Radio-frequency pulse compression for high-brightness ultrafast electron diffraction: design, characterization and application

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Abstract

Ultrafast electron diffraction (UED) is a technique for probing the dynamic structure of molecules and materials following laser excitation. With this approach, atomic scale dynamics are captured with electron pulses that stroboscopically freeze transient structures to a limit defined by the electron pulse duration. Progress in the field to date has mainly been hampered by electron-electron interactions (space-charge) which lead to a temporal broadening of the electron probe pulses and a subsequent deterioration of the effective time-resolution of the UED instruments. The work herein demonstrates that the limits to time-resolution previously defined by space-charge interactions can be nearly completely overcome by the careful design and implementation of an electron-optical column involving a radio-frequency cavity to temporally compress the broadened pulses back to their original duration. The performance of the ultrafast diffractometer operating in the radio-frequency compression geometry was characterized by ponderomotive scattering cross-correlation experiments which allowed for the direct measurement of the temporal impulse response function of the instrument. The result of the characterization is that electron pulses containing over 1 million electrons can be compressed to durations on the order of 100 fs; a nearly three orders of magnitude increase to the charge density at the specimen position (or signal per electron pulse). As a first experiment performed with the novel UED diffractometer, the lattice response of single-crystal graphite films was investigated and laser induced lattice disorder was measured on a time scale of 259 fs. The instrument, operating in a never before accessed charge density regime, directly measured a 1.4 THz optical phonon with a vibrational amplitude on the order of 0.06 pm.
Résumé

La diffraction d’électrons ultra-rapide est une technique permettant d’étudier la dynamique de structure de molécules et de matériaux à la suite d’une excitation laser. Dans le cadre de cette méthode, la dynamique à l’échelle atomique est enregistrée grâce à des pulses d’électrons qui gèlent les structures transitoires de façon stroboscopique, avec une résolution temporelle déterminée par la durée du pulse d’électrons. Les progrès dans ce champs de recherche ont majoritairement été limités par l’interaction électron-électron (espace-charge), qui engendre un élargissement temporel des pulses d’électrons et de ce fait détériore la résolution temporelle des montages de diffraction d’électrons ultra-rapide. Le présent travail démontre que les limites de résolution temporelle auparavant définies par les interactions espace-charge peuvent être presque complètement repoussées grâce à un design réfléchi et la mise en place d’une colonne électron-optique utilisant une cavité RF pour compresser les pulses d’électrons à leur durée initiale. La performance du diffractomètre ultra-rapide opérant dans la géométrie de compression RF a été caractérisée par des mesures de corrélation croisée de diffusion pondéromotrice, permettant ainsi une mesure directe de la réponse temporelle de l’instrument. Le résultat de cette caractérisation est que des pulses contenant un million d’électrons peuvent être compressés à une durée de l’ordre de 100 femtosecondes, ce qui représente une amélioration de trois ordres de magnitude de la densité de charge à l’échantillon (ou signal obtenu par pulse d’électrons). Comme première expérience effectuée sur le nouvel instrument de diffraction d’électrons ultra-rapide, la réponse du réseau d’un film de graphite monocristalline a été étudiée et le désordre créé par l’excitation laser mesuré sur une durée de 259 femtosecondes. L’instrument, capable d’opérer dans des régimes
de densité de charge jamais obtenus auparavant, a permis de mesurer directement un phonon optique à 1.4 THz d’une amplitude vibrationnelle de l’ordre de 0.06 pm.
Acknowledgements

First and foremost I would like to thank my supervisor, Prof. Bradley Siwick, for his support and encouragement throughout my graduate studies. Being one of his first students, I was lucky enough to help transform an empty room into a fully functional ultrafast electron diffraction laboratory. This opportunity allowed me to grow a great deal as a scientist and exercised my problem solving muscles on a daily basis. Brad always had his door open for stimulating conversations or for advice and was relentlessly excited about the science we were doing in the Otto Maass building.

Next I must mention Vance Morrison and Christopher Godbout who I worked closely with for many years. It was a tremendous pleasure to work with both of them and to build up the lab piece by piece in the first generation instrument geometry. Vance and I also spent hundreds of hours together in the lab during the characterization of the RF-compressed next-generation beamline.

I extend my thanks and acknowledgement to all the collaborators we have worked with throughout the years. The Eindhoven group under the supervision of Prof. Jom Luiten were very helpful in providing insight and advice with the RF compression research project. Jom and his students—most notably Thijs van Oudheusden and Peter Pasmans—were a pleasure to converse with about RF compression technology. The authors of the General Particle Tracer code used for many of the simulations presented in this thesis—Bas van der Geer and Marieke de Loos—were very helpful providing support when I needed to perform custom simulations. The Schwoerer group located in South Africa have been exceptionally helpful and generous, providing us with a working streak camera for instrument time-resolution measurements.
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On a more personal note I’d like to thank my parents and sister for their never ending support throughout all of my studies. Since I’ve been a small boy they have encouraged me to study hard and taught me to believe in my abilities. I must also thank all those who have enriched my life and inspired me to trust my creativity; this includes the many teachers and friends I’ve had the great fortune to have met along the way.

Last, I’d like to thank the Department of Physics at McGill University for a wonderful experience.
Preface

Chapter 4 of this thesis is based on a published journal article\(^1\) for which Vance Morrison and myself shared the first author role. My contribution to that work was the design, implementation and simulations related to the RF cavity technology required for creating high brightness, temporally compressed electron pulses. Vance Morrison contributed to the work by designing and implementing the characterization technology required to measure the temporal impulse response function of the UED diffractometer operating in the RF compressed geometry. My work has been highlighted in chapter 4 and only a short summary of the characterization methodology has been presented in this document. For a more complete description of the ponderomotive scattering experiments performed to characterize the RF compressed pulses please refer either to the journal article discussing the characterization of the pulse envelope of UED electron pulses\(^2\) or to the PhD thesis of Vance Morrison\(^3\).

The large amount of instrument design and characterization that was performed during my tenure at McGill University warranted a dissertation in the traditional


style format and Chapters 1, 2, 3 and 5 contains work published for the first time here. Chapter 6 is based on an article published in Ultramicroscopy\textsuperscript{4}.

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CHAPTER 1

Introduction

1.1 Dynamics of the atomic scale

The atom, although not the indivisible unit of matter John Dalton believed it to be, often remains as the fundamental building block when thinking about problems in condensed matter physics, chemistry and molecular biology. Much of solid state physics, for example, relies heavily on comprehending the way in which electrons and the positively charged atomic nuclei interact with one another. This interaction is a crucial consideration when modelling electronic band structures in solids and an atomic level view of the periodic crystal lattice is essential for accurate definitions of the electrostatic potential. Electron-lattice interactions are also responsible for the manifestation of superconductivity in certain materials, which occurs due to a net attractive interaction between electron pairs made possible by the screening of Coulomb forces by lattice vibrations [1]. Due to the fact that a deep understanding of material properties, phase transitions, chemical reactions and biological function all rely on a detailed structural description of molecules and materials, a great amount of research of the twentieth century was devoted to solving the equilibrium structures of matter. A complete picture of the microscopic world,
Figure 1–1: Schematic potential energy surface defining two stable molecular configurations and the activated complex. The potential energy defined by the activated complex is the barrier between reactants and products.

however, requires more than just an atomic description under conditions of thermal and chemical equilibrium; the ways in which networks of atoms and molecules respond (both electronically and structurally) under non-equilibrium conditions are of great importance to understanding many of the open questions in modern research.

The idea of an activated complex—a short lived transient structure which when sampled by the reactant molecules in a chemical reaction has a strong chance of decomposing to the product state—is an old one and was originally used as a theoretical construct for calculating reaction rates to higher degrees of accuracy [2].
1.2 Spatial and temporal requirements for resolving atomic motions

Transient structures defined in this way can be represented by saddle points on a potential energy surface for a set of reaction coordinates and the activated complex is thus a barrier between the local energy minima of stable compounds. This is shown schematically in Fig. 1–1. In the example shown there are two stable molecular configurations separated by a potential energy barrier (defined by the configuration of the activated complex). Perturbations to the activated complex configuration will either lead to a deterministic relaxation into one of the stable configurations (via a change in coordinate 1) or will lead back to the activated complex itself (via a change in coordinate 2). The accurate first-principles calculation of a potential energy surface requires knowledge of the forces acting on each atomic nuclei for every molecular configuration, which in turn requires a quantum-mechanical description of the dynamical electron distributions. The direct observation of the transition state is thus an often desired experimental goal with the promise to elucidate the empirical force gradients which drive systems under non-equilibrium conditions [3, 4]. Although barrier crossing dynamics are of great interest to physicists, chemists and biologists alike, they are not the only reason to seek an atomic level description under non-equilibrium conditions. Observing the motion of electrons and nuclei after small perturbations can give insights into the way systems channel energy through electron-electron, electron-nuclei and nuclei-nuclei interactions. Thus any data related to motions on the atomic scale would serve as an invaluable resource for both the theoretical modelling and experimental control of nanoscale systems.

1.2 Spatial and temporal requirements for resolving atomic motions

In order to resolve motions on the atomic scale, one must first consider the characteristic time and length scales on which electrons and atoms move. Since the expectation values of observables are constant in time for stationary states, ‘motion’
of particle wavefunctions can only take place when particles exist in a superposition of states (i.e. a wavepacket). The oscillation period of a particle in a superposition of two stationary states is just $\tau = \frac{2\pi \hbar}{\Delta E}$, where $\Delta E$ is the energy difference between the states. For electrons the time scales associated with wave packet motion are defined by energy spacings ranging from 1 keV - 0.1 eV and thus span single attoseconds to tens of femtoseconds depending on whether the electrons involved are in bound states (core and valence) or exist in a conduction band [5]. Vibrational periods of molecules are on the order of 10 fs - 1 ps (0.1 eV - 1 meV), much slower than the motion of the electrons orbiting the nucleus, and thus the Born-Oppenheimer approximation—which assumes electrons respond adiabatically to a change in nuclear position—is often a good approximation when considering molecular wave packet dynamics [3, 4, 6]. Resolving motion on the atomic scale can be broken into two experimental challenges due to this disconnect in time scale: fast electronic motion requires attosecond resolution, where slower electronic motion and nuclear motion requires femtosecond resolution.

Optical laser pulses are the ideal experimental tool for accessing these time scales. If the pulse duration is sufficiently short compared to the timescale of the motion of interest, the uncertainty principle guarantees that the energy bandwidth of the laser pulse will be larger than the separation between energy levels that need to be populated in order to drive the process. Furthermore, since experiments typically require that an enormous number of particles be simultaneously excited in order to obtain measurable results, pulse durations significantly shorter than the process of interest ensure that the dynamics of each sub-unit in the system can be defined by the same zero of time. After excitation, the motion can be captured using a second pulse of a similarly short duration that is delayed in time relative to the
excitation pulse. Experiments of this kind are called pump-probe experiments and can be schematically understood by observing Fig. 1–2. The probe pulse intensity or spectral character is modulated by the average configuration of the specimen over the interaction time of the pulse, and so one simply needs to monitor either the transmission of the probe through the specimen (as is shown in Fig. 1–2) or alternatively the reflection off of the specimen surface at different relative time delays in order to construct a time-domain picture of the response to excitation by the pump.

Recently it has become possible to generate extremely short attosecond electron and optical pulses by ionizing atoms and small molecules with intense infrared femtosecond laser pulses [5, 7]. The ionized electron wavepacket trajectory follows the electric field oscillation of the femtosecond pulse, initially travelling away from the atom and a half cycle later is accelerated back towards the parent atom from which it was extracted. The free electron finally collides with the atom and at this point the bound and free electron wavefunctions interfere with each other and produce an oscillating dipole which emits odd harmonics of the ionizing laser frequency. The emission time of the photon pulse is confined to the attosecond time scale by energy
filtering the lower harmonic photon energies [8]. The attosecond light pulse, due to the nature in which it is created, contains the amplitude and phase information of the electron wavefunction interference [7]. By analyzing the emitted attosecond pulse properties over a range of molecular alignments relative to the fs IR pulse it is possible to fully resolve electronic orbitals in small molecules such as N$_2$ [9]. Attosecond pulses have also been used in pump-probe transient absorption spectroscopy experiments that followed the real-time motion of valence electrons during the ionization of krypton over the span of several femtoseconds [10].

Femtosecond pump-probe technology complements attosecond science by exploring the longer time scales associated with excited state dynamics and relaxation. In metals and semi-conductors, for example, processes such as excited state energy relaxation, conduction band carrier dynamics, electron-electron scattering, electron-phonon scattering, and phonon-phonon scattering occur on time scales spanning 1 fs - 10 ps [11, 12]. Femtosecond science is not limited to the bulk solid-state, however, and can be extended to surfaces, liquids and solutions, the gas-phase, polymers, proteins and biological systems [13]. There are several techniques that operate under a femtosecond pump-probe approach, the difference amongst them being the choice of how to probe the system after excitation. When interested in excited state relaxation dynamics time-resolved electronic spectroscopies can be used to probe the transient population of electron energy levels. The probe centre wavelength is matched to the electronic transition of interest; for example, carrier relaxation in semiconductors requires a probe in the ultraviolet to near infrared range since band gaps are separated on the order of 1 eV [11]. Similarly, vibrational energy level populations and phonons are probed well by either time-resolved vibrational spectroscopy in the near to far infrared or by time-resolved Raman spectroscopy [14–16]. Very low energy transitions
in the 1 - 100 meV energy range can be accessed by time-resolved THz time-domain spectroscopy (tr-THz-TDS), which measures the transmission of a THz femtosecond probe pulse through a specimen in a coherent fashion, allowing for both the amplitude and phase information of the exiting pulse to be measured for every time delay between pump and probe \[17–19\]. This makes tr-THz-TDS an excellent tool for probing the frequency dependant photoconductivity of the excited state. Recently time and angle resolved photoemission spectroscopy (tr-ARPES) has been implemented in a femtosecond pump-probe context, allowing for momentum-dependant binding energy measurements to be carried out at material surfaces \[20,21\]. Resolving electron dynamics with tr-ARPES is especially useful for layered materials (due to surface properties being characteristic of the bulk in quasi 2D systems) and has been used to study transient charge-order in a charge density wave material \[20\] as well as electron-phonon relaxation in graphite \[21\].

All of these techniques are either weakly dependant or indirectly related to the actual structure (ie. nuclear coordinates) of the specimen, and thus are not ideal for exploring atomic trajectories. Structural dynamics are much more clearly revealed by techniques that monitor time-resolved diffraction signals because a diffraction pattern contains information related to the symmetry, composition and dimensions of the crystals or molecules under investigation. A time-resolved diffraction experiment proceeds in the exact same way shown in Fig. 1–2, except that the probe pulse is either an x-ray or electron pulse, both of which have the small wavelengths required to access the angstrom length scale characteristic of molecular bonds. The present work is concerned with how to measure the structural dynamics of molecules and materials, and so no more discussion will be devoted to measuring energy-resolved
1.3 Ultrafast Diffraction

Pulsed sources for both electron and x-ray time-resolved diffraction experiments have been developing in parallel over the past few decades and so it is appropriate to briefly discuss the experimental realities of both techniques. In any time-resolved diffraction experiment, roughly speaking, there are two main considerations that define the overall performance of the instrument. The number of scatterers per pulse transmitted through the specimen (pulse flux) defines how accurately the intensity of a diffraction peak can be measured and determines to what degree atoms can be spatially localized. The pulse duration puts a lower limit on the time-resolution of the instrument. The choice on whether to use electrons or x-rays should be guided based on which technique leads to the most accurate, efficient and reliable data collection. Unfortunately, there is much debate on this issue. Both technologies can currently perform time-resolved experiments on the ultrafast (sub-ps) time-scale, and so Ultrafast Electron Diffraction (UED) and Ultrafast X-ray Diffraction (UXD) are often complementary techniques. Historically the main technological challenge for UXD has been increasing pulse flux whereas short pulse durations have been relatively easy to achieve. UED has had precisely the opposite challenge.

There is a significant trade-off between UED and UXD that comes from the increased scattering cross section of electrons compared to x-rays; in the 80-300 keV range the electron scattering cross section is typically $10^5$-$10^6$ times larger than for 0.15 nm x-rays. This allows UED to generate a much larger signal per unit thickness (for the same number of incident scatterers) but also limits the maximum thickness of a UED specimen to the 100 nm scale. There are a few clear advantages to using
electrons instead of x-rays: first, x-rays are typically more damaging to specimens as they cause more frequent inelastic scattering events and deposit more energy per inelastic event, leading to approximately 1000 times the amount of deposited energy per elastic scattering event in biological specimens; second, the mean-free path of electrons better match the optical penetration depth of the pump-pulse, making it more simple to homogeneously excite the sample over the probed volume and also to achieve temporal overlap; third, electron-optical beamlines give more control over the transverse properties of the beam, allowing for sharper diffraction patterns as well as the ability to image specimens in real-space [22]. The main disadvantage of UED comes from the fact that electrons interact with one another via Coulomb interactions. These interactions (called space-charge interactions) are quite severe in the case of femtosecond pulses. Space-charge forces significantly affect both the temporal and spatial profile of the pulse as it propagates, placing limits on the pulse duration and transverse coherence length of UED electron pulses.

Facilities such as the Linac Coherent Light Source (LCLS) at Stanford University have dramatically improved upon the pulse flux of UXD sources by implementing what is known as an X-ray Free Electron Laser (XFEL), which has improved upon the pulse brilliance compared to synchrotron x-ray sources by ten orders of magnitude [23–25]. The enormous pulse flux ($10^{12}$ photons/pulse) and large transverse coherence length of the XFEL pulses have allowed for the structure of photosystem I to be solved using 70 femtosecond pulses, where the damaging nature of the x-rays did not limit the measurement since the time-scale for the damage was longer than the probe pulse duration [26]. The large coherence length of XFEL pulses compared to that which is currently possible for UED sources makes XFEL UXD experiments more ideal for the study of biological molecules. XFEL facilities do
have their downsides, however. Large scale facilities such as the LCLS have limited beam-time available compared to small table-top instruments typical of UED, and the investment cost to build the instrument is approximately three orders of magnitude larger for XFEL (which is a billion dollar instrument) compared to UED (a million dollar instrument). Furthermore, despite the large coherence of XFEL pulses, electron pulses may often yield better results for materials with smaller molecular volumes since UED pulses sample a more homogenous excitation. Since there are an enormous number of open problems that deserve serious study, both UXD and UED have their place in the field of structural dynamics today. The Siwick group has dedicated their efforts into building a novel instrument that represents a dramatic improvement to the performance of table-top UED technology.

Currently, the limiting properties of UED diffractometers are the pulse transverse coherence length and the instrument time resolution. There are thus two avenues to explore when considering instrument performance and typically these problems have been approached separately. Promising research that discusses ways to increase the transverse coherence length of pulsed electron beams to levels that exceed biomolecular dimensions include the implementation of cold atom electron sources which reduces the thermal velocity spread at the photocathode [27] as well as the potential for using single-electron pulses to avoid space charge induced reduction of transverse coherence [28]. The current work has focused instead on the problem of time resolution and before a solution can be presented, the way in which space-charge leads to temporal pulse broadening must be understood.
1.4 Femtosecond electron pulses and space-charge

The first set of time-resolved diffraction experiments that used a laser-actived electron source were performed by Gerald Mourou and Steve Williamson, who generated electron pulses with a Nd:yttrium aluminum garnet (Nd:YAG) laser and measured the laser-induced heating of thin-film aluminum with 20-100 ps time-resolution [29, 30]. In the initial characterization of their electron pulse durations using a streak camera, Mourou and Williamson measured durations of 100 ps—significantly longer than the expected duration of 15 ps based on the duration of the Nd:YAG optical pulse [29]. They concluded the difference was attributed to space-charge effects caused by the large number of excited electrons in the bunch.

