perturbative ionization of electrons, i.e., the electrons in the valence band absorb multiple photons to overcome the band gap energy (Δ).

8.4.2 Tunnel regime

When the field strength is relatively strong $\gamma \ll 1$, the ionization rate describes the tunneling effect. The tunnel ionization rate R_{TI} is given by,

$$R_{TI} = \frac{2}{9\pi^2} \frac{\Delta}{\hbar} \left(\frac{m\Delta}{\hbar^2} \right)^{3/2} \left(\frac{e\hbar E}{m^{1/2} \Delta^{3/2}} \right)^{5/2} \times \exp \left\{ -\frac{\pi m^{1/2} \Delta^{3/2}}{2e\hbar E} \left(1 - \frac{mw^2 \Delta}{8e^2 E^2} \right) \right\} \quad (8.5)$$

In the tunnel regime, the electric field is strong enough to distort the potential barrier in such a way that the electrons tunnel through this distorted barrier without gaining original bandgap energy.

8.5 Keldysh ionization rate in fused silica

In order to understand the role of Keldysh theory in distinguishing the multiphoton regime from the tunnel regime, the ionization rates for fused silica are calculated for a driving laser with carrier energy of 2 eV. The selection of fused silica is based on the fact that

the experimental parameters (bandgap [187], nonlinear refractive index [188], and reduced mass [189]) required for this simulation are available in the literature.

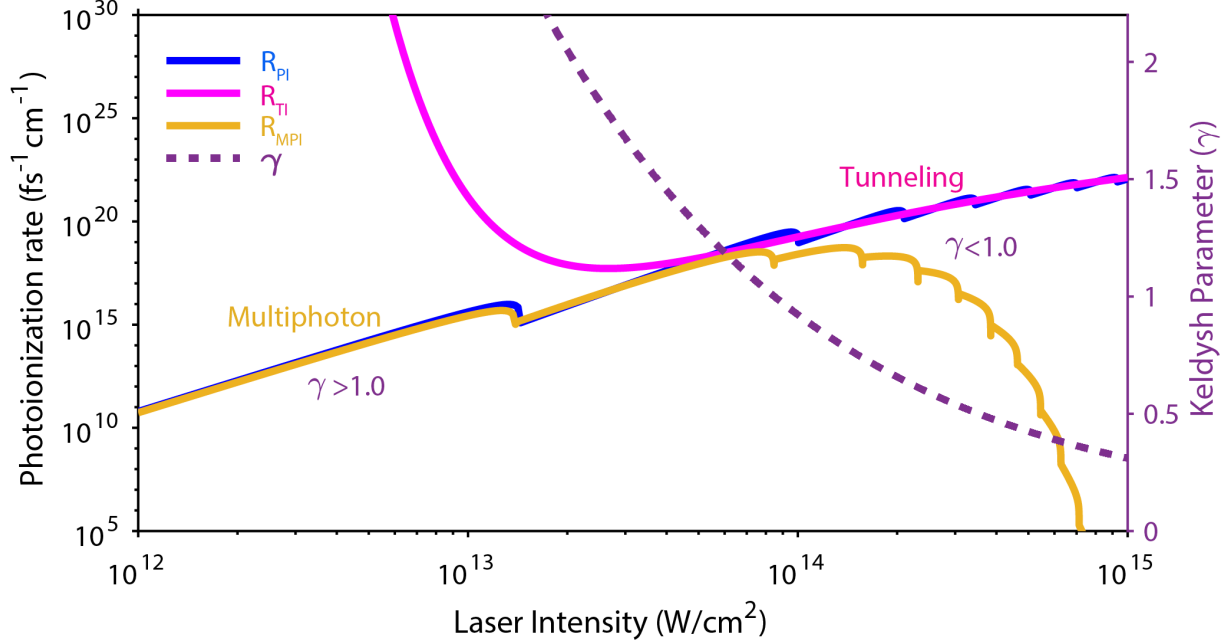


Figure 8.7: **Laser intensity dependent photoionization rate and Keldysh parameter of fused silica.** The blue, magenta and yellow solid lines illustrate the Keldysh theory-based photoionization, tunnel ionization and multiphoton ionization rates respectively. The value of the Keldysh parameter is represented by the purple dashed line.

Equation 8.1 is used to calculate the total photoionization rate, which is represented by the blue line in Figure 8.7. The yellow and magenta lines represent ionization rates for the multiphoton and tunnel cases, calculated using equations 8.4 and 8.5 respectively. The purple dashed line describes the value of the Keldysh parameter (γ) as a function of laser intensity. This Figure shows that when $\gamma > 1$, the multiphoton ionization rate follows the total photoionization rate, whereas when $\gamma < 1$, the tunnel ionization rate dominantly contribute to the total ionization. Around $\gamma \sim 1$, the multiphoton rate starts to deviate from the total rate. The electric field strength corresponding to $\gamma \sim 1$ represents the onset field for the transition from the multiphoton or perturbative regime to the tunnel regime. Therefore, $\gamma \sim 1$ is a good approximation to capture the perturbative to nonperturbative transition.

Table 8.1 shows the amplitude of the driving field strength needed for the materials to reach $\gamma \sim 1$. The field amplitudes are significantly higher than those observed experimentally. This fact reflects that, the Keldysh parameter is not appropriate to predict the PNT onset fields in solid-state materials accurately. The experimental bandgaps (Δ) and reduced masses (m^*) used for the above calculation are obtained from the existing literature [190, 191, 192, 193, 194, 195, 196, 197] and **QuantumATK** software respectively.

Crystal	Δ (eV)	m^* (m_e)	E (V/Å) for $\gamma = 1$	E (V/Å) from experiment
Diamond	7.1	0.181	0.82	0.23
MgO	7.8	0.297	1.10	0.37
MgF ₂	10.8	0.453	1.60	0.47
CaF ₂	12.1	0.445	1.69	0.63
LiF	14.1	0.630	2.16	0.62

Table 8.1: Information about the crystal parameters and onset field as evaluated from $\gamma \sim 1$ and determined from the experiments.

8.6 Potential under strong field

The inability of the Keldysh parameter to predict the PNT in solids calls upon the formulation of a parameter which can accurately predict the experimental onset fields. To this end, it is important to study the crystal potential under a strong field. For this purpose, I have followed the works [198, 199, 61, 141] on intense laser-induced band structure and crystal potential modification in this section.

Consider an electron in a periodic crystal driven by a time-periodic external field, such as a laser. The laser field $E(t) = E(t+T) = -E_0 \sin(\omega t)$ and the corresponding vector potential $A(t+T) = A(t)$ are periodic in time with laser period T . The potential $V(r) = V(r+a)$ is periodic in space with crystal's lattice constant a . In atomic units, the system can be described by the time dependent Schrödinger equation as follows:

$$H(t)\psi(t) = i\frac{\partial\psi(t)}{\partial t} \quad (8.6)$$

where the Hamiltonian of the system is,

$$H(t) = \frac{[p + A(t)]^2}{2} + V(r) \quad (8.7)$$

The spatial and temporal nature of the problem can be presented in the same term by allowing $\psi = \exp\left(-i \int p \cdot A(t) dt - \frac{i}{2} \int A(t)^2 dt\right) \phi$. This makes the canonical transformation to the new Hamiltonian of the moving electron convenient.

$$\left[\frac{p^2}{2} + U(r, t)\right] \phi = i\frac{\partial\phi(t)}{\partial t} \quad (8.8)$$

with,

$$U(r, t) = V\left(r + \int A(t) dt\right) \quad (8.9)$$

Here, U is spatially and temporally periodic provided the average of A is zero, $\int_0^T A(t)dt = 0$.

Now, by expanding the potential $V(r)$ in terms of reciprocal lattice vector k and Fourier coefficients V_k , $V(r)$ becomes $V(r) = \sum_k V_k e^{ik \cdot r}$ and representing $A(t) = -\int E(t)dt = -\frac{E_0}{\omega} \cos(\omega t)$ equation 8.9 can be rewritten as,

$$U(r, t) = \sum_k V_k e^{ik \cdot (r + \int A(t)dt)} = \sum_k V_k e^{ik \cdot r} e^{\frac{-ikE_0}{\omega^2} \sin(\omega t)} \quad (8.10)$$

Now the application of Jacobi-Anger expression in equation 8.10 leads to,

$$U(r, t) = \sum_{k,n} V_k J_n \left(\frac{kE_0}{\omega^2} \right) e^{i(k \cdot r - n\omega t)} \quad (8.11)$$

Here, J_N is the Bessel function of the first kind of order N . The time dependence of the above equation allows to divide it into time independent $U_0(r)$ and time dependent $U_n(r, t)$ parts.