Approximately ten years later, under the supervision of Ahmed Zewail at Caltech, J.C. Williamson et. al. were the first to perform UED experiments that used femtosecond pulses to excite a photocathode [31]. In 2001, the Caltech group performed the first direct measurement of a transient structure in a UED experiment performed on a gas-phase non-concerted elimination reaction of a haloethane [32]. This accomplishment was certainly a milestone, but there still remained a large problem within the field: space-charge induced temporal broadening was not understood in a rigorously quantitative way. It was clear the amount of broadening depended strongly on the number of electrons, extraction field, initial spotsize and propagation time, but due to the fact that streak-camera technology of the time could not typically resolve pulse durations shorter than 900 fs [33], an investigation into how the controllable experimental parameter space influenced the resulting pulse duration at the specimen could not be carried out empirically.
The first step forward in achieving sub-ps time-resolution was taken by Qian and Elsayed-Ali, who modelled electron pulse temporal broadening using a simple one-dimensional fluid model [34]. The model was improved upon by Siwick et al. who developed a mean-field theory and performed three-dimensional N-body computer simulations to test the validity of both the fluid and mean-field models [35]. The mean-field model was in excellent agreement with the simulations which were confirmed experimentally in 2008 using a ponderomotive scattering experiment (to be discussed in a later chapter) [36]. The mean-field model allowed the design of next-generation ‘compact’ diffractometers, which handled space-charge induced broadening by minimizing the length separating the electron source and the specimen within the limits of design, thereby reducing the propagation time and therefore the amount of broadening. The remaining parameter space influencing the pulse duration is then the extraction voltage, the number of electrons, the initial pulse duration and the rms UV spotsize at the photocathode—all of which can be easily controlled experimentally. The mean-field model thus allowed—for the first time—a way to prepare electron pulse durations below 1 ps at the specimen. Shortly after the model was published Siwick et al. performed pump-probe measurements on thin-film aluminum with 600 fs electron pulses and determined the mechanism for the femtosecond laser-induced order-to-disorder phase transformation [37]. It wasn’t long before pulse durations were reduced even further, and during the following 10 years a great deal of groundbreaking science was performed using UED, investigating many interesting phenomena such as: thermal and non-thermal mechanisms of melting [37–39]; electronic-bond hardening in gold [40]; coherent/thermal lattice dynamics of metals, semi-metals and semi-conductors [41–47]; a graphite-to-diamond phase transition [48]; three dimensional imaging of laser-aligned gas molecules [49];
and the ultrafast dynamics of charge-density wave materials after optical excitation [50, 51]. Despite the enormous success of these experiments—which achieved pulse durations as low as 200 fs—they all suffered from one unfortunate fact: no matter how close the specimen was placed relative to the electron source, there was always a fundamental trade-off between the bunch charge (or spatial resolution) and the pulse duration (or time resolution). This trade-off is made clear by observing Fig. 1–3, which shows the mean-field model calculations for 100 keV electron pulses. Electron pulse charge was often limited to less than $10^4$ electrons per pulse, a number that is too low for non-reversible studies of large molecules that require more statistics to localize the atoms. Furthermore, regardless of the complexity of the material in question, it is always advantageous to operate with as much charge per
Femtosecond electron pulses and space-charge

One solution is to increase the electron energy to the relativistic regime which damps the space-charge force and allows for longer propagation times for the same pulse duration limit. There are groups that currently implement this option [52–55], although there is much less work represented by relativistic UED compared to compact UED. Potential downsides of relativistic sources is a higher damage threshold due to inelastic scattering, larger apparatus due to the smaller electron wavelength, and the need for a control room due to the dangerous radiation produced by bremsstrahlung. An advantage of higher electron energy (apart from the improved time resolution) is the potential for studying thicker specimens due to an increased mean-free path. A second solution to the space-charge problem is to use single-electron pulses, which completely removes electron-electron interactions from the equation and allows for very short durations (< 50 fs) at the specimen. This of course is the worst case scenario in terms of statistics per pulse, but some groups have used high repetition rate MHz lasers to drive photocathodes in order to improve the average beam current [56, 57]. Single electron techniques can only be used for processes that recover quickly—if the sample does not reset between pulses then each excitation begins from a different starting point, which is especially problematic for the case of irreversible changes. A third solution—which is the solution the Siwick group has implemented at McGill—begins by asking this question: If the temporal
broadening of femtosecond electron pulses is a result of *internal* fields acting on the electron distribution, is it possible to use *external* fields to reverse this effect?

The answer to this question begins by investigating how the position-momentum distribution of the electron pulse evolves as it propagates. The previously mentioned N-body simulations performed to verify the mean-field model were also used to investigate the phase-space distribution of propagating electron pulses [35]. Fig. 1–4 shows that a gaussian distribution in position-momentum space evolves into a linear distribution under the influence of space-charge. This linear correlation, called

**Figure 1–4:** Development of a linear position-momentum distribution during femtosecond electron pulse propagation. Although the initial distribution is gaussian, the internal space-charge forces cause the distribution to become linear in a time on the order of 1 ns. Figure taken with permission from ref. [35]. Copyright 2002, AIP Publishing LLC. DOI: 10.1063/1.1487437.
a chirp, develops on the nanosecond time scale, and for electrons travelling at half the speed of light (100 keV electrons) this corresponds to a propagation distance of only 15 cm. It turns out that it is possible to completely invert the phase-space distribution and that this inversion leads to a bunch compression, allowing for both high bunch charge and short pulse duration to be achieved simultaneously, albeit in only a limited region of space.

1.5 Radio-frequency compression of electron pulses

The details of how to achieve high brightness electron pulses with short duration will be the focus of a significant part of this thesis, and so only the concept will be presented here. By using a radio-frequency cavity operating in a transverse-magnetic (TM) mode for which the electric field is polarized along the direction of the electron beam propagation, it is possible to use the cavity effectively as a temporal lens. Fig. 1–5 shows a cartoon of how such a temporal lens works. The electron beam, before passing through the cavity (which is drawn as a rectangular pillbox) has already developed a linear chirp and has a duration of many (∼ 10) picoseconds. The front of the bunch enters during a phase of cavity oscillation corresponding to a positive electric field (and thus a retarding force on the electrons) leading to the front electrons in the bunch being slowed down. By the time the middle of the bunch has entered the cavity the field strength is zero and thus there is no corresponding change of momentum. When the back electrons enter, they experience an accelerating force and leave the cavity travelling faster. Since upon exiting, the fast electrons are behind the slow ones, the bunch simply compresses itself ballistically at some distance away from the lens, which of course, is where we choose to locate the specimen. It turns out it’s not very hard to adjust the focal length of a temporal lens and that the
1.6 Details of this work

At the time this work began, the limits space-charge imposed upon UED instrument performance was well understood. From the onset the primary goal was to push the field into a new regime of instrument performance, not by the practical optimization of parameters under the established experimental constraints, but instead...
by implementing a completely novel electron-optical beamline. This thesis will document the steps taken to design and characterize the next-generation UED instrument located in the Siwick research laboratory. Chapter 2 discusses the instrument in a compact geometry. Due to the added complexity that comes with integrating a RF cavity into a UED beamline, it is helpful to first become acquainted with both the details of UED theory and also to look at some compact geometry UED data. Chapter 3 will introduce the theory of RF compression and will present our RF cavity design and simulations that demonstrate the range of parameter space we can control using the cavity. Chapter 4 will present the successful experimental characterization of the instrument in the RF compression geometry and show that our instrument has improved enormously compared to the former state of the art. Chapter 5 will present the material system studied in the RF compression instrument geometry—thin film graphite—which exhibited extremely fast transient diffraction signatures (< 300 fs) for very subtle diffraction peak intensity changes (< 1%). Chapter 6 discusses some potential implications of using very high charge density electron pulses at the specimen and how they may influence the spectral character of the resulting diffraction patterns. Chapter 7 presents a conclusion and also a brief discussion of the future of UED.
References


CHAPTER 2

Ultrafast Electron Diffraction - Instrumental, Theoretical and Experimental Details

2.1 Introduction

Time resolved electron diffraction experiments, if they are to be successful in resolving atomic motions on the femtosecond time scale, must take careful consideration of several experimental parameters, trade offs and constraints. One such constraint, as was discussed in the previous chapter, is that Coulomb repulsion leads to a very rapid temporal broadening of femtosecond electron pulses. Overcoming this obstacle will be the focus of Chapters 3 and 4. Space-charge, although a major consideration for UED, is not the only concern. There are other factors—such as the synchronization and temporal overlap of the pump and probe pulses—which if not properly handled can also limit the time-resolution of the experiment. Furthermore, time-resolution is not the only determining metric towards the performance of a UED diffractometer; diffraction pattern visibility and signal to noise, which depend on the electron beam illumination conditions, the quality of the
Figure 2–1: Schematic diagram of the UED instrument in the compact geometry. The laser system outputs 3 mJ, 35 fs IR pulses which are split into two separate paths. The first beam is used for pump and is delayed by an amount $\tau$ before arriving at the specimen. The second beam is first frequency tripled to 266 nm by a set of non-linear optics before being used to photoexcite the electron pulses at a copper cathode. The electron beam is accelerated up to 95 kV and travels towards the specimen where it diffracts. The diffraction pattern is detected at the CCD camera located downstream.

sample, and the sensitivity of electron detection at the diffraction plane are equally important for capturing atomic motions. A good starting point for understanding these considerations is the operation of an ultrafast diffractometer implemented in a compact geometry.

Fig. 2–1 shows a simplified schematic of a UED system in a compact geometry. The main components can be broken down as follows: i) A chirped-pulse-amplification (CPA) laser system, ii) laser optics necessary for both the pump and probe branches of the experiment, iii) a vacuum system that houses the generation of electron pulses, the specimen, and the detector, iv) a high-voltage accelerator
serves as the source of femtosecond electron pulses, v) an electron-optical beam line that includes a magnetic focusing solenoid lens and a flight tube, vi) a computer controlled in-vacuum specimen positioner system and vii) an electron detector with single-electron detection capability. Section 2.2 will first describe the design and/or implementation of each of these elements. Next, Section 2.3 gives a very short introduction to the theory of transmission electron diffraction in order to provide details that are essential to understanding UED data. After the necessary theory has been addressed, Section 2.4 presents a short discussion on how relevant experimental parameters in the system affect both the temporal and spatial resolutions of the instrument. Last, data collected from thin-film polycrystalline gold specimens in the compact geometry will be shown in Section 2.5.

2.2 The compact ultrafast diffractometer

2.2.1 The laser system

In a compact-UED diffractometer, the durations of both the pump and probe limit the time-resolution of the instrument. Thus it is essential that the laser system—which serves as both the pump pulse and also as the source for the photo-generation of electron pulses—be capable of generating laser pulses on the order of 100 fs with sufficient energy and wavelength tunability to excite materials and cause structural changes. Femtosecond laser technology today often exploits a technique known as Chirped-Pulse-Amplification (CPA) [1] which was first used to amplify 100 fs pulses from the nJ to mJ level in 1989 [2]. Fig. 2–2 shows the CPA concept. The seed pulse from the laser oscillator cannot be directly amplified to the mJ level without damaging the titanium-sapphire (Ti:sapphire) gain medium used for power amplification due to the large peak intensities characteristic of femtosecond pulses. To circumvent this problem, the seed pulse first passes through a pair of dispersive
diffraction gratings which stretch the pulse duration by a factor of one thousand. The linearly chirped picosecond pulse that leaves the stretcher can then be amplified to the mJ level in a Ti:sapphire based regenerative amplifier. The amplified pulses which exit the laser cavity are recompressed by a second set of diffraction gratings. CPA systems today are highly efficient and commercially available. The CPA system on which the Siwick group UED instrument is based is a Spectra Physics XP® amplified fs laser system that uses the Millennia Pro® and Empower® pump lasers responsible for creating population inversions in the Ti:sapphire crystals, a Tsunami® laser oscillator which generates the seed pulses, and the Spitfire Pro XP® CPA regenerative amplifier. The pulses which leave the Spitfire Pro XP are 35 fs in duration, 3
mJ in pulse energy, have a centre wavelength of 800 nm and operate at a maximum repetition rate of 1 kHz.

### 2.2.2 Optics

The laser pulse train that leaves the CPA amplifier becomes the clock which keeps the experiment synchronized. By splitting the original pulse train in two, the relative time delay of the pump and probe arms of the experiment is defined entirely by their path length difference. The optics on the laser table must thus perform the following functions: 1) Provide a user-controllable path length difference over a range (in the temporal domain) of hundreds of picoseconds, with a step size less than 100 fs. 2) Convert the frequency of the photocathode excitation pulse above the work function of the metal photocathode inside the electron accelerator to allow for the generation of an electron beam. 3) Independently control the transverse sizes of the pump and probe beams to allow for the appropriate illumination conditions of both the pump at the specimen and the probe laser at the photocathode.

The relevant length scales in order to satisfy requirement 1, when referencing 1 ns and 100 fs at the speed of light are 30 cm and 30 µm, respectively. These disconnected length scales were simultaneously satisfied by using a computer controlled commercial translation stage with positioning accuracy and step size on the order of 1.5 µm and total travel distance of approximately 30 cm. The stage was fitted with a retro-reflecting optic which ensures that the incoming and outgoing beam at the stage position are parallel to one another, and if aligned correctly, guarantees that the outgoing beam always follows the same path independent of the translation stage longitudinal position. The relative delay of the pump and probe pulses is set by sending only the pump laser arm into the translation stage, so that the stage position uniquely defines the relative time delay at the specimen, \( \tau \) (see Fig. 2–1).
The photocathode excitation pulse creates a distribution of electrons on the front surface of a bulk copper cathode held at 95 kV. The work function at copper surfaces ranges from 4.5 - 4.9 eV, depending on the average orientation of the crystal domains, the average domain size, and the surface roughness [3–6]. Thus it will not be possible to excite (in a single photon excitation process) electrons using the fundamental frequency of the ultrafast laser. The third harmonic of 800 nm (266 nm or 4.66 eV), however, is above the work function of the copper cathode used in the instrument and it is a simple matter to frequency triple the red fundamental by using non-linear optical media. Beta-Barium Borate (BBO) is a highly non-linear optical material that is commonly used in concert with Ti:Sapphire laser systems to generate new laser frequencies by means of non-linear optical processes such as second harmonic generation, sum-frequency and difference-frequency generation and optical parametric amplification. A thorough treatment of non-linear optics is presented by Boyd [7], the details of which are beyond the scope of this thesis. Referring to the schematic presented in Fig. 2–1, third harmonic generation can be summarized as follows. The 800 nm beam interacts with the first BBO crystal in the line and generates 400 nm light through a second-harmonic generation process. Momentum-conservation (or phase matching) requires that the generated 400 nm photons are polarized perpendicular to the 800 nm photons (Type-1 phase matching) [8]. The group-velocity mismatch of 800 nm and 400 nm through BBO causes the two pulses to leave the crystal at different times. This time offset is corrected by a calcite crystal which has a birefringence that allows for the opposite group-velocity mismatch as in BBO. The temporally overlapped 400 and 800 nm pulses then enter a second BBO crystal and generate 266 nm photons by sum-frequency generation through a Type-2 phase matching process [8]. All three frequencies are collinear upon exiting the
second BBO crystal and the third harmonic is isolated by using a prism compressor and aperture.

The transverse beam size of the UV photocathode excitation pulse and the 800 nm pump are defined by the distance of the 50 and 75 cm focal length lenses to the cathode and specimen, respectively, as shown in Fig. 2–1. The UV is focused to approximately 100 μm at the cathode and the pump is sized to a variable spot size that depends on the required excitation fluence and the minimum size necessary for a homogenous illumination across the probed specimen area (typically on the order of 0.5 - 2 mm).

2.2.3 Vacuum System

The diffractometer must be held at a vacuum pressure below 10^{-5} mbar for two reasons: first, to prevent the high voltage accelerator from discharging and second, to allow the propagating electron beam to travel to the specimen and detector with minimal interaction with matter in order to preserve the beam quality and total charge.
The vacuum system was designed in a modular fashion as can be seen schematically in Fig. 2–3. Two chambers were built to house separately the electron accelerator and the specimen/detector, shown in panels A and C, respectively. The two chambers are each pumped by their own turbo pump and are sealed by a combination of ConFlat (CF) and Klein (KF) flanges. A gate valve separates the two chambers, allowing for the electron accelerator to stay at vacuum (and thus at high voltage) when the specimen chamber is at atmosphere. This allows the frequent cycling of the specimen chamber between vacuum and air necessary for the alignment of the electron and laser at the specimen without having to turn off the voltage. The pump down time of the specimen chamber is approximately thirty minutes to achieve a vacuum of $10^{-5}$ mbar and has a base pressure of approximately $10^{-7}$ mbar. The electron accelerator chamber achieves a lower base pressure of approximately $10^{-8}$ mbar since there are fewer KF flanges and only metallic and ceramic (UHV compatible materials) inside the chamber. Panel B of Fig. 2–3 shows how the vacuum system is set up in the RF compression geometry; in the compact geometry, panel B is not present and the two chambers are connected directly via the gate valve. The chambers and beam tubes have several ports and feedthroughs including: optical windows that are transparent to the laser beams, a high-voltage feed-through rated up to 100 kV, a pressure monitor for each chamber, and instrumentation feedthroughs allowing for control of the in vacuum sample positioner system and other experimental needs.

### 2.2.4 High-voltage electron accelerator

There are many reasons to work at relatively high electron energy in a UED experiment. Relativistic beams, for example, suffer from less space-charge induced temporal broadening and penetrate deeper into materials than do low energy electron beams. Building a relativistic accelerator is a larger undertaking however; there is
greater risk of electrical breakdown at higher voltages and there are also dangerous x-rays produced by bremsstrahlung, requiring experiments to be performed from a control room. If one desires a more compact accelerating structure due to laboratory space constraints, the electron energy should be limited to the 80-300 keV range of conventional transmission electron microscopes (TEM). At this energy it is possible to stay near the single-scattering limit (i.e., each electron only scatters once during its trip through the specimen) for sample thicknesses on the order of 100 nm.

The electron accelerator design is shown in Fig. 2–4. The accelerator diode structure is front illuminated by the UV laser beam and uses a bulk copper photocathode as the electron source. (The copper is only at the tip, the rest of the cathode and the anode are made of stainless steel). The anode is a hole cut in the 12” CF vacuum flange. The shape and size of both the cathode and anode are important parameters which determine the electric field distribution near the centre axis of the electron beam trajectory. If the anode is made too small, for example, there will be significant radial fields which interact with the electron beam. The interaction of such radial fields cannot easily be reversed by conventional electron optics and can lead to a deterioration of beam quality. The geometry of our accelerating diode is based on work performed by Thijs Van Oudheusden [9], which was optimized so that the on-axis fields were dominated by longitudinal components. Although the shapes and dimensions of the anode and the top surface of the cathode were based on the Oudheusden work, the rest of the accelerator assembly (the way in which the ground is separated from high voltage via the Maccor insulator) was redesigned, due to the fact that early prototypes suffered from profound high-voltage instability which limited operating voltages to less than 65 kV.
Figure 2–4: High voltage electron accelerator design. The stainless steel anode and cathode are isolated from one another by a Maccor insulator geometry. Field emission from the cathode is shielded from the insulator by stainless steel guard rails.

High Voltage Breakdown

DC electrical breakdown—the phenomena of an insulator becoming conductive—is usually understood in terms of the familiar Paschen Law, which relates the breakdown voltage $V$ to the product of the pressure $p$ and gap distance $d$ between the
cathode and anode (which in reality relates also to the diameter of the cathode/anode plates relative to the gap distance [10]) . The conductivity of gases in the presence of electric fields can be increased significantly when the gas atoms are ionized by electrons [11–13]. An ionizing electron frees a second electron from the atom it collided with, and this secondary electron—depending on its mean-free path—may acquire sufficient energy in the field to cause another ionization process in a second atom. As $pd$ approaches both positive and negative infinity the breakdown voltage monotonically increases and there is a global minimum usually in the range of 0.1-10 mbar-cm (the exact functional form of Paschen’s law depends also on the constituent gas molecules in the system). At high pressure collisions are too frequent and the gas conductivity is low since ionized electrons will not acquire sufficient energy to cause a cascade of ionizations; at low pressure there are not enough collisions to allow for a stable ionization driven current to flow from cathode to anode [12].

At very low pressures the Paschen Law predicts higher breakdown voltages than can be realized experimentally; in reality, once the pressure is low enough to prevent a discharge across the ambient gas molecules, breakdown is typically independent of pressure [14]. These pressure independent breakdown mechanisms relate to the electric field strength and distribution, the material properties of the cathode, anode and insulator as well as their geometrical lengths, shapes and relative distances. Metals at high voltage field emit electron currents in proportion to the square of the field strength [15] and these field emitted electrons are the most common driving force of electrical breakdown. They serve as the original source of ionization of gas molecules in a vacuum gap, but at sufficiently low pressure can still cause major problems. There are two mechanisms in particular that limited our original prototype accelerator voltages.
The first mechanism that is relevant is caused by field enhancement due to surface imperfections; sharp metal protrusions on the cathode in the vacuum gap will field emit higher than average currents which can significantly heat both the cathode protrusion itself and also the parts of the anode that receive large field emitted electron power densities. At a critical voltage, material from either the cathode or anode is vaporized and the local pressure in the gap fluctuates enough to lead to a cascading ionization in the same way explained above [16–21]. If the field enhancement of a protrusion is sufficiently large and the breakdown mechanism is the vaporization of the protrusion itself, the field enhancement of the protrusion is lowered since the resulting protrusion shape is usually more dull after the breakdown event. Once all protrusions have been dulled through what is known as a conditioning process, the anode becomes the likely location for vaporization. If, however, the anode material dissipates heat effectively, the anode will not limit the stability of the accelerator in the 100 kV range [20, 21].

A second mechanism that can lead to breakdown is called surface tracking and is defined by an electrical breakdown event that takes place across the surface of the insulating material separating the cathode from the anode. Experiments that were performed with an insulating dielectric such as Pyrex glass separating a cathode and anode directly in the vacuum gap revealed that the dielectric insulation lowered the breakdown voltage significantly compared to experiments performed with nothing but vacuum insulating the gap [14, 22]. The material properties of the insulator such as the surface resistivity and surface roughness, as well as the insulator length, shape and location are related significantly to the surface tracking induced breakdown voltage; the geometry of the cathode-vacuum-insulator triple junction is also very influential on the breakdown voltage which can be increased by a factor
of approximately 2 by appropriate triple junction designs [14, 22–24]. The proposed mechanism for surface tracking breakdown is that field emitted electrons at the triple junction bombard the surface of the insulator and cause the surface to release secondary electrons. The surface develops a positive charge which electrically connects the anode to the cathode leading to sustained current discharges and eventually to breakdown.

Early prototypes of our accelerator failed mainly due to the geometry of our insulator. Our attempts at conditioning the accelerator early on lead to permanent damage of the insulators; our first insulator became conductive at approximately 65 kV and our second design attempt lead to a macroscopic puncture of the insulator wall. Our third attempt proved to be successful and is based on the following three design principles/constraints: 1) The accelerating diode must stay stable for field strengths as high as 120 kV/cm, which is the field required for a 100 kV voltage drop. 2) Field emitted electrons should terminate at a conductor, not an insulator. 3) The surface protrusions on the cathode which limit the breakdown voltage should be removed by a controlled conditioning process. The cathode is separated by the anode via a machinable insulator made of Maccor (see again Fig. 2–4), which was roughened by coarse grain sandpaper. The junction of the Maccor and high voltage stainless steel was shielded by burying the Maccor inside the steel, which was rounded in order to limit field emission striking the Maccor at the triple junction. The field emitted electrons from the outer part of the rounded stainless steel were handled by adding stainless steel guard rails which connect to ground and hide the Maccor rods that connect to the anode (the guard rails draw the field emission current rather than allowing this current to bombard the Maccor). Conditioning of the accelerator in this final configuration was accomplished by a computer controlled algorithm.
that slowly ramps the voltage while simultaneously monitoring the power supply current. When any currents were measured (above field emission levels) without any change in voltage, the voltage was either held constant or reduced in order to discourage surface tracking. Breakdown at the cathode has a signature of a rapid decrease in voltage and simultaneous spike in current. Although the vaporization of protrusions leads to a more stable accelerator, if the power supply is allowed to quickly return to voltage after a breakdown event the increased pressure in the gap can lead to further breakdown which may create new protrusions [21]. The algorithm limits the creation of new protrusions by turning off the power supply immediately after a breakdown event is detected so that the vacuum pumps have time to remove material from the chamber. After every breakdown event the power supply ramps back up slowly and after a few days to a week the accelerator is capable of maintaining stable 95 kV voltages indefinitely, so long as the voltage is never turned off. Fig. 2–5 shows the geometry and field map distributions of our electron accelerator simulated using POISSON SUPERFISH [25]. Panels B and C, which present the field distributions near the centre axis, show that when \( r < 1 \text{ mm} \) the fields are dominated by longitudinal components to better than 96%.

2.2.5 Magnetic solenoid lenses

It is essential to control the transverse properties of electron pulses in a UED experiment. The pulses created at the photocathode have significant internal transverse space-charge fields which lead to a divergent transverse trajectory despite the longitudinal accelerating fields in the accelerator. In order to obtain a sharp diffraction pattern at the detector, the electron beam must be refocused transversely by external fields. Magnetic solenoid lenses were used to focus the electron beam and
Figure 2–5: Cylindrically symmetric electron accelerator field distributions. A: Geometry of accelerator. Equipotential lines are shown in red and the arrowheads show the magnitude and direction of the electric field. B: Main figure shows the longitudinal electric field at r=0. The inset shows longitudinal fields at various r values normalized to the field at r=0. C: Transverse electric field distributions near the electron beam centre axis.

were designed to require approximately 10-15 A of current. The design and optimization of the magnetic lenses used in our experiment is described in detail in Thana Ghunaim’s MSc thesis [26] and thus the lenses will only be briefly described here.

The magnetic lens must be placed as close as possible to the cathode in order to reverse the space-charge induced transverse divergence while the electron beam spotsize is still relatively small. This leads to a practical problem, since there may
Figure 2–6: Solenoidal magnetic lens design. A: Geometry of iron shielded lens. Magnetic field lines are shown in red and the purple arrowheads show the magnitude and direction of the field. The solenoid is represented by the gray area containing wire loops represented by black circles (current flows into the page). B: Longitudinal magnetic field $B_z$ at $r = 0$ for both the shielded and unshielded solenoids. C: Longitudinal magnetic field $B_z$ at $z = 0$ for both the shielded and unshielded solenoids. Simulations performed using POISSON SUPERFISH.

be significant magnetic fields present inside the accelerator gap which can lead to a deterioration of beam quality. In order to avoid this, a soft-iron shield was designed around the solenoid in order to achieve a more sharply peaked field distribution around the centre of the solenoid. Fig. 2–6 shows the shielded design geometry, as well as the shielded and unshielded field distributions. Panel B shows that the shielded lens reduces the magnetic field significantly (> 85 %) in the accelerator gap (located between $z=-6$ and $z=-5$ cm) compared to the unshielded design. Panel C shows that the longitudinal magnetic field distribution is uniform to better than 1% over the width of the electron pulse, which is approximately 1-2 mm upon entering the
solenoid. Note that in the RF geometry presented in the next chapter two magnetic lenses must be used, and the second lens is simply the unshielded geometry of Fig. 2–6.

In the ‘thin lens’ approximation to the paraxial ray equation when modelling a magnetic solenoid lens, one assumes an individual electron position does not change significantly while in the lens, i.e. it is assumed the focal length of the lens is much longer than the thickness of the lens. Following a treatment by Reiser [27], it can be shown that:

\[ r'_i - r'_o = -r \frac{e^2}{4\gamma^2 m^2 v_z^2} \int B_z^2 dz, \]

where \( r' = \frac{dr}{dz} \) for the electron with radius \( r \) from the longitudinal axis, the subscripts \( i \) and \( o \) refer to the image and object trajectories of the electron (i.e. after and before the lens, respectively), \( e, m, \gamma, \) and \( v_z \) refer to the charge, mass, Lorentz factor and longitudinal velocity of the electron and \( B_z \) is the axial magnetic field. Inspection of Eq. 2.1 reveals that a linearly correlated electron pulse, i.e. one in which \( r'_o = kr \) for some constant \( k \), will focus to a perfect point due to the fact that the right hand side of Eq. 2.1 depends linearly on \( r \) and the integral is constant. Calling \( k_2 = \frac{e^2}{4\gamma^2 m^2 v_z^2} \int B_z^2 dz \), the focal length \( f \) is:

\[ f = -\frac{1}{k - k_2} \]

and thus depends inversely on the constant \( k \) and the integral of the magnetic field squared. Since \( k_2 \) is larger for a sharp distribution of \( B_z \) the iron shielded magnetic lens allows for smaller focal lengths for equivalent driving currents. In reality, one cannot focus to a perfect point for two reasons: first, Coulomb repulsion eventually takes over at sufficiently small beam sizes and/or sufficiently high bunch charges and
these internal space-charge forces act as a negative lens affecting both the minimum spot size at the beam waist and the actual focal length; second, even in the absence of space-charge the finite emittance of a real electron pulse (to be defined explicitly later this chapter) means that a perfect linear correlation is not achievable and there is always an instrumental limit to the sharpness of a diffraction pattern.

2.2.6 Specimen positioning system

Spatial overlap between the pump and probe is achieved by using a 3-axis computer controlled set of translation stages (Micos® MT-40) that are fixed inside the specimen vacuum chamber. Each translation stage has a range of motion of 3 cm and has a step size and repeatability on the order of 3 µm. The stages are assembled together and support a single bar which attaches to the specimen holder. A schematic of the sample positioning system is shown in Fig. 2–7. The specimen holder is attached to the positioning system bar via a 2-axis tip-tilt stage which allows the fine tuning of the angle of the electron beam relative to the surface normal of the specimen. The 2-axis tip-tilt stage has a range of motion of ± 2 degrees, but is fixed via a set screw and can be rotated to up to a 45 degree angle relative to the z-axis in the x-direction, allowing for experiments to be performed where the electron beam penetrates the specimen at much larger angles. The sample holder, shown in Fig. 2–7, panel B, is a square metal frame with a 2.5 cm edge length. Thin film metallic samples can be mounted directly to the frame since it is simple to prepare films that have transverse macroscopic dimensions on the cm scale. Samples which could not be grown to the cm scale were deposited on 3 mm TEM grids which were in turn supported by a silicon wafer with etched windows. The window sizes were between 250 - 750 µm and on each wafer a single larger window was etched with edge size of approximately 2 mm. The larger window provided sharp edges which can be
used for measuring the electron and laser spotsizes and positions. It is important that the laser spotsize be significantly larger than the probed area of the specimen, so that the excitation is homogeneous. Typically we ensured that the laser spotsize was at least twice as large as the electron beam spotsize.

Spatial overlap between the pump and probe was achieved via the large window in the silicon wafer using the following procedure. The window was initially positioned such that the entire laser/electron beam travels through the window without clipping. The laser transmission was measured by a power meter after the window and the electron transmission was measured with the CCD detector. The sample positioning stages were then scanned in both the x and y directions (one at a time) and at each stage position the laser and electron transmission through the window was measured. Scans were performed starting from full transmission and continued until the beams were fully clipped by the wafer. The resulting transmission data

**Figure 2–7:** Specimen positioning system. A: Shows a side view of the sample holder and positioner. B: Shows a front view of the sample holder.
was fit using an error function for the gaussian parameters $c_x$, $c_y$, $\sigma_x$ and $\sigma_y$ of both beams. This procedure was iteratively repeated until the sizes of the beams were appropriate for the experiment and the centres of both beams were coincident.

### 2.2.7 CCD detector

The signal to noise of the diffraction pattern is a very important consideration for time-resolved diffraction experiments in that the integrated signals for each time delay define the location of atoms under study. The CCD detector used in this instrument, the Ultrascan \( \textregistered \) 1000 from Gatan Inc., is capable of single electron detection and serves UED experiments well. A phosphor scintillator sits on top of the CCD and is fiber-optically coupled to the pixels of the CCD. When a Pelletier cooler is used to lower the CCD temperature to -25 degrees C, the background noise on the camera is typically ± 2 counts per pixel. We calibrated the camera by varying the electron pulse charge over a range of energies and measured the charge directly with an electrometer and faraday cup after which we captured the total number of counts registered on the CCD under the same conditions. The calibration revealed that the number of counts per electron on the CCD was $0.1862U - 0.5660$, where $U$ is the electron energy in kV. This equates to approximately 18 counts per electron at 95 kV, consistent with the camera specifications and also significantly above the measured noise level of the detector. Since laser light is inside the chamber during each camera exposure, it is important to shield the camera from counts associated with stray laser reflections. An aluminum coating of 1 µm deposited on top of the scintillator provides such a shield. A layer of this thickness is opaque to 800 nm light but will not significantly scatter 95 kV electrons beyond the fiber-optic connections (ie. electrons will be registered by the same pixels as they would in the absence of any aluminum). Due to an error by the manufacturer, the camera was not coated
with a sufficient amount of aluminum and the detector was initially transparent to 800 nm light. We coated the detector ourselves by sputtering $\sim 300$ nm of aluminum using McGill facilities. Fig. 2–8 shows a low intensity divergent laser exposure on the camera before and after the aluminum coating was sputtered. The amount of laser induced counts on the detector was reduced by nearly three orders of magnitude after the coating, but there were some pinholes that remained. These pinholes are likely due to the initial surface roughness of the phosphor, which lead to certain pixels being ‘hidden’ from the sputtered aluminum particles by neighbouring surface imperfections. In order to prevent hot pixels from adding noise to the analysis of time-resolved diffraction patterns, great care was taken experimentally to limit the amount of stray laser that impinges upon the detector, either by blocking the light with a beam stop or by reflecting it out of the chamber through one of the laser
ports. Whatever intensity remained was measured in a background image with the electron beam off. The laser-background images were used to either subtract from the images with the electron beam on, or if necessary, were used as a mask that excluded hot pixels from data analysis.

2.2.8 Control Software

All of the components of the UED instrument described in this section must be controlled via automation software in order to synchronize the experiment and allow for data collection to proceed without suffering from human error. MATLAB® was used to write the software that controls the laser delay stage, the sample positioning stages, the pump and probe optical shutters, and the CCD camera acquisition. All tasks were modularized into a single graphical-user-interface (GUI) so that the user could set-up an experiment in the most efficient manner. Once the user finishes the initial beam-alignments, the GUI allows the user to enter a set of pump-probe time delays and specimen positions to be repeated $N$ times for a user defined camera exposure. The data acquisition then proceeds by the following iterative algorithm: i) Move laser delay stage to the next user defined position stored in the array, ii) Open pump and probe laser shutters and begin CCD integration for an exposure time defined by the user, iii) Close the laser shutters while the CCD reads out, iv) Save the image into a time-stamped file with the time delay and the scan index saved in the filename, v) Move the specimen to a new position if necessary (for non-reversible experiments) or skip this step for reversible experiments, vi) Repeat steps i)-v) until the last time-delay in the stored array is reached, vii) If the time-delay is the last in the stored array, either repeat all time delays for a new scan index or stop acquisition if $N$ pictures per time delay have been taken. This algorithm is first used to find temporal overlap between pump and probe pulses by using a coarse set of
time delays and analyzing the time-resolved diffraction data to find the onset (‘time zero’) of the transient diffraction signatures. Once time zero is found to within 1 ps, the complete set of time-delays (with finer resolution and larger range) is stored and the final experiment is performed by re-running the acquisition.

2.3 Transmission Electron Diffraction

A complete treatment of diffraction theory is beyond the scope of this work and only the key ideas will be shown here. The summary presented in this section follows closely the treatment by Fultz and Howe [28]. Relatively high energy electrons (> 30 keV) are often assumed to scatter weakly through a thin film of material. This weak scattering condition is the starting point for kinematical diffraction theory and is defined by the first Born approximation. The first Born approximation assumes that the incident free-electron wavefunction is undiminished after scattering and that the electron scatters only once while inside the material. These assumptions lead to, in the case of a single electron scattering off of a single atom:

\[
\Psi_{\text{scatt}}(\Delta \mathbf{k}, \mathbf{r}) = \frac{e^{i2\pi \mathbf{k} \cdot \mathbf{r}}}{r} f(\Delta k) \\
\Psi_{\text{scatt}}^2 = \frac{m}{2\pi \hbar^2} \int V_{\text{at}}(\mathbf{r}') e^{-i2\pi \Delta \mathbf{k} \cdot \mathbf{r}'} d^3 \mathbf{r}', \quad (2.3)
\]

where \( V_{\text{at}} \) is the atomic potential of a specific atom, \( \Delta \mathbf{k} \) is the difference between incident (\( \mathbf{k}_0 \)) and scattered (\( \mathbf{k} \)) wave vectors (\( k = \frac{1}{\lambda} \)), \( \mathbf{r} \) is the vector connecting the atom and the measurement position, and \( \Psi_{\text{scatt}}^2 \) represents the measured scattered intensity at a far field detector after many scattering events have taken place. Note that individual electron wave amplitudes do not sum coherently at the detector, instead it is their intensities that add together. (Each electron interferes with itself in a way defined by the potential). When dealing with crystals instead of single atoms, the Born approximation can be used once again, but the atomic potential \( V_{\text{at}} \)
must be replaced by the integrated potential due to all atoms in the crystal. From here forward we will ignore the spherical wave component \( e^{i2\pi \vec{k} \cdot \vec{r}} / \vec{r} \) of Eq. 2.3 since this depends on the relative geometry of the source, specimen and detector, i.e. for a fixed geometry and beam direction, the scattered intensity depends only on the fourier transform of the scattering potential, \( f(\Delta \vec{k}) \), which is called the atomic form factor. It can be shown that the scattered electron wave function after interaction with a material with \( N \) atoms, after applying the first Born approximation to the collective potential is:

\[
\psi(\Delta \vec{k}) = \sum_{j=1}^{N} f(\Delta \vec{k}, \vec{R}_j) e^{-i2\pi \Delta \vec{k} \cdot \vec{R}_j},
\]

(2.4)

where \( \vec{R}_j \) is the position of the \( j^{th} \) atom and \( f \) depends on \( \vec{R}_j \) to account for the possibility of dealing with polyatomic crystals. A crystal is a periodic structure that can be defined by a Bravais lattice plus a basis, where:

\[
\vec{R}_j = m\vec{a}_1 + n\vec{a}_2 + o\vec{a}_3 + \vec{r}_p
\]

\[
\vec{R}_j = \vec{r}_g + \vec{r}_p
\]

(2.5)

defines the location of the \( j^{th} \) atom in the crystal. The vectors \( \vec{a}_i \) depend on the symmetry (or space group) of the crystal and define the Bravais lattice via \( \vec{r}_g \), where \( m, n, \) and \( o \) are integers. It is not necessary that there be atoms at the Bravais centres. At each lattice site, there may be a basis of atoms \( \{r_p\} \) that define the coordinates of each atom relative to the site origin, for \( p = 1 : P \), where \( P \) is the number of basis atoms. A reciprocal lattice can be formulated using the direct (real
space) lattice via:

\[
\begin{align*}
\vec{b}_1 &= \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\
\vec{b}_2 &= \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\
\vec{b}_3 &= \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}.
\end{align*}
\] (2.6)

These vectors define any arbitrary reciprocal lattice vector by

\[
\vec{g}_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3,
\]

where \( h, k \) and \( l \) are integers. The real space and reciprocal Bravais lattices have the useful property:

\[
\vec{a}_i \cdot \vec{b}_j = \delta_{ij}.
\] (2.7)

Substituting Eq. 2.5 into Eq. 2.4 and re-arranging:

\[
\psi(\Delta k) = \left( \sum_{m=1}^{N_m} \sum_{n=1}^{N_n} \sum_{o=1}^{N_o} e^{-i2\pi \Delta k \cdot \vec{r}_g} \right) \left( \sum_{p=1}^{P} f(\Delta k, \vec{r}_p) e^{-i2\pi \Delta k \cdot \vec{r}_p} \right),
\]

\[
\psi(\Delta k) = S(\Delta k)F(\Delta k)
\] (2.8)

where \( S(\Delta k) \) is called the shape factor and is defined by the first term enclosed by large brackets, \( F(\Delta k) \) is called the structure factor and is defined by the second term in large brackets, and \( N_m, N_n \) and \( N_o \) are the number of unit cells along the directions \( \vec{a}_1, \vec{a}_2 \) and \( \vec{a}_3 \), respectively. \( S(\Delta k) \) depends only on the shape (via \( \vec{r}_g \)) and size (via \( N_m, N_n \) and \( N_o \)) of the crystal and \( F(\Delta k) \) depends only on the atomic/molecular structure inside each unit cell (via \( f \) and \( \vec{r}_p \)). Since the maximum of \( e^{-i2\pi \Delta k \cdot \vec{r}_g} \) is 1, and occurs when \( \Delta k \cdot \vec{r}_g \) is an integer, \( S(\Delta k) \) is maximum when \( \Delta k \) is a vector of the reciprocal lattice, as can be confirmed with Eq. 2.7. Thus we have arrived at the Laue condition for constructive interference:

\[
\Delta k = \vec{g}_{hkl}.
\] (2.9)
For each allowed reflection \([h,k,l]\), the structure factor \(F(\mathbf{\Delta}k)\) determines the relative intensity compared to other allowed reflections.