$$U(r, t) = \sum_k V_k J_0 \left(\frac{kE_0}{\omega^2} \right) e^{ik \cdot r} + \sum_{k,n \neq 0} V_k J_n \left(\frac{kE_0}{\omega^2} \right) e^{i(k \cdot r - n\omega t)} = U_0(r) + U_n(r, t) \quad (8.12)$$

Time independent $U_0(r, E_0) = \sum_k V_k J_0 \left(\frac{kE_0}{\omega^2} \right) e^{ik \cdot r}$ describes the effective potential of the crystal. The second term is time dependent, and it represents the transitions between the different states of $U_0(r)$ by the absorption or emission of photons at harmonics ($N\omega$) of the driving field [200, 201, 202].

$$U_0(r, E_0) = \sum_k V_k J_0 \left(\frac{kE_0}{\omega^2} \right) e^{ikr} \quad (8.13)$$

where, $k = n \frac{2\pi}{a}$ and n is an integer. The properties of this crystal potential can be modified by the laser field amplitude (E_0). For example, when the laser field is strong enough, the effective crystal potential can be suppressed completely so that the electron wave packets become nearly free (Figure 8.8.c, yellow line).

Here, a heuristic model is introduced which assumes that the first Fourier coefficient represents the effective crystal potential of the solids and for large band gap materials, the amplitude of the Fourier coefficient can be approximated to the bandgap of the corresponding material. Thus the effective potential becomes,

$$\tilde{U}_{eff}(\omega, E_0) = E_g J_0 \left(\frac{kE_0}{\omega^2} \right) \quad (8.14)$$

The dependence of $\tilde{U}_{eff}(\omega, E_0)$ on J_0 suggests that the laser field will reduce the amplitude of the effective crystal potential from E_g , as a function of driving field strength. This is

supported by previous theoretical works that show the intense laser-induced potential and bandgap modification in bulk solids [61, 203]. In this context, the onset of extreme nonlinearity in bulk solids is anticipated to arise, when the amplitude of the effective potential drops below the energy associated with the lowest-order nonlinearity of the material (Figure 8.8.b and c). Consequently, for a centrosymmetric crystal illuminated by an intense laser with carrier photon energy 2 eV, the extreme nonlinearity will start at a field strength that reduces $\tilde{U}_{eff}(\omega, E_0)$ to 6 eV, energy of the lowest-order harmonic.

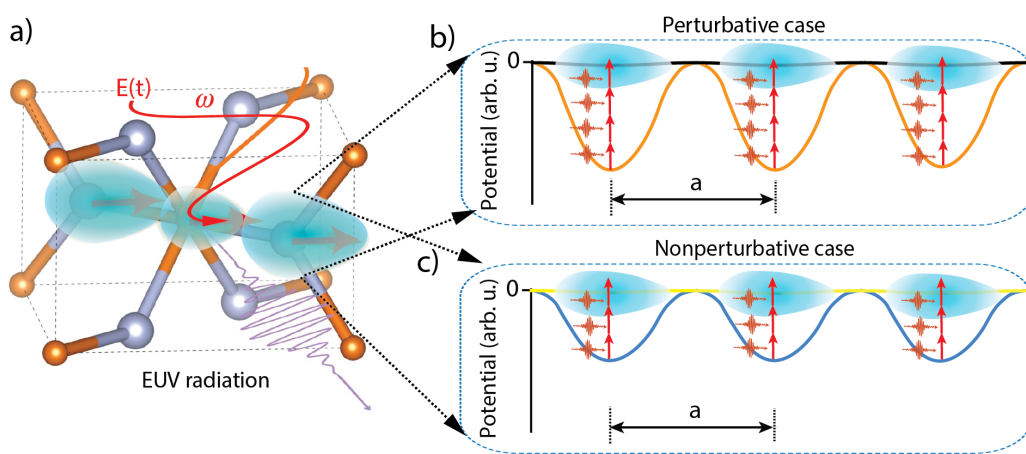


Figure 8.8: **Crystal under strong fields.** b) Schematic of the deformation of effective crystal potential under comparatively lower laser field strength. Here more than three photons with energy 2 eV are required for an electron to overcome the potential barrier. c) Schematic of the crystal potential under a comparatively stronger field strength, where three photons are sufficient enough to overcome the potential barrier. The blue-shaded areas represent valence electron clouds. Adopted from ref. [61]

Figure 8.9 shows the drop in $\tilde{U}_{eff}(\omega, E_0)$ with the increase in driving field strength. $\tilde{U}_{eff}(\omega, E_0)$ of diamond, MgO (orange), MgF₂ (yellow), CaF₂ (purple), and LiF (green) decrease to 6 eV at field strengths of 0.24, 0.34, 0.55, 0.70 and 0.56 V/Å respectively and these define their onset values. Figure 8.10 compares the experimental onset field values (magenta) with those calculated from effective potential (teal) and Keldysh parameters (olive). This comparison indicates that the estimated onset field, as determined by the Keldysh parameter, is approximately 3 to 4 times greater in magnitude than the values obtained from experiments. In contrast, the predictions derived from the drop of the effective potential closely align with the experimental results.