An important property of the shape factor, especially in the case of crystals with a small number of unit cells along any given direction, is that although maximum at reciprocal lattice points, there remains significant intensity off the Laue condition. This can be appreciated by rewriting the shape factor as:

\[
S(\mathbf{\Delta}k) = \sum_{m=1}^{N_m} e^{-i2\pi \mathbf{\Delta}k \cdot m\mathbf{a}_1} \sum_{n=1}^{N_n} e^{-i2\pi \mathbf{\Delta}k \cdot n\mathbf{a}_2} \sum_{o=1}^{N_o} e^{-i2\pi \mathbf{\Delta}k \cdot o\mathbf{a}_3}.
\] (2.10)

Each sum in Eq. 2.10 can be represented by a truncated geometric series:

\[
S_r = 1 + r + r^2 + \ldots + r^{N-1}
\]

\[
S_r = \sum_{i=0}^{N} r^i - \sum_{i=N}^{\infty} r^i
\]

\[
S_r = (1 - r^N) \sum_{i=0}^{\infty} r^i
\]

\[
S_r = \frac{1 - r^N}{1 - r}
\] (2.11)

where \(r = e^{-i2\pi \mathbf{\Delta}k \cdot \mathbf{a}_i}\), for \(i = 1,2,3\). It can be shown using Eq. 2.11, the intensity due to the shape factor is:

\[
S^* S(\mathbf{\Delta}k) = \frac{\sin^2(\pi \mathbf{\Delta}k \cdot \mathbf{a}_1 N_m) \sin^2(\pi \mathbf{\Delta}k \cdot \mathbf{a}_2 N_m) \sin^2(\pi \mathbf{\Delta}k \cdot \mathbf{a}_3 N_m)}{\sin^2(\pi \mathbf{\Delta}k \cdot \mathbf{a}_1) \sin^2(\pi \mathbf{\Delta}k \cdot \mathbf{a}_2) \sin^2(\pi \mathbf{\Delta}k \cdot \mathbf{a}_3)}.
\] (2.12)

Each term in Eq. 2.12 has a maximum value of \(N^2\) at reciprocal lattice points defined by \(g_{hk}\), and has a width that decreases with \(N\), i.e. large crystals have sharply peaked reciprocal lattice points. In transmission electron diffraction experiments, specimens are typically hundreds of microns in the transverse direction, but only 10-100 nm in the transmission direction, which we define to be \(z\). Fig. 2–9 shows the Laue condition for diffraction for a thin film specimen. The incident beam direction
is \( \vec{k}_{in} = \frac{\hat{n}_{in}}{\lambda} \), where \( \hat{n}_{in} \) is a unit vector. Energy conservation requires that the scattered wave vector \( \vec{k}_{out} \) be the same length as \( \vec{k}_{in} \) and so it is not possible to intersect the centre of each reciprocal lattice point. Each lattice point, however, is elongated by approximately \( \frac{2}{Nz a_z} \), (where \( a_z \) is the lattice constant along the \( z \) direction) and for a sufficiently aligned electron beam and specimen, it is possible to intersect multiple diffraction conditions simultaneously. The higher the electron
energy, the longer the $k$-vectors become, and as a result the sphere of intersection between the scattered wave vectors and the reciprocal lattice points (known as the Ewald sphere) becomes flatter and more diffraction conditions are simultaneously satisfied. At 100 keV it is possible to satisfy many orders of reflections for a given orientation. This fortuitous advantage of transmission electron diffraction comes with a price: the interpretation of the positions and intensity of Bragg peaks in a diffraction pattern for a single specimen orientation is susceptible to error due to the extent of the shape factor. Take for example, a situation in which the beam orientation angle $\alpha$ shown in Fig. 2–9 is small. The first order peak intersects the Ewald sphere a distance $\xi$ away from the centre of the reciprocal lattice point and as a result the change in wave vector $\Delta k$ is longer than the true reciprocal lattice spacing. This results in a diffraction spot with a peak position error at the detector. As we move to higher order reflections, $\xi$ does not remain constant, and we have the additional problem of different amounts of error depending on which reflection we observe. Furthermore, the ratio of diffracted intensities between different reflections, which we would normally use to define the structure factor, is also influenced by these angle dependent error terms. In time resolved experiments, there is the additional problem of the fact that the lattice constants may change dynamically and thus the errors defined by $\xi$ are also time dependent. One way to simplify experiments and eliminate these sources of error is to study polycrystalline specimens. Polycrystalline specimens have thousands of crystal domains oriented randomly to the electron beam, and thus sample a nearly continuous distribution of $\xi$ values for a given reflection, effectively integrating the reciprocal lattice point. The time-resolved amplitude and position data in polycrystalline experiments is thus much more reliable than the single crystal counterpart at fixed orientation. Single crystal experiments must be
very careful when handling these errors and the work on single-crystal graphite in Chapter 5 will describe how they were handled in our lab.

2.4 Figures of merit for a UED diffractometer

The overall performance of a time-resolved diffractometer depends on the how well the instrument can measure and resolve diffraction pattern peak intensities and also on how short a time interval structure can be frozen for each time delay between pump and probe. This section will define explicit figures of merit which allow quantification of UED instrument performance.

2.4.1 Beam brightness and emittance

The previous section showed that a diffraction pattern from a periodic crystal contains a great deal of information related to the crystal structure. The relative peak intensities define the relative position of atoms in each unit cell, the peak positions define the reciprocal lattice constants and the peak widths along the $x$, $y$ and $z$ directions of the crystal define the macroscopic size and shape of the domains under investigation. The ability to extract these material properties is impacted in essential ways by the electron beam brightness:

$$B = \frac{N}{\varepsilon_{n,x} \varepsilon_{n,y} \varepsilon_{n,z}},$$

(2.13)

where $N$ is the number of electrons in the pulse and $\varepsilon_{n,i}$ is called the normalized rms emittance along the $i^{th}$ direction. Maximizing the brightness experimentally is desired for the following two reasons. Increasing $N$ leads to a larger number of scattered electrons and thus higher signal to noise in the diffraction pattern, allowing for a more accurate and precise structure factor definition. Emittance is a quantity related to the focusability of the electron beam and limits the diffraction pattern
sharpness at the detector plane. Peak broadening as a result of emittance will first limit the ability to extract domain shape and size information and eventually will limit the accuracy of peak intensity and position information when emittance becomes so large that peaks begin to overlap with one another. In general, at any point in the propagation of a cylindrically symmetric electron beam, the normalized rms emittances are defined as [27]:

\begin{align*}
ε_{n,x} &= \beta \gamma \left( \overline{x^2 x'^2} - \overline{xx'}^2 \right)^{1/2} \\
ε_{n,y} &= \beta \gamma \left( \overline{y^2 y'^2} - \overline{yy'}^2 \right)^{1/2} \\
ε_{n,z} &= \frac{1}{mc} \left( \overline{t^2} \overline{U_c^2} - \overline{t_c U_c}^2 \right)^{1/2}
\end{align*}

(2.14)

where $\beta = v/c$, $\gamma$ is the Lorentz factor, $x' = dx/dz$, $y' = dy/dz$, $t_c$ is the separation in time between an electron and the centre of the pulse and $U_c$ is the energy of an electron in the reference frame of the pulse. At a beam waist the transverse emittances are entirely uncorrelated and analogously at a temporal focus so is the longitudinal emittance:

\begin{align*}
ε_{n,x} &= \beta \gamma \sigma_x \sigma_{x'} \\
ε_{n,y} &= \beta \gamma \sigma_y \sigma_{y'} \\
ε_{n,z} &= \frac{1}{mc} \sigma_U \sigma_t.
\end{align*}

(2.15)

When there is no coupling between motions in different directions and when there aren’t any significant non-linear self or external fields, Liouville’s theorem states that the volume of phase space is conserved and it can be shown that so are the normalized emittances. The *thermal emittance* per degree of freedom is defined as
the finite emittance that exists immediately after photoemission and is given by [29]:

\[ \varepsilon_{n,i} = \sigma_i \sqrt{\frac{\hbar \omega - \Phi_e}{mc^2}}, \]  

(2.16)

where \( \hbar \omega \) is the photon energy used to excite the cathode and \( \Phi_e \) is the effective work function of the metal. The effective work function is lowered as a result of applied electric field \( E_0 \) which reduces the potential barrier seen by surface electrons (called the Schottky effect). The effective work function is quantified by the Schottky term \( \Phi_e = \Phi_0 - \sqrt{\frac{e^3 E_0}{4\pi \varepsilon_0}} \). For copper metal photocathodes excited by UV light with a FWHM transverse size of approximately 100 microns, the thermal transverse emittance is on the order of 0.02-0.05 mm-mrad [29]. The conservation of normalized emittance when there are no particle-particle interactions or non-linear fields present makes the thermal emittance a lower-limit to the emittance at the specimen location and prevents an infinitely sharp diffraction pattern. A finite emittance broadens the diffraction peak for two reasons: the transverse emittances define an uncorrelated spread in the incident \( k \) vectors described in the previous section, and the longitudinal emittance \( \varepsilon_{n,z} \) defines a spread in wavelengths. Large unit cells have smaller diffraction angles resulting in Bragg peaks at the detector being spaced closer together. The diffraction linewidth due to emittance thus limits the largest unit cell that can be probed. The transverse coherence length, defined as the length scale over which a unit cell can be probed in a coherent fashion, is given by [30]:

\[ L_c = \frac{\hbar \sigma_x}{mc\varepsilon_{n,x}}, \]  

(2.17)

where \( L_c \) and \( \sigma_x \) have been calculated at a beam waist.

In a UED experiment there exist very significant space-charge forces at the cathode and there is always some degree of emittance growth. A linear increase to
the total pulse charge does not lead to a linear increase in beam brightness because more charge leads to larger space charge forces and thus more emittance growth. The maximum beam brightness and transverse coherence of UED electron beams, however, are not the limiting factors to the overall performance of the instrument when studying small molecules (which is limited to a much larger extent by the pulse duration of bright pulsed beams) and so producing the highest brightness beams possible (at the cathode) was not a major aspect of this work. The thermal emittance of the electron beam was minimized by ensuring the UV beam size at the cathode was small and emittance growth was limited by ensuring that the UV beam quality was high in order to prevent hot spots from leading to local spikes in Coulomb forces.

2.4.2 Pulse Flux

The trade-off between the total bunch charge defined by $N$ and the pulse duration $\sigma_t$ at the specimen was the limiting factor in UED performance for small molecules at the onset of this work. Since beam brightness is not a current limitation when unit cells are sufficiently small, a much more pertinent figure of merit is the pulse flux through the specimen:

$$J = \frac{Q_{\text{bunch}}}{\sigma_t \sigma_x^2}, \quad (2.18)$$

where $Q_{\text{bunch}}$ is the total bunch charge in Coulombs, and $\sigma_t$ and $\sigma_x$ are the rms pulse duration and spotsize, respectively. The trade-off between $Q_{\text{bunch}}$ and $\sigma_t$ discussed in chapter 1 limits $J$ a great deal in a compact geometry but is not the only concern. The transverse spotsize $\sigma_x$ is also a very important consideration. Specimens are often on the 100 micron transverse length scale and require electron probes with spot sizes
of approximately the same size. At this length scale transverse space-charge forces become significant and need to be considered.

2.4.3 Overall time resolution

The time resolution of the experiment depends on more than just the electron pulse duration, but instead can be approximately described as follows [31]:

$$\tau_{\text{experiment}} = \left( \tau_{\text{pump}}^2 + \tau_{\text{probe}}^2 + \tau_{\text{synchronization}}^2 + \tau_{\text{geometry}}^2 \right)^{1/2},$$  \hspace{1cm} (2.19)

where $\tau_{\text{pump}}$ and $\tau_{\text{probe}}$ are the pump and probe pulse rms durations, $\tau_{\text{synchronization}}$ is the rms error due to synchronizing the relative arrival time of the probe with respect to the pump, and $\tau_{\text{geometry}}$ is the rms error associated with the geometrical and/or velocity mismatch between the pump and probe pulses and depends on the relative angles between the surface of the specimen and both pulses. In the compact geometry, the dominant term is the pulse duration of the probe. The synchronization error in the compact geometry is defined entirely by the stability of the electron accelerator power supply, which has a reported stability of 0.001% over an 8 hour period. At 100 kV this corresponds to a synchronization error of only 0.23 fs/cm for every cm separating the source from sample. The error due to the pump-probe geometry is due to the laser and electron pulses being non-collinear. When the electron pulse is aligned perfectly to the surface normal of the specimen, the error due to the pump-probe geometry is just: $\tau_{\text{geometry}} = \sigma_x \sin \theta / c$, where $\theta$ is the angle between pump and probe and $\sigma_x$ is the spot size of the electron beam. The pump angle was thus always made as small as possible and was typically on the order of 10°.
2.5 Polycrystalline Gold Data

The first set of experiments that were performed using the compact diffractometer were on thin films of single-crystal and polycrystalline gold and were conducted as a test of the instrument performance. After excitation by a femtosecond laser, the electronic distribution in the gold specimen is initially out-of-equilibrium. After a short thermalization time the electrons equilibrate to a Fermi-Dirac distribution defined by temperature $T_e$ which is hot as compared to the lattice temperature $T_l$ [32,33]. The energy of the electrons then couple to the lattice via electron-phonon scattering processes until the entire system (electron+lattice) have equilibrated to the same final temperature. These set of processes are often described by a two-temperature model [32, 33]. When the thickness of the film is sufficiently small compared to the ballistic range of the initial hot non-thermal electrons, the electron distribution thermalizes into a homogenous temperature distribution, ie. there is no significant temperature gradient across the film thickness due to the optical penetration depth of the laser. For gold the ballistic range of electrons was calculated to be 100 nm [34], significantly longer than the 20 nm films used in the experiments reported here. Under these conditions the two temperature model excludes hot electron diffusive terms and can be written as [33]:

$$C_e(T_e) \frac{\partial T_e}{\partial t} = -g(T_e - T_l) + F(t)$$
$$C_l \frac{\partial T_l}{\partial t} = g(T_e - T_l),$$  \hspace{1cm} (2.20)

where $T_e$ and $T_l$ are the respective temperatures of the electron and lattice, $C_e$ and $C_l$ are the respective specific heats, $g$ is the electron-phonon coupling rate constant and $F(t)$ is the time-dependant absorbed energy density source term that is defined by the laser excitation pulse. The electronic specific heat depends (to first order) linearly on
the electron temperature and as a result Eq. 2.20 predicts that the 1/e time constant of the electron temperature relaxation after excitation (and due to the coupled nature of the equations, also the time constant of the lattice temperature rise) is increased for larger laser excitations. The validity of the two-temperature model has been explored extensively in all-optical pump-probe experiments. It has been shown that in the limit of very small absorbed energy densities (ie. a perturbative limit) and low initial lattice temperatures, the two-temperature model fails to adequately describe the electron energy relaxation due to longer electron thermalization times that approach and can even surpass the electron-phonon relaxation time [35]. However, at room temperature and moderate excitation, the two-temperature model has been shown to agree well with the time-resolved data for sub 100 nm thin film gold specimens [33], which under these excitation conditions has a thermalization time on the order of 10 -100 fs in the 0.1 - 1 mJ/cm$^2$ absorbed fluence regime [36]. The increased electron temperature relaxation time dependance on excitation fluence under room temperature conditions has recently been shown using femtosecond pulsed surface plasmon resonance [37]. Since all of these experiments have tested the validity of the two-temperature model by exploring the electron relaxation dynamics, UED provides an excellent opportunity to further test the model by exploring the lattice temperature dynamics.

UED experiments are sensitive to the temperature of the lattice through the diffracted peak intensities which depend on the lattice temperature via the well known Debye-Waller factor [28]:

$$I(T, s) = I_0 e^{-2B(T)s^2},$$  

(2.21)
where \( s = \sin \theta / \lambda \) is known as the scattering vector, \( \theta \) is half the angle between incident and scattered \( k \) vectors, \( B(T) \) is the Debye parameter and depends on the mean-squared vibrational amplitudes \( < u^2 > \) of the atoms about their equilibrium

**Figure 2-10**: Polycrystalline gold data analysis. A: Raw data of 20 nm gold film. B: Average diffracted intensity \( I \) and change \( \Delta I \) as a function of \( s \) for an excitation fluence of 0.59 mJ/cm². Colours represent time delay and range from -7 ps (blue) to 37 ps (red). C: Subtraction of inelastic background. Two linear backgrounds are fit to the \([111]+[200]\) and \([220]+[311]\) peak pairings. D: Bragg peak intensities are measured by fitting lorentzian functions to the background subtracted diffraction data.
positions and $I_0$ is the intensity of the given reflection at $T = 0$ K. The temperature dependance of $B(T)$ for gold was parameterized by Gao and Peng based on the experimentally determined phonon density of states [38,39]. Using Eq. 2.21 it is not hard to show that:

$$-\ln(1 - \Delta I) = 2s^2(B(T) - B(T_R))$$

$$\Delta I = \frac{I_{TR} - I_T}{I_{TR}},$$

where $I_T$ and $I_{TR}$ are the measured Bragg peak intensities and $B(T)$ and $B(T_R)$ are the Debye parameters at the excited and room temperatures, respectively.

The data from experiments performed on a 20 nm thin film of gold supported by a copper mesh is shown in Fig. 2–10. Panel A shows a characteristic diffraction pattern taken at a fixed pump-probe time delay. The electron pulses contained approximately 10000 electrons per pulse corresponding to a total time resolution at the sample (after accounting for the error due to pump-geometry) of approximately 800 fs. The details of the characterization of the instrument time-resolution in the compact geometry can be found in ref. [40]. The experiment was performed at a repetition rate of 250 Hz and each time delay represents an average of 20 patterns taken at a 2 second exposure. The images of Fig. 2–10, panel A were averaged by integrating the diffracted intensities at a constant radius from the diffraction pattern centre. Fig. 2–10, panel B shows the radially-averaged diffracted intensity for all time-delays, where the colours change from blue to red as the time delay changes from -7 to 37 ps. Notice that the Bragg peak intensities experience a time-dependant suppression and that the intensity in the region labelled 'thermal diffuse' increases with time following laser excitation. Both features are consistent with a temperature change of the lattice. The diffraction peaks sit on top of a background that results
from inelastic scattering events and the radial averaged data must be background subtracted for accurate determinations of the Bragg peak suppressions. Fig. 2–10, panels C and D show both the background subtraction which fit linear background terms to small sections of the data (panel C) and the subsequent fit to the Bragg peaks using a sum of Lorentzian functions (panel D).

The UED data for fs-laser excited polycrystalline gold thin films is shown in Fig. 2–11. Panel A shows the intensity dynamics of both the Bragg peaks and the thermal diffuse background. The time scale for the suppression of the Bragg peak intensities is consistent with the time scale for the increase in the thermal diffuse background intensity. The suppression of Bragg peak intensities increased as a function of $s$ in a manner consistent with the Debye-Waller Eq. 2.22, as shown in panel B of Fig. 2–11. These observations all support a mechanism of lattice heating governing the time-dependent intensity changes of the diffraction patterns. The slope of the fitted lines in panel B defines $B(T) - B(T_R)$. Assuming the temperature of the un-pumped films is 300 K, the extracted slopes were used to calculate the measured temperature change $\Delta T$ that resulted from laser excitation. The temperature change that would be expected based on thermodynamical approximations is:

$$\Delta T = \frac{F}{L \rho S}$$

$$F = a E (1 - R) (1 - e^{-\alpha L})$$

where $L$ is the film thickness, $\rho$ and $S$ are the density and specific heat of gold, $R$ and $\alpha$ are reflectivity and absorption coefficient of gold at 400 nm, $E$ is the incident pulse energy and $a = \frac{1}{\pi (w_{pump}^2 + w_{probe}^2)}$ is a geometrical term related to the pump-probe overlap and respective sizes, where $w_{pump}$ and $w_{probe}$ are the FWHM/(2\sqrt{ln2})
Figure 2–11: Lattice heating dynamics in fs-laser excited polycrystalline gold. A: Bragg peak and thermal diffuse background dynamics for an excitation fluence of 0.35 mJ/cm$^2$. B: Fit to Debye-Waller model. C: Laser induced temperature change as a function of excitation fluence. D: Lattice heating time constant $\tau$ dependence on excitation fluence.

Fig. 2–11, panel C shows a comparison of the measured temperature change from the UED data to that predicted by Eq. 2.23. The errorbars on the thermodynamically estimated data points were calculated by assuming a 95% confidence interval of $\pm$ 3 nm on the sample thickness of the film. The temperature changes calculated by both methods are consistent with one another. Fig. 2–11,
panel D shows the fitted time constants to the suppression data for the three fluences explored. The lattice heating time constant increases with increasing fluence, as is expected based on the two-temperature model Eq. 2.20. The electron-phonon coupling constant $g$ was extracted by simulating the time dynamics of the lattice temperature using the two-temperature model for the same excitation conditions as the experiment, and varying $g$ for the best fit to the experimentally determined time constants. The extracted value with 95% confidence is $g = (2.4 \pm 0.7) \times 10^{16}$ W m$^{-3}$ K$^{-1}$ and is consistent with values reported in the litterature [33]. It should be noted that there is another reported UED study on the laser-induced heating of gold carried out by Ligges et. al. [42] who measured a slightly lower coupling constant $(2.1 \times 10^{16}$ W m$^{-3}$ K$^{-1}$) extracted from a single excitation fluence (ie. no fluence dependance) experiment.

The compact diffractometer described in this chapter was used to successfully perform time-resolved diffraction experiments capable of resolving the fs-laser induced heating of a thin-film of gold for temperature changes on the order of 10 K. The next two chapters will be devoted to the task of improving the time-resolution of the instrument and at the same time allow for a much brighter electron pulse to serve as our structural probe. The pulse flux of the electron probes used for the polycrystalline gold experiments was approximately 2 pC m$^{-2}$ fs$^{-1}$. It will be shown that the use of RF-compression technology increased this figure of merit of our instrument by approximately three orders of magnitude, and that in principle pulse flux approaching $5 \times 10^{5}$ pC m$^{-2}$ fs$^{-1}$ are in reach in the near future.
References


3.1 Introduction

Temporal refocusing strategies have opened up the possibility of orders of magnitude enhancement to the pulse flux attainable in UED experiments [1]. These approaches make use of the space-charge driven expansion of femtosecond laser generated electron pulses to produce the energy-correlated distributions required for radio-frequency compression strategies. This method does not try to circumvent the space-charge problem but instead takes advantage of space-charge dynamics to enable six-dimensional phase-space imaging of the electron pulse. Transverse imaging is accomplished by regular solenoid lenses and longitudinal imaging by RF-pulse compression; space-charge induced pulse-broadening is no longer a fundamental limitation but something that can be controlled by spatio-temporal focusing with appropriate beamline elements.

Using an RF cavity to temporally compress electron pulses in the context of UED experiments was first proposed by Thijs Van Oudheusden et al in 2007 [1] in collaboration with Dr. Bradley Siwick. The original simulations performed showed
that a 0.1 pC electron pulse could be compressed to an rms duration of 20 fs using an RF temporal lens. The optimization of the RF-cavity design model used in the simulations was performed by Erwin de Jong and the RF-cavity implemented in our lab is based off of the original optimization [2]. The details of the design will not be rigorously repeated in this work but a short summary will be provided in Section 3.2 in order to elucidate what field strengths and distributions the cavity can achieve. It will be shown that these fields are sufficient to provide the necessary momentum inversion required for temporal compression. Once the cavity design has been addressed, the remainder of the chapter will be devoted to exploring the relevant experimental parameter space that significantly influences the spatial and temporal quality of the focused electron beams. The behaviour of the cavity as a longitudinal/temporal lens acting on a space-charge limited pulse of electrons will first be explored and compared to the ideal case of a non-interacting distribution in Section 3.3. Next, the limits of pulse flux will be explored in Section 3.4 by considering whether or not the electron pulse distributions at the temporal focus (or alternatively, the position of the specimen) are sufficient for the formation of a resolvable diffraction pattern. Last, a short treatment on how cavity amplitude and phase fluctuations, as well as electron beam charge fluctuations, influence the pulse duration and pump-probe synchronization at the sample position will be given in Section 3.5.

3.2 RF cavity design considerations

3.2.1 Pillbox Model

The most simple starting point in understanding how a RF cavity can be used as a lens is the pillbox cavity. Shown in Fig. 3–1, a pillbox has a disk shape with dimensions \( d \) in the longitudinal direction and \( R \) in the cylindrically symmetric transverse
direction. When the cavity is driven in the lowest order transverse-magnetic (TM010) mode, there exists only longitudinal components to the electric-field distribution, and only transverse components to the magnetic-field distribution. Specifically:

\[
\vec{E}(r, z, t) = E_0 J_0 \left( \frac{2.405 r}{R} \right) \cos(\omega t + \phi_0) \hat{z} \\
\vec{B}(r, z, t) = -i \frac{E_0}{c} J_1 \left( \frac{2.405 r}{R} \right) \cos(\omega t + \phi_0) \hat{\phi},
\]

(3.1)
where $J_i(x)$ is the $i^{th}$ Bessel function of the first kind [3]. In the TM$_{010}$ mode the pillbox resonant frequency $\omega$ depends only on the length $R$:

$$\omega \approx 2.45 \frac{c}{R}.$$

(3.2)

where $c$ is the speed of light in vacuum. If we consider the situation in which only two electrons travelling with mean velocity $v$ and separated in the time domain by $\tau$ enter the cavity at $r = 0$, it is simple to calculate the change in momentum of each electron. If we assume the front electron arrives at the entrance to the cavity at $t = t_0$ with velocity $v + \delta v$ and the back electron arrives at a time $\tau$ later with velocity $v - \delta v$, then the electrons exit the cavity with momenta:

$$p_{\text{front}}' = \gamma m(v + \delta v) - \int_{t_0}^{t_0 + d/v} eE_0 \cos(\omega t + \phi_0) dt$$

$$p_{\text{back}}' = \gamma m(v - \delta v) - \int_{t_0 + \tau}^{t_0 + d/v + \tau} eE_0 \cos(\omega t + \phi_0) dt$$

(3.3)

where $\gamma$ is the Lorentz factor defined by $v$. We will assume that the cavity phase is chosen such that an electron located directly in between the front and back electron would experience no net change in momentum upon exiting the cavity. This assumption requires that $t_0 = (\pi/2 - \phi_0)/\omega - \tau/2 - d/(2v)$. Next, we assume that both the propagation time through the cavity ($d/v$) and the time separation $\tau$ are small compared to the period of oscillation $2\pi/\omega$, allowing us to use the small angle approximation after integrating Eq. 3.3. Applying these assumptions and integrating yields:

$$p_{\text{front}}' - p_{\text{back}}' = 2\gamma m \delta v - \frac{eE_0 \omega \tau d}{v}.$$

(3.4)
Thus we see that if a pulse of electrons is linearly correlated (i.e. if $\delta v = k\tau$) the resulting momentum distribution will also be linearly correlated so long as the resonant frequency $\omega$ and cavity length $d$ are chosen appropriately such that the largest $\tau$ in the pulse (defined by the very front and very back electron) sample a sufficiently small portion of the sinusoid. In order to estimate the minimum field requirements for compressing pulses, we simply require that the momentum difference in Eq. 3.4 is negative. Electron pulses on the order of 0.1 pC and 100 keV will arrive at the cavity with durations on the order of $\sigma_t = 10$ ps for cathode-cavity distances in the range of 15-50 cm and under these conditions an RF frequency of 3 GHz is sufficiently slow to ensure the pulses sample a fairly linear segment near the zero-crossing of the sinusoid. For 100 keV electrons with $\sigma_t = 10$ ps, $\sigma_U = 1$ keV, and a cavity defined by $d = 1$ cm and a resonant frequency of 3 GHz, the front electron has a smaller momentum than the back electron for field strengths as low as 0.7 MV/m. Eq. 3.4 does not account for space-charge forces however and depending on the level of pulse charge, the minimum field strength required can be significantly higher. Also, it is of practical convenience to operate the lens with a controllable focal length, which decreases as a function of $E_0$. As will be shown in the second half of this chapter, a range of 1-10 MV/m allows for a great deal of experimental flexibility and so we will define that to be the range of field strengths to be desired for UED experiments.

Despite the analytical convenience of a pillbox model and the fact that it is clearly capable of inverting a linear distribution without disrupting the position-momentum correlations, it is not the ideal choice for implementing in practice. In the 3 GHz frequency range Eq. 3.2 requires that the pillbox radius $R$ be on the order of 4 cm. At this length scale the electric field strength remains significant for values of $r$ much larger than the typical transverse size of UED electron pulses ($\approx 1$ mm).
3.2 RF cavity design considerations

Figure 3–2: Fieldmap of the power-efficient RF-cavity. The length and direction of the arrows represent the magnitude and direction of the local electric field.

and so a great deal of energy is wasted. The drive power requirement for fields as high as 10 MV/m was simulated to be 17 kW [2]. Generating RF power to this level requires the use of a klystron and thus a pillbox is not the most cost-effective design possible.

3.2.2 Power efficient cavity design

Fig. 3–2 shows the geometry and electric field distribution of the power efficient RF-cavity used in our lab. The shape of the cavity was optimized using Poisson Superfish with the following goals in mind: 1) To tune the resonant frequency to 3 GHz. 2) To ensure the effective cavity length $d$ was sufficiently short ($\approx 1$ cm) so that $d/v$ was small compared to the RF period of 333 ps in the 100 keV range.
3.2 RF cavity design considerations

3) To localize the electric field distribution close to the longitudinal axis so to not waste energy at large $r$ values where electrons are not present. 4) To maximize the efficiency of the cavity by minimizing the dissipated energy at the cavity walls as a result of surface currents induced by the magnetic field distribution. As shown in Fig. 3–2, the power efficient design works by having two distinct regions with significantly different dimensions: a narrow ‘throat’ region which has high fields compared to the large ‘top’ region. The peak electric field on axis are much higher for the same input power since the fields are much less uniform throughout the entire volume compared to a pillbox. The length of the throat in the $z$-direction effectively defines the cavity length $d$ and the shape of the top was optimized to maximize the volume to surface area ratio which minimizes the amount of power dissipation. The resonant frequency is influenced by all cavity dimensions and so could be easily tuned to 3 GHz after satisfying the field distribution requirements. The result of the optimization is that the simulated power efficient cavity was capable of achieving 10 MV/m on-axis electric fields using only 1 kW of drive power and represents a power reduction of 95% compared to a pillbox [2].

The simulated field maps were sent to Advanced Energy Systems who machined the RF cavity using bulk copper to better than 10 micron machining precision. The machine drawings are shown in Fig. 3–3. Cooling channels which penetrate the cavity walls (but not the cavity itself of course) were installed so that the equilibrium temperature of the cavity walls could be controlled by an external recirculating chiller. As the temperature of the cavity changes so does its volume, leading to a change in resonant frequency [4]:

$$\frac{df}{dT} = f_0 k_T, \quad (3.5)$$
where $f_0$ is the cavity resonant frequency and $k_T$ is the linear thermal expansion coefficient of copper. The cooling channels thus give us the ability to fine tune the resonant frequency in order to match the drive frequency of our RF amplifier, which outputs RF pulses with a centre frequency of 2.9985 GHz. Two loops were installed into the cavity volume, one to serve as the drive loop which excites the $\text{TM}_{010}$ mode, and the second serves as a pick-up loop which gives us the ability to monitor the amplitude and phase of the fields in the cavity. The monitor loop is recessed very far away from the high field regions so to not perturb the field distributions that will interact with the electron pulses. The signal level in the pick up loop was measured to be -33 dB relative to the drive input. Both loops were carefully coupled to the cavity to ensure that maximum power is delivered to the cavity itself.
Upon receiving the cavity, measurements were performed to ensure that the resonant frequency, power efficiency and on-axis field distributions agreed with the simulations. The cavity properties were explored using a network analyzer provided by the Department of Electrical Engineering at McGill. A network analyzer sends an input signal to the cavity and then monitors the reflected signal that returns. The ratio of the forward and reflected power defines the absorbed power, and so, by sweeping a range of frequencies it is possible to determine the resonant frequency as well as the resonant bandwidth. The quality factor $Q$ of a resonant cavity is defined as the ratio of the energy stored divided by amount of power loss per cycle and is related to the bandwidth of the power absorption via [5]:

$$Q = \omega_0 \frac{\text{energy stored}}{\text{power loss}} = \frac{2f_0}{\text{BW}}, \quad (3.6)$$

where $f_0$ and $\omega_0$ are the linear and angular resonant frequency of the cavity in Hz and BW is the FWHM bandwidth of the absorbed power vs. frequency curve. The resonant frequency and bandwidth was measured as a function of the cavity temperature and these measurements are shown in Fig. 3–4, panel A. When the cavity is driven off of resonance there is a reduction in the absorbed power $P$ and a corresponding phase shift of the electric field oscillation. The bandwidth did not vary significantly and over the full range of temperatures the average bandwidth measured was 770 kHz and corresponds to a quality factor $Q = 7800$. The slope of the fitted line is $-46$ kHz/°C and is in good agreement with what is expected theoretically by Eq. 3.5. In the range explored the resonant frequency is ideal. It is possible to match perfectly the resonant frequency to the drive frequency of the RF amplifier in order to achieve maximum power absorption (at approximately 16°C) but at room temperature there still remains significant power absorption due to
the fact that room temperature resonance is only 250 kHz away from the RF pulse frequency, and thus is well within the cavity bandwidth. The on-axis electric field distribution was measured by using a 1.5 mm radius spherical Delrin® bead which was used to perturb the volume of the cavity. A volume perturbation will lead to a resonant frequency shift defined by [6]:

$$\frac{\Delta f}{f_0} = 2\pi r_0^2 \left( E_a^2 - \frac{1}{2} H_a^2 \right), \quad (3.7)$$

where \( r_0 \) is the radius of the perturbing volume and \( E_a \) and \( H_a \) are normalized quantities related to the electric and magnetic fields at the position of the perturbed volume, such that the integral over the volume of the cavity of \( E_a^2 \) or \( H_a^2 \) is unity. Since the on-axis magnetic field is zero in the TM\(_{010}\) mode, positioning the bead along the \( z \)-axis will cause a volume perturbation that is defined entirely by the local electric field. The bead position inside the cavity was scanned using a micrometer stage and the resonant frequency was measured with the network analyzer at each unique
position. From the resulting data, $\Delta f/f_0$ was normalized to the maximum value and was compared to the simulated $E^2$ profile on-axis normalized to its maximum. The results are shown in Fig. 3–4, panel B, and the data agrees very well with the simulations.

The characterization performed on the cavity with the network analyzer showed that the manufactured cavity can be used in UED experiments. The measurement of the on-axis field profile confirmed that the cavity length $d$ is 1 cm as it should be. The resonant frequency is within the control bandwidth of our RF amplifier and the measured $Q$ factor is only 15% lower than the simulated value. Since $Q$ is proportional to the stored energy, and the stored energy is proportional to the electric field squared, it is possible to predict the maximum achievable field strength by using:

$$E_{\text{lab}} = E_{\text{sim}} \sqrt{\frac{Q_{\text{lab}}}{Q_{\text{sim}}}},$$

where the subscripts lab and sim refer to the laboratory and simulated values, respectively. Since $Q_{\text{sim}} = 9134$, $Q_{\text{lab}} = 7800$ and $E_{\text{sim}} = 10.21$ MV/m, the maximum field strength achievable in practice is approximately 9.5 MV/m. As will be clear by the end of this chapter, this field strength is sufficient to achieve incredibly high charge densities compared to the state-of-the-art compact UED diffractometer.

### 3.3 Beam-line simulations

Due to the analytical challenge in correctly modelling space-charge forces in large N-body problems, investigations into the focusing properties and temporal lens behaviour of the RF-cavity are much more readily handled by numerical simulations which track a collection of particles as they propagate through a series of electric and magnetic field distributions. Where pertinent the simulation results presented
3.3 Beam-line simulations

below will be compared against a simple analytical model that was formulated for non-interacting particles.