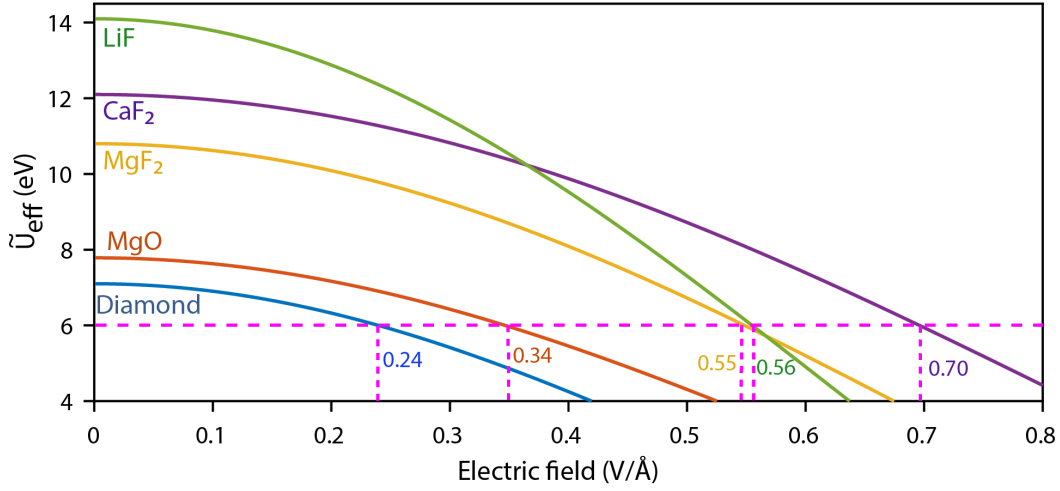


Figure 8.9: **Onset field calculation under strong laser excitation.** Drop of the effective potential or the bandgap with the laser field strength for Diamond (blue), MgO (orange), MgF₂ (yellow), CaF₂ (purple) and LiF (green). The onset field is defined as the point where $\tilde{U}_{eff}(\omega, E_0)$ drops below 3rd harmonic energy (6 eV). The onset fields are 0.24, 0.34, 0.55, 0.70 and 0.56 V/Å for diamond, MgO, MgF₂, CaF₂ and LiF respectively.

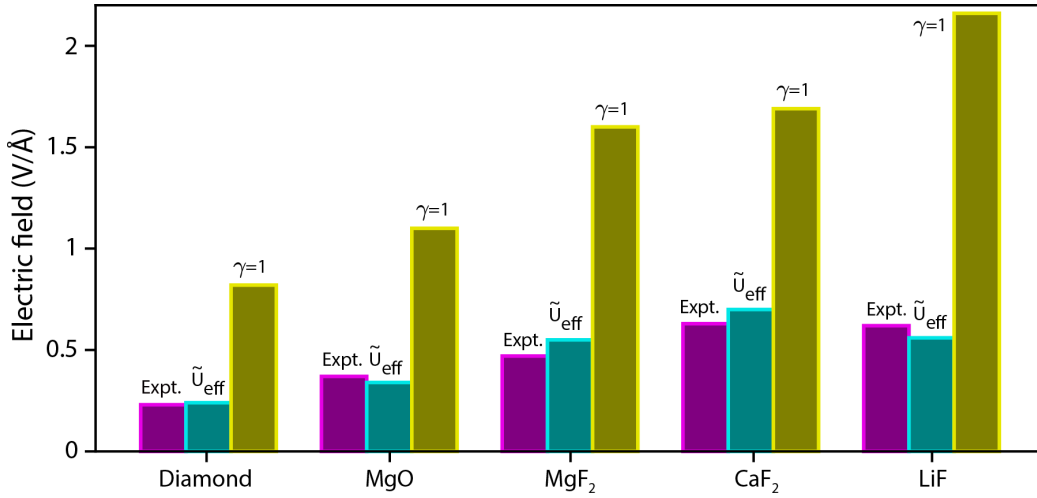


Figure 8.10: **Onset field strengths of extreme nonlinearity.** Comparison of the experimental onset fields (magenta) with those predicted by $\tilde{U}_{eff}(\omega, E_0)$ (teal) and Keldysh parameter $\gamma = 1$ (olive) for all five materials. Here, 'Expt.' stands for experimental.

In conclusion, perturbative and nonperturbative harmonic yields have been generated in various dielectric materials in this study. The nonlinearity of the harmonics have allowed to conclude that the Keldysh parameter ($\gamma \sim 1$) is not a good approximation for predicting the onset of extreme nonlinearity in bulk solids, while the effective potential model offers a reliable estimation of the onset field.

Chapter 9

Conclusions and outlook

9.1 Conclusions

A new perspective on the ultrafast phase transition dynamics of VO_2 is presented in this thesis, where it is shown that ultrashort laser pulses do not directly drive the room temperature monoclinic VO_2 to the rutile phase, but instead trigger it to the excited rutile phase. As a result, the thermalization-relaxation responses of $\text{R}^*\text{-VO}_2$ are imprinted on the reflectivity change measured by the pump-probe experiments. On the same note, the experimental study has allowed to explain why there are generally different time scales reported in separate transient optical experiments of VO_2 in the literature. They are not due to electronic or structurally driven responses, but the result of the thermalization-relaxation response of metals which depend on the probe wavelengths. By utilizing the experimental thermalization-relaxation dynamics of $\text{R}^*\text{-VO}_2$, it has been possible for the first time to disentangle the M1-VO_2 population dynamics and the underlying electron dynamics of $\text{R}^*\text{-VO}_2$ from the laser-excited M1-VO_2 response. The transition rate as evaluated from the M1-VO_2 population dynamics reveals that the transition from M1-VO_2 to R-VO_2 occurs in steps. Additionally, the vanadium-vanadium bond length alternation related to the phase transition has also been extracted for the first time in the current thesis. Real-time TDDFT simulations support the experimental observation of anharmonic step-like transition. Overall, our experimental results reveal that the photoinduced phase transition is driven by the anharmonic swing of the V-V bonds and not by an instantaneous Mott mechanism.

The high harmonic experimental setup, described in this thesis, represents a significant advancement in the control of high harmonic generation and measurement in solids. The improvements include the simultaneous measurement of a broad range of harmonic orders extending into the EUV region with two laser sources of carrier energy 2.0 eV and 1.5 eV, the accurate determination of the driving laser field strength, and the measurement of nearly perfect symmetric orientation-dependent HHs, make the setup a

state of the art tool for harnessing the physics of high harmonic generation in solids.

The onset of extreme nonlinearity in a variety of solid materials is presented for the first time through the perturbative to nonperturbative transition of the harmonics of the driving field of carrier energy 2 eV. Successful HHs have been generated in five solid crystals: Diamond, MgO, MgF_2 , CaF_2 , LiF. Harmonics of the crystals, starting from a comparatively lower bandgap material diamond (7.1 eV) to a very high bandgap material lithium fluoride (14.1 eV) demonstrated a clear PNT when the electric field amplitudes of the driving laser pulse are gradually increased. The Keldysh parameter $\gamma \sim 1$ fails to predict the onset electric field amplitudes, whereas the effective potential model captures the onset fields very well.

9.2 Outlook

It would be interesting to investigate the excited phase responses observed in M1-VO_2 within other correlated materials, specifically in transition metal oxides. Such studies could explore similar ultrafast pathways including electronic thermalization-relaxation responses, providing important insights into their laser-induced phase transition mechanism.

The advanced HHG setup could be used to picture the two-dimensional valence potential or electron density in crystalline solids by performing 360° orientation-dependent high harmonic generation. Consequently, with the help of the goniometer's three-dimensional rotation stages, other crystallographic planes can be accessed to reconstruct a three-dimensional valence potential or electron density of the crystal. Furthermore, by introducing a pump-probe facility to the current setup, we may also track the time-dependent change in electron density in crystals like VO_2 , which undergoes a phase transition upon laser excitation.

The examination of the perturbative to nonperturbative transition for materials with a lower bandgap than those used in our experiments utilizing infrared laser sources would be exciting. A generalized theoretical description of HHG, which captures the perturbative to nonperturbative transition in materials including semiconductor as well as insulators shall be needed to accurately predict the onset of extreme nonlinearity in bulk solids.

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