3.3.1 The General Particle Tracer Code

The General Particle Tracer [7] code is a commercial software suite capable of full 3-dimensional particle tracking capabilities in the presence of external fields. It contains built in field map distributions as well as functions which allow user defined field maps to be imported into the environment. As a result, the field maps presented earlier for our electron accelerator, solenoid lenses and RF cavity were used in all simulations and the results presented below reflect the specific performance of our apparatus. Each field map serves as a tunable element which can be positioned at a user defined beamline location and also can be scaled by a user defined constant. For the RF-cavity field map, there is also a user defined phase term that allows the cavity to be synchronized to the arrival time of the electron pulses. Once all the field maps are defined, the simulations proceed by first defining the initial electron distribution—that we locate at the tip of the cathode inside the accelerator field map—which requires setting the initial total electron pulse charge as well as the initial spot size, pulse duration and energy/momentum distribution. The code allows for \( N \) ‘macroparticles’ in the simulation, which does not necessarily need to be the total number of electrons that are defined by the total electron pulse charge \( Q \), such that the charge per macroparticle is \( q = Q/N \). In the limit of \( q \to e \) GPT performs an MD simulation on the system of \( N \) interacting electrons. Setting \( q > e \) allows simulations to proceed more quickly, however, and becomes especially necessary at electron pulse charges approaching \( 10^6 \) electrons. At each timestep in the simulation, the force acting on each particle is calculated by considering the local electric and magnetic field at the particle position, as well as the total space-charge field due to
the other \(N - 1\) macroparticles. There are two space-charge algorithms which need to be mentioned. The first is the exact model, which considers all pair-wise interactions between particles and thus takes computational time on the order of \(N^2\). This leads to the algorithm becoming unreasonably slow when \(N > 1000\). The space-charge model used instead was a Particle-In-Cell (PIC) [8] solver which ignores pair-wise interactions and instead concerns itself only with forces due to the average charge density of the electron pulse. Both algorithms were tested in the low electron pulse charge regime (100-1000 electrons per pulse), the results of which showed that the qualitative trends of all relevant beam properties were the same for both the pair-wise and PIC model. The PIC model suffered from absolute value errors on the order of 10-50 \% in the low-moderate charge density regime, and was as high as 100\% in the very high charge density limit. The results below should be viewed in the context of order of magnitude calculations as well as providing insights into the qualitative behaviour. Most simulations performed used an electron pulse charge of 0.1 pC, which contains \(6.25 \times 10^5\) electrons. PIC simulations were performed to test what level of \(N\) was required for the simulations to converge, and it was consistently found that 25000 electrons agreed within 1-2 \% of the simulation results for \(N = 625000\). Thus all simulation results below used 25000 macroparticles.

Fig. 3–5 shows a schematic representation of the parameter space explored in the simulations, as well as a sample simulation result to help put the schematic into context. Electrons are birthed at the position \(z_0 = 0\) which is also the position the accelerator field map is placed. The initial distribution used in the simulations were: \(\sigma_{x,i} = 43\ \mu m, \sigma_{Uz,i} = \sigma_{Ux,i} = 0.2\ eV, \sigma_{t_i} = 43\ \text{fs}, V_{acc} = 95\ \text{kV}\) and variable electron pulse charge \(Q\). All standard deviations reported are rms values and can be multiplied by 2.35 to obtain full-width-at-half-maximum (FWHM) values. The first
3.3 Beam-line simulations

Figure 3–5: Schematic geometry of beam-line particle tracking simulations. The cathode, solenoid magnetic lens 1, RF-cavity and solenoid magnetic lens 2 are positioned at $z_0$, $z_1$, $z_2$ and $z_3$, respectively. The specimen is positioned at the temporal focus $z_4$ and the detector is positioned at the spatial focus $z_5$.

The magnetic lens was fixed at position $z_1 = 6$ cm and the current of the lens was chosen such that the electron beam was collimated after leaving the lens. The RF-cavity was positioned at a variable position $z_2$ and has user-controllable peak electric field strength $E_0$ and phase $\phi_0$. For all simulations (except those at the very end of the chapter) $\phi_0$ was set so that the center electron in the pulse received no change of momentum upon exiting the cavity. The second magnetic lens was positioned at the
variable position $z_3$ and has a variable current. The purpose of the simulations will be to study the properties of the electron pulses at positions $z_4$ (the temporal focus and specimen position defined by the cavity parameters) and $z_5$ (the spatial focus and detector position defined by the second solenoid parameters). We define the quantity $L = z_5 - z_4$ to be the length between the two foci, which in an experimental context defines the absolute spacing between diffraction orders at the detector.

### 3.3.2 Analytical Model

Recently it has been shown that a microwave cavity operating in a TM$_{010}$ mode can be described as a temporal lens analogously to a traditional optic or magnetic lens in the limit of zero space-charge [9]. In the paraxial ray, weak lens and thin lens approximation, it is assumed that the period of oscillation is long compared to the pulse duration, and that the change in momenta and longitudinal position of an electron in the rest frame of the pulse does not change significantly while interacting with the RF field. Under these approximations, equations for the focal length and pulse duration at the temporal focus as a function of the electric field strength and cavity phase can be derived. The focusing power of the cavity is given by [9]:

$$P_L = \frac{ed\omega}{m\gamma^3v^3}E_0\sin\phi_0,$$

where $P_L$ is related to the focal length $f_L$ by $P_L = 1/f_L$, $m$ and $e$ are the mass and charge of an electron and $d$, $\omega$, $\gamma$ and $v$ are the cavity and electron pulse properties defined in Section 3.2.1. Note that in this formalism a phase $\phi_0 = \pi/2$ corresponds to the phase at which the centre electron receives no momentum change. When it is assumed that space-charge effects can be neglected, the duration at the temporal focus is only a function of the input duration to the cavity, the electric field strength,
3.3 Beam-line simulations

cavity phase and the normalized longitudinal emittance. Specifically:

\[
\sigma_{t,z} = \left( \frac{mv}{e\beta d\omega} \right) \frac{\varepsilon_{n,z}}{E_0 \sin \phi_0 \sigma_{t,z}^2} \tag{3.10}
\]

The point at which space-charge forces become dominant can be approximated by calculating the average kinetic and potential energy of the electron pulse. The average kinetic energy (in the rest frame of the pulse) upon leaving the cavity can at most be completely converted into potential energy, which defines the space-charge limited temporal focus. When it is assumed the pulse has a constant charge density and has dimensions \( R \) in the transverse direction and \( L_z \) in the longitudinal direction, it can be shown that the potential energy for a given set of dimensions is [1]:

\[
U_p = \frac{3Q^2}{20\pi \varepsilon_0 L_z} \frac{\arctan(\Gamma)}{\Gamma}, \tag{3.11}
\]

where \( \Gamma = \sqrt{R^2/L_z^2} - 1 \). The average kinetic energy in the rest frame of the pulse after leaving the cavity is [9]:

\[
U_k = \gamma^4 U P_E^2 v^2 \sigma_{t,z}^2, \tag{3.12}
\]

where \( U \) is the mean energy of the pulse in the lab frame. Equating the two energy equations, we find the critical field \( E_0 \) for which space-charge begins to dominate the behaviour of the focused duration:

\[
E_{\text{crit}} = \frac{m\gamma v^2 Q}{2e\beta d\omega \sin \phi_0 \sigma_{t,z} \sqrt{3 \arctan(\Gamma) \frac{\arctan(\Gamma)}{5\pi \varepsilon_0 L_z U \Gamma}}}. \tag{3.13}
\]

### 3.3.3 Simulations on the focusing properties of the cavity

In order to test how well these expressions represent the behaviour of the RF cavity under conditions influenced by space-charge, simulations were performed for \( Q = 0.1 \) pC over a range of electric fields between 1-8 MV/m. The dependance on
the input pulse duration $\sigma_{t,z_2}$ was tested by repeating the simulations at different $z_2$ positions (since the pulse duration increases monotonically as the beam propagates, the duration at the input of the cavity depends on $z_2$). At each unique $z_2$ position the phase was set so that $\phi_0 = \pi/2$. The initial cathode conditions were not varied. For each unique $E_0$, the position of the temporal focus was measured in order to determine $P_L$ using $z_4 - z_2 = f_L$. The duration at $z_4$, the normalized longitudinal emittance and the energy spread at the temporal focus position were also measured. The magnetic lens at $z_3$ was turned off so that the temporal behaviour could be studied in isolation.

The results of the simulations are shown in Fig. 3–6. Panel A shows the measured pulse duration at the temporal focus. At small electric field strengths, the simulated data fit well to a hyperbolic $\frac{a}{bE_0 - c}$ function. At a critical field this function stopped fitting well and instead the data fit best with a linear function of $E_0$. The critical field depended on the position of $z_2$ and moved to higher fields at shorter $z_2$ distances. The minimum achievable focus occurred at small $z_2$ distances, measuring 25 fs rms at $z_2 = 15$ cm and 8 MV/m, twice as short as that measured for $z_2 = 50$ cm and 2 MV/m. These results agree well with the trends predicted by the analytical model; at low fields the focusing is limited by emittance and obeys the form of Eq. 3.10 and after a critical field defined by Eq. 3.13 space-charge forces become too severe and larger electric fields are no longer beneficial. This becomes more clear by observing Panels C and D. The measured energy spread (shown in Panel C) increases linearly over the entire range of electric fields for all cavity positions. The normalized longitudinal emittance (Panel D), on the other hand, is fairly constant at low fields and begins to grow quadratically after the same critical field position found in Panel A. This suggests that until the space-charge limit is reached, the cavity operates
in an emittance limited fashion. The normalized emittance measured at the input to the cavity over the entire range of cavity positions studied was constant within 10% and this is reflected by the fact that until the critical fields are reached, the normalized emittance at the temporal focus was independent of $z_2$. The vertical dashed lines of Panel D show the theoretical values of $E_{\text{crit}}$ (Eq. 3.13) defined by the
cavity positions $z_2$ and the experimentally relevant parameters. The theoretical $E_{\text{crit}}$ agrees reasonably well with the simulations. Panel B shows the measured focusing power $P_L$ as a function of $E_0$. For comparison the analytical prediction Eq. 3.9 is plotted as a solid orange line. The minimum field required to induce focusing is higher than that predicted by Eq. 3.9 since the analytical prediction assumed a zero emittance beam. There is an inherent energy spread which needs to be overcome by the cavity and thus there is a minimum electric field required to achieve a temporal focus. The energy spread upon entering the cavity is fairly insensitive to $z_2$ but since the pulse duration is very dependant on $z_2$ the minimum field required increases as $z_2$ decreases. This is because a short pulse samples smaller peak fields than does a long pulse and gets a smaller momentum inversion for the same cavity field $E_0$. The simulated data deviated from the linear dependance of $P_L$ on $E_0$ predicted by Eq. 3.9 and fit better with a quadratic function. This is likely due once again to space-charge; after the critical field has been surpassed space-charge acts as a significant negative lens, defocusing the pulse and moving the temporal focus further away than was predicted by the kinematical formula.

An interesting feature of the RF cavity is that while it operates at fields below $E_{\text{crit}}$ it is possible to temporally collimate the pulse, as is made clear by the inset in Panel C. At the precise minimum field required to induce focusing, the energy spread of the pulse is significantly reduced to the level of a few eV. Although using the cavity in this mode would not be beneficial for femtosecond experiments since the pulse duration would remain on the order of 10 ps, it would allow for a very monochromatic beam to be used in picosecond diffraction experiments to improve the spatial quality of the measured diffraction pattern, or potentially to be used for time-resolved electron-energy-loss-spectroscopy experiments [10,11].
3.4 Pushing the limits of pulse flux

To summarize, the RF-cavity works very well as a temporal lens but care must be taken when designing a beam-line. For every unique cavity position, there is a finite range of electric fields for which the cavity produces the shortest pulses and the pulses tended to shorter durations at smaller $z_2$ distances. Furthermore, the critical fields shown here depended strongly on the pulse charge $Q$ and this parameter needs to be considered in the case of working in different charge regimes.

3.4 Pushing the limits of pulse flux

Now that the general features of the temporal focusing properties of the lens have been explored, the next relevant simulation to perform is on how to achieve the highest charge density possible at the specimen position. In a UED diffractometer in which there is only one magnetic lens after the RF cavity there is no independent control of the spotsize at the specimen due to the spatial focus being constrained by the detector position (see once again Fig. 3–5). There are limits to how close the detector can be placed after the specimen since a sufficient amount of path length is required in order to resolve a diffraction pattern. Even if the diffraction pattern is resolvable in theory, the finite pixel size of a detector will limit how far apart Bragg peaks need to be in order to measure accurately. A single lens system will limit the maximum pulse flux due to these reasons. A two lens system adds a second degree of freedom, however, allowing the first lens to focus transversely at the specimen, and the second lens to refocus at the detector. In order for this to work the spatial quality at the beam waist of the first lens must be high. The spatial focus of the first lens can be thought of as the object plane (where the diffraction pattern comes to a focus) and the CCD the image plane (where it is imaged by the second lens).

In order to address what level of pulse flux can be used in UED and still achieve a resolvable diffraction pattern, the temporal and spatial properties of the electron
Figure 3–7: Spatial and temporal beam waist properties for various specimen to detector distances. A: Shows the temporal (blue) and spatial (red) standard deviations of electron pulses simulated at the temporal focus as a function of the separation $L$ between the temporal and spatial waists. B: Shows the temporal and spatial standard deviations simulated at the spatial focus as a function of the separation $L$.

Pulses must first be studied at the temporal and spatial foci. The relevant independent variable to study is the separation $L = z_5 - z_4$ between the foci. Simulations were performed for a pulse charge of 0.1 pC and the set of source/cavity parameters which yielded the shortest pulses for $z_2 = 15$ cm and $E_0 = 4$ MV/m. The focusing magnetic lens was positioned 10 cm behind the RF cavity, (ie. $z_3 = z_2 + 10$ cm). The current of the magnetic lens was then varied and the quantities $\sigma_t$ and $\sigma_x$ were measured at the positions $z_4$ and $z_5$. The results of this scan is shown in Fig. 3–7.

For increasing foci separations above $L = 10$ cm, the temporal duration at the specimen position $z_4$ did not change significantly and the transverse spotsize increased monotonically. For separations less than 10 cm, the increased charge density (and higher space-charge fields) at the temporal focus begins to influence the duration itself and the degradation of the temporal focus is accelerated for $L < 5$ cm. Over the whole range of $L$ studied ($L > 0.5$ cm), the duration remained less than 150 fs.
The range of $\sigma_x$ measured at $z_4$ was dramatic, at $L = 25$ cm it is approximately 700 $\mu$m and at $L = 1$ cm it is approximately 50 $\mu$m. Since the charge density scales with $1/\sigma_x^2$, this represents a range of pulse flux spanning two orders of magnitude. Accessing the small $L$ regime experimentally is thus a very worthwhile task. Fig. 3–7, panel B shows the properties at the spatial focus position. The spatial waist size is reduced as $L$ is decreased and is fairly small over the entire range. The temporal focus size also reduces as $L$ is decreased (since there is less time for space-charge to temporally broaden the compressed pulse) and as a result for small $L$ the charge density of the pulse is high throughout the entire transit between the temporal and spatial foci. The implication of this is addressed in Chapter 6, since it is natural to question how space-charge will affect the Bragg peak distributions during diffraction pattern formation.

A simple criteria can be made to determine whether or not a diffraction pattern is resolvable for a given $L$. First we will assume the specimen is at the position $z_4$. Next we assume that either the detector is at position $z_5$, or alternatively, a second magnetic lens has been placed after $z_5$ with the goal of imaging the diffraction pattern which is sharpest at $z_5$. Using the Bragg formula for diffraction \[12\] and assuming the specimen space group is simple cubic with lattice constant $d$, the distance in real-space between the zero-order transmitted beam and the first order diffraction peak is:

$$ r_{10} = L \tan 2\theta $$

$$ \theta = \sin^{-1} \left( \frac{\lambda}{2d} \right). $$

The spotsize $\sigma_x(z_5)$ will define both the minimum spot size of the transmitted main beam and also the width of the diffraction rings in the object plane. Thus, the
3.4 Pushing the limits of pulse flux

**Figure 3–8:** Diffraction pattern resolvability. A: Shows a simulated powder diffraction pattern with a resolvability defined by $\Omega=0.2$. B: Shows a simulated powder diffraction pattern with a resolvability defined by $\Omega=0.5$. C: Simulated $\Omega$ at the spatial focus as a function of the separation $L$. D: Simulated pulse flux at the temporal focus as a function of $L$ with resolvability ranges indicated by bands of various colours.

diffraction pattern is resolvable so long as $r_{10}$ is large compared to $\sigma_{x}(z_5)$. We can define a quantity related to the degree of overlap between diffraction orders:

$$\Omega = \frac{2\sigma_{x}(z_5)}{r_{10}}. \quad (3.15)$$

Setting $\Omega = 1$ and solving for $r_{10}$ we see that the first order diffraction peak overlaps with the main beam at the $1\sigma$ level. Similarly for $\Omega = 0.5$ and $\Omega = 0.3$ the peaks
overlap at the $2\sigma$ and $3\sigma$ levels, respectively. Fig. 3–8 shows the calculated $\Omega$ values as well as the measured pulse flux for the data shown in Fig. 3–7, where a 0.4 nm unit cell was assumed. The results are very promising, almost all of the simulated data would lead to a resolvable pattern to the $1\sigma$ level and a great deal of it is resolvable better than $3\sigma$. The level of resolvability actually required will of course depend on the specimen unit cell dimensions and whether it is polycrystalline or single crystal (since single crystal data is separated azimuthally, it requires less strict overlap criteria than polycrystalline data). Nevertheless, pulse flux as high as 0.5 $\mu$C m$^{-2}$ fs$^{-1}$ is potentially in reach in the near future. The state-of-the-art compact experiments of the past decade achieved pulse flux as high as $2 \times 10^{-4}$ $\mu$C m$^{-2}$ fs$^{-1}$ [13] and so there is room for over three orders of magnitude increase to the pulse flux as well as the potential for a 4-10 fold improvement of the time-resolution of UED experiments. With a more sophisticated illumination system pre-specimen it may be possible for even higher charge density regimes to be accessed.

3.5 Simulations at a fixed specimen position

The simulations performed to this point did not restrict our attention to a specific z position when addressing the temporal properties at $z_4$. As the parameter space was explored, the absolute value of $z_4$ did not stay constant since we were only interested in relative lengths such as $f_L = z_4 - z_2$ and $L = z_5 - z_4$. In practice, however, the specimen must stay fixed in space during an experiment and thus the way in which experimental parameters affect the temporal properties at a fixed position is a relevant question to explore. An experimental method for determining the correct phase for a given specimen position that involves measuring the temporal properties of the electron pulses in situ is a necessary experimental goal. The way in
which the electron pulses were characterized in practice will be the focus of the next chapter and here we will present simulation results which aid in those measurements.

At each unique specimen position there is a global minimum pulse duration which requires both the ideal phase \( \phi_{\text{opt}} \) and the ideal amplitude \( E_{0,\text{opt}} \). The ideal phase was found to be slightly different that \( \phi_0 = \pi/2 \), but for all practical purposes \( \pi/2 \) suffices as the ideal phase. Observing Eq. 3.9, we see that the focal length \( f_L \) is related inversely to the product \( E_0 \sin \phi_0 \). When we are operating at or below the optimal electric field \( (E_0 < E_{0,\text{opt}}) \), any choice of \( \phi_0 \) that is different than \( \phi_0 = \pi/2 \) will result in an increased focal length (since \( \sin \phi_0 \) is at most 1). When the focal length is no longer matched to the specimen position, the measured duration necessarily gets longer. If, however, we are at a large electric field strength such that \( E_0 > E_{0,\text{opt}} \) we have also caused the focal length to decrease and so there will exist two values of \( \phi_0 \) that bring the focus back into the specimen plane. We therefore expect two local minima in a phase scan when we are at electric fields above that which is ideal. This behviour is shown in Fig. 3–9, Panel A. The way the focal length responds to both amplitude and phase allows us to develop an algorithm for tuning the cavity parameters to their optimal values. If we are below the optimal electric field we will observe only one minima during a phase scan and when above we will observe two, and in either case the optimal phase is clear. We can therefore iterate between adjusting \( E_0 \) and \( \phi_0 \) until we arrive at the global minima, each time knowing if we have gone too far in one direction.

Now that we understand how to tune to the ideal cavity parameters, a second relevent question is to what degree experimental fluctuations will influence the pulse duration at the specimen position. The stability of the UV power will in turn lead to charge fluctuations and the pulsed nature of the RF amplifier which drives the cavity
3.5 Simulations at a fixed specimen position

Figure 3–9: Simulations at a fixed specimen position. A: Simulated pulse duration at \( z = 77 \) cm as a function of the cavity phase for various electric field strengths and cavity position \( z_2 = 50 \) cm. B: Simulated pulse duration at \( z = 77 \) cm, \( \phi = \phi_0 \) and \( E_0 = 1.985 \) MV/m as a function of the electron pulse charge. C: Simulated pulse duration at \( z = 77 \) cm and \( \phi = \phi_0 \) as a function of the electric field strength. D: Pump-probe synchronization error due to phase fluctuations. The magnitude of the arrows represent the average exit velocity kick the pulses receive after interacting with different portions of the sinusoid. A phase slip of \( \Delta \phi_0 \) leads to an electron pulse arrival time error \( \Delta t \).

may lead to both phase and electric field strength fluctuations, not to mention that temperature fluctuations in the room will also lead to fluctuations/drifts of all three of the aforementioned properties. Observing Fig. 3–9, panels A,B, and C, it is clear
that when the system is originally tuned to the optimal values, the pulse duration remains less than 100 fs rms over the range of 0.1 rad for $\phi_0$, 0.15 pC for $Q$, and 0.4 MV/m for $E_0$. Measurements on the charge stability and the electric field stability in the lab are well below these limits and it is not expected for them to contribute significantly to time-resolution degradation. A much more serious concern is the phase stability, which needs to be much better than 0.1 rad due to another reason. Although a small change in $\phi_0$ does not affect the pulse duration significantly, it does lead to a modulation of the mean energy of the pulse post-cavity, due to the fact that the average electron will interact with a different part of the RF sinusoid. This is shown schematically in Fig. 3–9, Panel D. A phase slip $\Delta \phi_0$ leads to a change in arrival time of the electron pulse at the specimen position given by [9]:

$$\Delta t = -L_s \frac{P_L}{\omega} \Delta \phi_0,$$

(3.16)

where $L_s$ is the distance between the cavity and specimen. UED experiments work by defining the relative time between pump and probe pulses and so an unknown arrival time fluctuation leads to an improper time-stamping of a given diffraction pattern. When the specimen is located at the temporal focus, Eq. 3.16 can be simplified since $L_s = 1/P_L$ in this case; in fact, the amount of arrival time jitter at the specimen is not dependent on $L_s$ when the system is optimally compressed. In order to ensure arrival time stability better than 100 fs, Eq. 3.16 requires phase stability on the order of 1 mrad.

With the simulated RF cavity having been shown to operate correctly, and with a good understanding of how the experimental parameter space influences the spatial and temporal properties of the electron pulses, we are now in a position to implement the cavity in practice and attempt to measure high brightness sub-ps
electron pulses. The following chapter will present a detailed description of how the electron pulses were synchronized to the RF-cavity and then temporally characterized at the specimen position, the results of which demonstrated a dramatic improvement compared to the pulse flux reported in Chapter 2.
References

CHAPTER 4

Experimental Characterization of the RF Cavity Compressed UED Instrument

4.1 Introduction

The previous chapter presented the concept, design and modelling of an RF compressed electron beamline for UED. The practical details of RF cavity design, operation and performance was also discussed. This chapter will focus on the experimental characterization of the performance of the RF compression system in practice and with emphasis on the time resolution of the diffractometer. First we discuss the femtosecond laser/RF cavity synchronization system that is at the heart of this approach in Section 4.2. Second, we describe the all-optical characterization of the temporal impulse response function (IRF) of the diffractometer in Section 4.3. The ponderomotive cross-correlation characterization measurements presented in Section 4.4 will show that the RF compressed beamline functions in a way consistent with the simulations of the last chapter; that is, electron pulses with charge in excess of 1 million electrons can be compressed by the RF system to durations on the order of 100 fs. The IRF, however, depends not only on the pulse
duration, but also on the magnitude of the RF phase-synchronization jitter (which leads to fluctuations of the electron pulse arrival time at the measurement position). A statistical analysis will be presented in Section 4.5 which quantifies the degree to which these two contributions—pulse duration and phase jitter—may be limiting the system. We end the chapter with a discussion in Section 4.6 of the day-to-day characterization of the instrument time resolution using a novel laser-activated streak camera which adds a great deal of experimental flexibility when performing time-resolved diffraction experiments.

4.2 RF cavity timing electronics

The relevant quantities which define the time resolution of the instrument are the pulse duration $\sigma_t$ and the jitter on the arrival time of the electron pulse relative to the pump laser $\sigma_\tau$. Together, these two quantities define the IRF full-width-at-half-maximum:

$$\text{IRF FWHM} = 2\sqrt{2\ln 2} \sqrt{\sigma_t^2 + \sigma_\tau^2}. \quad (4.1)$$

The IRF FWHM limits the fastest process which can be studied with the instrument and must always be considered simultaneously with the average number of electrons inside the pulse. As was shown in the previous chapter, the phase stability of the RF cavity must be on the order of 1 mrad for an IRF FWHM on the order of 100 fs. We thus need a system for synchronizing the arrival time of the mean electron in the pulse to the correct phase leading to ideal compression—on a pulse-to-pulse basis—in order to make $\sigma_\tau$ as small as possible. This section will detail the way in which the RF cavity was synchronized to the laser system.

The problem of synchronizing the electron pulse to the correct cavity phase begins by considering the case of allowing all oscillators in the lab to run freely based
**Figure 4–1**: RF cavity synchronization and amplification system. The 75 MHz laser oscillator pulse train generates an electrical signal used by the PLL to phase-lock the RF cavity oscillation with the femtosecond laser. Electron pulses generated at the photocathode arrive at the RF cavity and interact with electric fields defined by the electric field strength $E_0$ (set by the amplifier) and phase $\phi_0$ (set by the PLL). These settings lead to a temporal focus at the position indicated by the dashed red line. The pulse will arrive at the temporal focus position at some time $t$ after interacting with the cavity and will have a duration $\sigma_t$.

on their own reference clock. Since the laser oscillator is not generally commensurate with the RF cavity frequency of 3 GHz, the phase of the cavity electric field each electron pulse samples in a free-running mode varies significantly pulse-to-pulse and $\sigma_T$ is large. Note that a perfect frequency of 3 GHz would be commensurate with a perfect frequency of 75 MHz and the precision on the absolute frequencies will determine the level of phase slipping. If the oscillator frequency is $\nu_o = (75 \pm \Delta)$ MHz and the RF cavity frequency is $\nu_c = 3$ GHz, $\Delta$ needs to be less than 0.2 mHz in order to stop phase slipping on the mrad level over a time period of 1 s. Temperature fluctuations in the lab make this level of precision impossible to
achieve in practice and so a free-running pair of oscillators will not be sufficient for a low-jitter compression system.

There are two possible strategies for synchronizing the two oscillators: (1) lock the laser to the 3 GHz signal that drives the cavity or (2) lock the cavity to the laser repetition rate frequency ($\sim 75$ MHz). Approach (1) requires a feedback system with rapid control over the laser cavity length and is in principle possible, albeit with low bandwidth ($\sim 1$ kHz). We choose to implement option (2) since the electronic oscillator which generates the 3 GHz signal has a control bandwidth more than 3 orders of magnitude higher than the laser cavity ($\pm 1.5$ MHz). Fig. 4–1 shows a schematic of the timing system used in our lab. The RF cavity is synchronized to the oscillator by using a phase-locked-loop (PLL) electronics module which sets the phase of the RF pulse before being amplified by the kW RF amplifier. The PLL can be viewed as the knob which sets $\phi_0$ by applying a phase-shift to the phase-locked signal and the RF amplifier is the knob which sets $E_0$. Together these two knobs define both the arrival time $t$ and the pulse duration $\sigma_t$ at the specimen.

The PLL compares two signals together: the first is its own internal 3 GHz oscillator signal and the second is an electrical signal that is created by splitting the 75 MHz laser oscillator pulse train before it enters the CPA amp and allowing a small amount of it to impinge upon a fast-photodiode (see Fig. 4–1). Fig. 4–2 shows a more detailed diagram of the PLL electronics. Inside the PLL, the 75 MHz electrical pulse train is filtered for its 375 MHz harmonic ($\omega_1$) and the 3 GHz PLL internal frequency is filtered for its 375 MHz sub-harmonic ($\omega_2$). These two signals arrive at a double-balanced-mixer (DBM) which responds non-linearly to the two inputs and outputs a signal: $y = A \sin((\omega_1 - \omega_2)t + \phi_1 - \phi_2)$. This difference signal is then used in a feedback loop to continuously control the voltage controlled oscillator (VCO)
which sets the internal PLL frequency. The VCO continuously adjusts the frequency \( \omega_2 \) until \( \omega_1 = \omega_2 \). At this point the difference frequency voltage is minimized and the time-dependance on the difference signal vanishes: the two signals are thus in phase. The PLL implemented in our lab is a commercially available product from AccTec B.V. [1]. Its loop electronics have been characterized for the amount of phase jitter and drift over the frequency range which defines the control bandwidth of the VCO, the results of which demonstrated a total rms phase jitter of 18 fs and a drift of 20 fs/h [2].
4.3 Characterization of the instrument IRF

In order to characterize our system in a way that reflects performance in a pump-probe geometry, ponderomotive scattering measurements were performed, the details of which are shown in Fig. 4–3. A discussion of the rigorous details of the ponderomotive measurement is beyond the scope of this thesis and can be found in the following work [3–7]. The basic principle behind the measurement is that a free electron experiences a net, time-averaged force when it interacts with an inhomogeneous optical field; that is, the electron motion consists of a quiver oscillation and a time-averaged drift component in the direction of low field strength [3]. The time-averaged ponderomotive force can by expressed by [4]:

$$\vec{F}(\vec{r}, t) = -\frac{e^2 \lambda^2}{8\pi^2 m\epsilon_0 c^3} \nabla I(\vec{r}, t),$$

where $e$ and $m$ are the mass and charge of an electron, $\lambda$ is the laser wavelength and $I$ is the laser intensity. The strength of the force is proportional to the gradient of the local field intensity. For a single laser pulse, the field spatial gradient is determined by the details of the laser pulse envelope, $c\sigma_{t,\text{laser}}$, where $\sigma_{t,\text{laser}}$ is the laser pulse duration. Using a single laser pulse to perform the cross-correlation of UED electron pulses requires laser powers beyond that typical of table-top systems [4]. In order to achieve larger field gradients a technique was developed which functions by first splitting the laser in two and then carefully aligning the two beams so that they arrive at the specimen overlapped in space and time and travelling in counter-propagating directions (Fig. 4–3, panel A). At the moment of spatial and temporal overlap, a standing wave is created and the local field gradient in the pulse is determined by $\lambda/2$ (Fig. 4–3, panel B). Since $\lambda/2 << c\sigma_{t,\text{laser}}$, the standing wave approach enhances the field gradient significantly ($\sim$ factor of 25) compared to a single pulse approach.
4.3 Characterization of the instrument IRF

Figure 4–3: Details of the ponderomotive scattering measurement. A: Shows a schematic of the characterization geometry. The electron pulse arrives at the specimen position with a time delay $\tau$ relative to the arrival of two counter-propagating pump pulses. B: Shows the standing wave which occurs when two counter-propagating laser pulses overlap in time and space. C: Shows the resulting electron spot measured at the CCD for the three delays indicated in Panel A.

This technique was demonstrated to be capable of characterizing sub-ps electron pulses in a compact geometry [5] and has also been used to characterize the local internal charge density (pulse envelope) of UED electron pulses [6].

The IRF characterization procedure can be understood by observing Fig. 4–3. In panel A, the pulsed electron beam intersects with the counter-propagating pulsed laser beams at 90° to determine the measurement/interaction region. Immediately before this point the electron beam is apertured by a pinhole to 100 $\mu$m in order to better match the transverse spots size of the electron beam to the pulse envelope of the laser beams. The pinhole leads to a higher level of signal to noise, since a larger
percentage of the measured electrons will interact with the scattering potential of the laser beams. The electron beam profile is detected with the CCD camera located downstream from the interaction point. The relative timing of the electron and laser pulses at the interaction point is determined by two optical delay stages; the first stage delays the laser beams relative to the electron pulse by $\tau$ and the second stage delays one of the split beams relative to the other by $\tau_p$. The second delay stage allows the two laser beams to arrive at the electron/laser beam crossing point at the same time leading to the standing wave shown in Fig. 4–3, panel B. When $\tau$ is set such that the electron pulse does not overlap with this standing wave at the crossing point (indicated by $\tau_1$) there is no ponderomotive interaction and the spot on the CCD is undistorted as seen in Fig. 4–3, panel C. The other two images shown in panel C represent different levels of electron/laser temporal overlap; $\tau_2$ shows the case for interaction with the tail of the electron pulse, and $\tau_3$ shows the case of interaction with the centre of the electron pulse. The total ponderomotive scattering signal, $I$, measured at the CCD for each delay setting $\tau$ is defined by [5]:

\[ I(\tau) = \int |X| D_\tau(X,Y)dXdY, \]  

(4.3)

where $X$ and $Y$ are the pixel coordinates on the CCD and $D_\tau(X,Y)$ is the number density of electrons measured at $(X,Y,\tau)$. $I(\tau)$ has been shown to be determined by a convolution between the temporal profiles of the laser and electron pulse as well as the time required for electrons to cross the laser beam waists ($\tau_{\text{cross}} \propto \frac{\sigma_{x,\text{laser}}}{v}$, with $v$ being the mean electron velocity) [5]. This crossing time dependance becomes clear when observing Fig. 4–3, panel A: if the electron pulse length (measured in the $z$-direction) is much shorter than the beam waist of the laser ($\sigma_{t,\text{electron}} < < \frac{\sigma_{x,\text{laser}}}{v}$) then $I(\tau)$ provides a ‘map’ of the laser spot field distribution, ie. $I(\tau)$ \(\propto\).


\[ e^{-(v \tau)^2/\sigma_{x,laser}^2} \] rather than being representative of the the time-dependent charge distribution in the electron pulse. The width of impulse response function of the measurement can be expressed as:

\[
\text{IRF}_{\text{MEAS}} \text{ FWHM} \approx \sqrt{\sigma_{l,\text{laser}}^2 + \left(\frac{\sigma_{x,\text{laser}}}{v}\right)^2}.
\] (4.4)

The beam waist of the laser pulses was set using a pair of 5 cm focal length convergent lenses leading to \(2\sqrt{2\ln2}\sigma_{x,\text{laser}} \approx 15 \mu\text{m}\). This, along with the laser FWHM pulse duration of 30 fs leads to \(\text{IRF}_{\text{MEAS}} \text{ FWHM} \approx 100\) fs. For instrument IRF FWHM values greater than \(\text{IRF}_{\text{MEAS}} \text{ FWHM}\), the laser properties do not dominate and \(< I(\tau) >\) is a direct measure for the time-averaged local charge density in the electron pulse measured at \(\tau\). The FWHM of the \(< I(\tau) >\) vs \(\tau\) curve therefore defines the width of the instrumental IRF as both \(\sigma_t\) and \(\sigma_\tau\) will affect the average local charge density.

4.4 Results

4.4.1 Initial Beam Settings and Alignment

The pinhole aperture shown in Fig. 4–3 was created by positioning a layer of aluminum foil at 45° to the electron beam/laser directions and allowing one of the laser pulses to focus onto the foil (which creates the pinhole aperture). The aperture was first used to spatially overlap the two laser pulses. The pinhole was scanned across each laser beam waist (one at a time) and the transmission was measured with a power meter. Each scan defines the \((x,y,z)\) position of the laser waists and this procedure was iterated until both waists were localized within 2-3 \(\mu\text{m}\) of each other. The aperture was then translated 2 mm (in the \(z\)-direction) in front of the interaction point of the two laser pulses in order to serve as the pinhole for the electron beam (translating in \(z\) ensures the electron beam is spatially overlapped with the
laser pulses). Electron pulses were prepared at the cathode using the third harmonic of the laser as described in Section 2.2.2. A 100 µm circular aperture, strongly overfilled with the UV laser illumination, was imaged 1:1 on the cathode so that the initial charge distribution immediately after photoexcitation is best described by a nearly top-hat distribution (rather than Gaussian). Temporal overlap of the two laser pulses and electron beam was found by performing a two-dimensional scan of both optical delay stages and measuring the ponderomotive signal $< I(\tau, \tau_p) >$ at each pair of delays. Once a signal above noise level was found the temporal overlap of the laser pulses was optimized at a fixed $\tau$ by maximizing $< I(\tau, \tau_p) >$ as a function of $\tau_p$. The ideal $\tau_p$ only needed to be determined once and after it was optimized all subsequent measurements were one-dimensional in $\tau$. For a given set of photocathode/RF cavity experimental parameters, the mean arrival time of the electron pulse relative to the laser pulses, $< \tau >$, and the IRF FWHM are determined by scanning $\tau$ and measuring the profile of $< I(\tau) >$. The mean arrival time and IRF FWHM were extracted by fitting a Gaussian function to the profile or by calculating the statistical moments of $< I(\tau) >$ for instrument settings that did not lead to Gaussian time-averaged charge distributions.

The amount of charge was varied between 10-500 fC and although each charge required different cavity settings, charge was not found to limit the resulting IRF FWHM. The data reported below was taken using 0.1 pC electron pulses. The first magnetic lens was tuned in order to approximately collimate the electron beam through the RF cavity. The distance between the photocathode and the measurement position as well as the distance between the cathode and RF cavity constrains the temporal focal length required to achieve the minimum IRF FWHM. The cathode-cavity distance was determined to be 54.3 cm by the instrument machine drawings.
The cathode-measurement position distance was determined by recording the change in mean arrival time $<\tau>$ at two different electron beam energies with the RF cavity turned off; in this mode, the change in arrival time depends only on the change in energy and the propagation distance. The measurement position was determined to be 80.3 cm from the source, a number consistent with the machine drawings of the instrument. With everything being constrained in this way, the only parameters left are $E_0$ and $\phi_0$ and so the experimental results can be compared to the simulations of the previous chapter.

The optimal phase $\phi_0 = \pi/2$ was first roughly approximated by varying $\phi_0$ while monitoring the electron beam transverse spotsize. There are significant transverse magnetic fields on-axis inside the RF cavity which tend to focus the electron beam near $\phi_0 = 3\pi/2$ and defocus the electron beam near $\phi_0 = \pi/2$. The maximum electron beam spotsize roughly coincides with the optimal phase. The phase was refined further by measuring the IRF FWHM at various $\phi_0$ values in the proximity of the rough approximation and at an electric field strength setting $E_0 > E_{0,\text{opt}}$. This procedure yields two IRF FWHM local minima as described in Section 3.5. A first guess at the optimal phase is then defined to be centred between the two local minima. At this point $E_0$ is reduced until a global minima is found. Small adjustments to $\phi_0$ and $E_0$ were made iteratively about the global minimum settings in order to further refine the minimum IRF FWHM.

4.4.2 Ponderomotive Characterization of RF compression

Fig. 4–4 demonstrates the temporal focusing properties of the RF cavity for an electron bunch charge of 0.1 pC. The impulse response at the measurement position is shown for several amplitude settings up to the point of optimal compression in panel A. It is clear from Fig. 4–4 that as $E_0$ is increased towards optimal compression the
local charge density increases and the FWHM impulse response of the instrument decreases (see panel B for FWHM values). For amplitudes less than the optimal field, the RF cavity is operating in an under-focused mode and the temporal focus is located beyond the measurement position and vice versa for amplitudes greater than the optimal field. At optimal compression the impulse response is relatively insensitive to cavity amplitude instabilities; amplitude fluctuations of $\sim 3$ percent only lead to an increase in the IRF FWHM of $\sim 50$ fs.

The performance of the system is much more sensitive to phase stability. Changes in relative phase affect both the temporal focal length and the mean arrival time $<\tau>$. Fig. 4–5 shows the behaviour of both the mean arrival time $<\tau>$ and the measured impulse response function for an amplitude $E_0 = 1.66$ MV/m over a range of relative phase settings. This electric field strength is above the optimal value and so there are two phase settings that bring the (sub-optimal) temporal focus into coincidence with the measurement position since the $\sin \phi_0$ term makes
Figure 4–5: IRF dependence on RF cavity phase. A: Shows the measured cross-correlation at $E_0 = 1.66$ MV/m at various phase settings centred at $\phi_0 = \pi/2$. The delay $\tau$ shown here represents a fixed laser delay setting and the time offsets between the impulse response functions shown as different colours is entirely due to the RF cavity setting. The inset shows the mean arrival time $<\tau>$ (or time-offset) for each cavity phase setting (colours of the inset match the colours in the main figure). B: Shows the measured IRF FWHM extracted from the cross-correlation data, where the colours correspond to the data in panel A. The dashed line shows the best fit to the data using GPT simulations.

Eq. 3.9 symmetric about $\pi/2$, (see panel B). The mean arrival time was found to depend linearly on the phase (over the range of $\phi_0$ shown in the figure), and the measured slope at 1.66 MV/m was found to be approximately 63 ps/rad at $\sim 2.998$ GHz, (see inset of panel A). This slope agrees within 10% of the theoretical slope predicted by Eq. 3.16. Thus, in order to maintain arrival time stability less than 100 fs, phase stability of less than 0.0016 rad is required. This corresponds to electron pulse arrival time fluctuations at the cavity of less than 84 fs with respect to $\phi_0$.

Throughout the course of several months daily measurements similar to those shown in Fig. 4–4 and Fig. 4–5 were performed to characterize the day to day (and hour to hour) fluctuations in the IRF and also to investigate the parameter space
which may be limiting the system performance. Poor UV beam quality as well as large pointing jitter of the 75 MHz optical pulse train on the fast photodiode were determined to significantly increase the minimum achievable IRF FWHM. The UV quality affects the initial space-charge forces that broaden the electron pulses during propagation and influences the linearity of the position-momentum distribution upon entrance to the RF-cavity. Pointing jitter of the 75 MHz pulse train will lead to intensity fluctuations measured by the diode when the pointing jitter width approaches the diode size. Intensity fluctuations at the photodiode are linearly related to the phase-synchronization error of the PLL circuit [2]. The results shown here are those under the most ideal UV illumination and 75 MHz pulse train pointing conditions, which once optimized, remained stable and yielded reproducible results.

The remaining parameter space we could control in the lab did not yield significant changes to the measured IRF. The smallest IRF FWHM measured with the ponderomotive cross-correlation system is the data at 1.57 MV/m in Fig. 4–4. The FWHM of the gaussian fit to the data was 350 fs and after deconvolving out the impulse response of the measurement the extracted IRF FWHM is 334 ± 10 fs. It should be noted that the ponderomotive measurements reported here were conducted in parallel to those at the University of Toronto under the supervision of Prof. Dwayne Miller. Both our work and theirs was submitted for publication within 2 months of each other and the results in both studies were consistent with one another, although our measured IRF FWHM is slightly shorter [8,9].

4.5 Synchronization Drift and Jitter

The first demonstration of an RF-compressed electron pulse was performed by Thijs van Oudheusden et. al. in 2010 [10]. The measurements were performed by positioning a second 3GHz RF cavity immediately after the compression cavity. The
second cavity operated in the TM110 mode and was designed to quickly ‘streak’ the electron pulse transversely by an amount proportional to the electron pulse duration, $\sigma_t$. The measured pulse durations in the van Oudheusden work were less than 235 fs FWHM. The streak camera measurements were not sensitive to stability of the laser and electron pulse synchronization characterized by $\sigma_\tau$, however, since there was no laser to serve as reference for the definition of $\tau$.

The results reported here are inherently sensitive to both the pulse duration of the compressed electron bunches as well as the rms jitter of the laser/electron pulse synchronization system. Fig. 4–5 showed that an RF cavity phase change leads to a linear time offset of the electron pulse at the measurement position and that phase stability better than 1 mrad is needed for sub-100 fs synchronization jitter. This section will present data and analysis which investigates both the long and short time scale phase-stability of the instrument.

### 4.5.1 Slow Drift

In order to begin investigating the relative time scales of phase slipping, data was collected which continuously monitored $<I(\tau)>$ as a function of the laboratory time in minutes, as shown in Fig. 4–6. The data shown was collected by scanning $\tau$ from -1 to 1 ps without adjusting the RF cavity parameters. As the laboratory time progresses, the centre of the temporal impulse response function, $<\tau>$, does not stay constant relative to the fixed laser delay settings. This drift of $<\tau>$ is due to drift in the RF cavity phase and represents a ‘time zero’ offset between the electron pulse and the laser pulses. A complete IRF can be measured with sufficient signal-to-noise using 250 shots to define $<I(\tau)>$ for approximately 10-40 values of $\tau$. A single pass through all $\tau$ values takes 20-90 seconds and so we can monitor IRF centre drift on this time scale. Measurements of this type take too long to track the
Figure 4–6: Long time scale phase drift. The colour from blue to red shows the magnitude of $\langle I(\tau) \rangle$. The mean arrival time offset of the electron pulse relative to the laser delay, $\langle \tau \rangle$, defined approximately by the red portion of the data, does not stay constant on the time scale of several minutes.

Shot-to-shot variations of $\langle \tau \rangle$, however, since each electron pulse is separated in time by 1 ms. The shot-to-shot rms synchronization jitter $\sigma_{\tau}$ will be explored by a different type of measurement presented in the following section. Fig. 4–6 shows the drift in $\langle I(\tau) \rangle$ over the course of 45 minutes. The system regularly exhibits periods with essentially zero drift on $\langle \tau \rangle$ and there are other times when the drift on $\langle \tau \rangle$ is significant and on the order of 0.1-1 ps per hour. Luckily drift is an easily recognizable signature and can be tracked in a UED experiment. As will be shown in Appendix D, drift can actually be corrected in data analysis so long as there is an accurate definition of $\langle \tau \rangle$ made regularly. Measurements similar to those shown in Fig. 4–6 showed that the laser oscillator frequency was found to be
related linearly to the phase of the cavity by the amount of 3.8 fs/Hz. The oscillator frequency measured a very stable value on the short time scale and as a result it is not believed to contribute significantly to the shot-to-shot phase jitter. In order to avoid oscillator frequency related phase drift a feedback circuit was designed to keep the oscillator frequency fixed to 1 Hz. The drift that remains when the oscillator is locked is attributed to temperature fluctuations of the cavity (which lead to a shift in resonance and a subsequent phase change) and also PLL related synchronization drift.

4.5.2 Statistical analysis of the shot-to-shot jitter

As explained above, the average scattering signal $< I(\tau) >$ is not performed on the pulse-to-pulse level since an accurate measurement of the IRF takes at least 20 seconds. The shortest IRF FWHM measured (330 fs) is significantly longer than the expected pulse duration of 100 fs predicted by the GPT simulations. Since it is not possible to make complete IRF measurements on the shot-to-shot level, the reason for the discrepancy between experiment and simulation is ambiguous; the IRF FWHM is either being limited by phase jitter $\sigma_\tau$ or by a systematic problem related to the compression which limits the pulse duration $\sigma_t$. In order to attempt to detangle these two contributions to the total IRF FWHM, we will first present a simple statistical model which will define both the width of the IRF as well as the size of the signal fluctuations for a fixed $\tau$ assuming that the pulse duration and the rms synchronization jitter are described by normal distributions. The model will be then compared to measurements which were collected at a fixed $\tau$.

At a fixed laser delay $\tau$, $< I(\tau) >$ is measured on the CCD by averaging the interaction of the electron beam with the laser beams over many pulses. In the case
of an exposure of $N$ pulses each individual electron pulse will interact with the individual laser pulses and add to the total signal in the exposure. We assume the contribution to the total measured signal from each electron/laser pulse interaction will depend on instantaneous relative time offset $\tau_i$ between the $i^{th}$ electron/laser pulses. We also assume the signal depends on the instantaneous electron pulse duration. In the case of small phase fluctuations the fluctuations on the compressed pulse duration $\sigma_t$ were shown in the previous chapter to be negligible and so we assume that the instantaneous pulse duration is constant for a given set of RF cavity settings. Based on these assumptions, the contribution to the total ponderomotive signal measured at $\tau$ due to the $i^{th}$ pulse in the exposure is:

$$I_i(\tau, \tau_i) = \frac{I_0}{\sqrt{2\pi\sigma_t}} e^{-\frac{(\tau-\tau_i)^2}{2\sigma_t^2}}. \quad (4.5)$$

The probability of the pulse arriving with a given $\tau_i$, assuming that the mean arrival time is $<\tau> = 0$ is just:

$$P(\tau_i) = \frac{1}{\sqrt{2\pi\sigma_\tau}} e^{-\frac{\tau_i^2}{2\sigma_\tau^2}}, \quad (4.6)$$

The expectation value of the measured intensity at $\tau$ is then exactly calculated by:

$$<I(\tau)> = \int_{-\infty}^{\infty} I_i(\tau, \tau_i) P(\tau_i) d\tau_i$$

$$<I(\tau)> = \frac{I_0}{\sqrt{2\pi(\sigma_t^2 + \sigma_\tau^2)}} e^{-\frac{\tau^2}{2(\sigma_t^2 + \sigma_\tau^2)}} \quad (4.7)$$

Eq. 4.7 is simply the result of the convolution between the probability distribution functions which define the jitter and duration, and is the reason we have defined the IRF FWHM in the form of Eq. 4.1. A second expectation value of interest is the standard deviation of $I(\tau)$ at a fixed $\tau$. The standard deviation is most easily calculated by using:
Figure 4–7: Investigation into the synchronization phase jitter. Signal fluctuations are evident in repeated measurements taken at $\tau = 0$ after having measured the IRF FWHM of the instrument to be $425$ fs.

$$
\sigma_I(\tau) = \sqrt{< I^2 > - < I >^2},
$$

and so we only need to calculate $< I^2 >$, which after a using Eq. 4.5 and Eq. 4.6 can be shown to be:

$$
< I^2(\tau) > = \frac{I_0^2}{4\pi w \sqrt{\sigma_t^2 + w^2}} e^{-\tau^2/(2(\sigma_t^2 + w^2))},
$$
where $w = \sigma_t / \sqrt{2}$. For measurements performed at $\tau = 0$, the expected standard deviation is then:

$$\sigma_I(0) = \sqrt{\frac{I_0^2}{4\pi w \sqrt{\sigma_t^2 + w^2}}} - < I(0) >^2. \quad (4.10)$$

These quantities were used to put limits on the range of jitter that are likely to be influencing the measured IRF FWHM. Fig. 4–7 shows the way in which signal fluctuations were collected at the peak of the IRF. After using the instrument to measure the IRF, the jitter and duration standard deviations were constrained by the relation $2\sqrt{2\ln2}\sqrt{\sigma_t^2 + \sigma_{t'}^2} = 425$ fs. Data was then collected continuously at a fixed delay $\tau = 0$, where each exposure contained a total of $N = 250$ electron pulses. The measurement was repeated a total of 500 times and the signal fluctuations collected are shown in Fig. 4–7. The measured mean of the 500 measurements was used to determine $I_0$ by using Eq. 4.7:

$$I_0 = \bar{I}_{\text{measured}} \sqrt{2\pi(\sigma_t^2 + \sigma_{t'}^2)} \quad (4.11)$$

For a finite sample of $N$ pulses, the error on the mean that arises from jitter is just $\sigma_J = \sigma_I / \sqrt{N}$ and after constraining $I_0$, $\sigma_J$ can be solved explicitly for each possible value of $\sigma_{t'}$ using Eq. 4.10. The measured standard deviation can be defined as:

$$\sigma_T = \sqrt{\sigma_J^2 + \sigma_M^2}, \quad (4.12)$$

where $\sigma_T$ is the measured standard deviation of the 500 measurements, $\sigma_J$ is the contribution from the phase jitter and $\sigma_M$ is the contribution from all other sources such as charge fluctuations, electron beam pointing fluctuations, pump laser pointing/energy fluctuations and CCD camera related noise. The contributions to $\sigma_M$ from all sources (except pump laser pointing) was measured by collecting data at
the baseline of the IRF where there is no ponderomotive interaction. This put a lower limit on $\sigma_M$ which was measured to be 0.11. An upper limit on $\sigma_M$ was estimated by similar measurements performed with the RF cavity turned off. (Measurements with the cavity off are not affected by electron beam arrival time fluctuations and so $\sigma_J = 0$, allowing for $\sigma_M$ to be measured directly). The details on the estimation of the upper limit of $\sigma_M$ are discussed in Appendix A. The upper limit on $\sigma_M$ was determined to be 0.19.

The three unknown parameters are thus the pulse duration $\sigma_t$, the phase jitter $\sigma_\tau$ and the measurement noise $\sigma_M$. Since the former two are constrained by the IRF FWHM, it is sufficient to treat them as a single parameter and we choose to float $\sigma_t$. The remaining parameter $\sigma_M$ was floated from 0.08 to $\sigma_T = 0.34$. For each set of parameters ($\sigma_t, \sigma_M$) we can define a quantity $\Delta$ which quantifies how well the analytical quantities agree with the measured value:

$$\Delta = \frac{(\sigma_T)_{\text{measured}} - \sqrt{\sigma_I^2/N + \sigma_M^2}}{(\sigma_T)_{\text{measured}}/\sqrt{2N-2}},$$

(4.13)

where the numerator is constrained by the IRF FWHM and the measured mean $\bar{I}$ in the way described above. The denominator normalizes $\Delta$ to the error on the measured standard deviation $(\sigma_T)_{\text{measured}}/\sqrt{2N-2}$ so that $\Delta$ reflects how many standard deviations away a given set of parameters agree with the measured data.

The results of this analysis are shown in Fig. 4–8. For each value of $\sigma_M$ within the range of constraints, the value of $\sigma_t$ which minimizes $\Delta$ was determined analytically as shown in the inset. For most of the range of $\sigma_M$ explored, the data suggests a significant jitter is influencing the IRF FWHM. Up until an 85% contribution of $\sigma_M$ to the total standard deviation, the extracted FWHM pulse duration is less than 100 fs. Only at the extreme case of the entire standard deviation being defined by
Figure 4–8: Analysis of phase jitter. The inset shows the minimum value of \( \Delta \) at a fixed \( \sigma_M \). The main figure shows the pulse duration which minimizes \( \Delta \) as a function of the unknown noise term \( \sigma_M \). The black vertical lines show the estimated range of allowed \( \sigma_M \) values.

\( \sigma_M \) does the jitter term vanish. This extreme seems very unlikely due to the care that was taken in minimizing the influence of pump-laser fluctuations. The delay stage used to ensure the temporal overlap of the laser pulses (\( \tau_p \), see again Fig. 4–3) contains three mirrors which ensures that a small laser pointing fluctuation before the beam-splitter will result in both laser beams moving together at the measurement position (pointing fluctuations are self compensating) [11]. Furthermore, the range of allowed \( \sigma_M \) (shown by the black vertical lines in Fig. 4–8) estimated from the baseline and RF cavity off experiments suggest the most likely pulse duration is sub-100 fs. Even if the laser beam energy/pointing fluctuations were twice as large
as extracted from experiment, the duration would still be less that 150 fs FWHM. There is additional evidence that suggests the IRF FWHM is limited by phase-jitter. Fig. 4–4 shows that the GPT simulations fit much better away from the instrument optimal compression settings which can be explained by the smaller impact of jitter on the IRF FWHM for long pulse durations. Also, the single-shot streak camera results performed by the Eindhoven group were exclusively sensitive to the pulse duration of the compressed electron pulses and they reported pulse durations less than 235 fs FWHM [10]. Although the results shown in Fig. 4–8 should not be viewed as a direct measure of the pulse duration (since the extracted durations relied on a simple idealized model) they do strongly suggest that the performance of the RF system is limited by phase-synchronization and not by the temporal lensing of the RF cavity.

Despite being limited to an IRF FWHM of 330 fs the increased charge density at the specimen now achievable using the instrument has increased by over two orders of magnitude. The IRF FWHM achieved is the same as that for a compact instrument that uses $10^4$ electrons per pulse and yet we successfully compressed bunch charges in excess of $10^6$. The simulations in the previous chapter suggest that with a new vacuum system design allowing for shorter propagation distances (and smaller transverse spot sizes at the specimen), the current RF compressed charge density can be improved upon again by two more orders of magnitude. These upgrades will be implemented in the near future in concert with a more thorough investigation into the shot-to-shot stability of the RF cavity phase, as will be addressed in Chapter 7. The ponderomotive scattering geometry presented in this chapter is not easily
converted back and forth from the pump-probe geometry required for diffraction experiments, so a technique for measuring the IRF on a day-to-day basis is essential for the success of future studies.

4.6 Day to day operation of the timing system

In order to gain the flexibility of moving the specimen to different positions, as well as the need to compensate for temperature related drifts in the lab, an ultrafast streak camera was installed on the specimen holder. This allows the experimenter to characterize in situ the instantaneous IRF of the system, since the streak camera (which measures the IRF) moves with the specimen as it travels in response to the sample positioner system. The streak camera used was manufactured by the Schwoerer group in South Africa who developed the streak camera for characterizing the pulse duration of sub-ps electron pulses [12]. The reported IRF FWHM of the streak camera is 150 fs with 50 fs timing jitter.

The details of the streak camera are shown in Fig. 4–9. Panel A shows a simple schematic of the streak camera set-up. Before the arrival of both the laser and electron pulses, a circuit with a parallel plate capacitor is charged so that there is a static electric field between the plates. At time zero, the 800 nm laser pulse impinges upon the Gallium Arsenide (GaAs) photo-switch and closes the circuit leading to a damped harmonic oscillation of the electric field between the plates. Not shown in the schematic is the power supply. The harmonic ringing of the circuit is decoupled from the charging of the plates by carefully tuning the resistive properties of the circuit so that the charge-up time is sufficiently long compared to the period of oscillation. The resonant properties of the circuit are such that the period of oscillation is approximately 200 ps. Since the electron pulses to be characterized are much shorter than this, they interact with linear segments of the oscillation. The
pulse as a whole experiences a transverse momentum kick and is deflected by an amount $\Delta x$ at the CCD camera. By measuring this deflection as a function of $\tau$ it is possible to calibrate the streak velocity of the camera. Fig. 4–9, panel B shows the calibration data of our streak camera for which we measured streak velocities ranging
from 0.2-0.4 mm/ps depending on the voltage used to charge the plates. Once the calibration is performed \( \tau \) is set so that the mean electron experiences no change in momentum at the first zero-crossing of the ring-down. The front electrons are then streaked towards \(+x\) and the back electrons towards \(-x\) so that the transverse width of the spot on the camera can be converted into an IRF FWHM. A reference spot width is measured with the streak camera off and the contribution to the width due to streaking is extracted from:

\[
\sigma_{x,\text{streaked}} = 2\sqrt{2\ln2} \sqrt{\sigma_{x,\text{measured}}^2 - \sigma_{x,\text{reference}}^2},
\]

(4.14)

The IRF FWHM is then defined by \( \sigma_{x,\text{streaked}}/v_s \), where \( v_s \) is the streak velocity. Fig. 4–9 panels C and D show two streak camera IRF measurements, the first taken at the non-ideal \( \phi_0 \) and the second under ideal cavity parameters. Impulse response functions consistent with the ponderomotive results are measured on a daily basis and the streak camera is thus an excellent tool for regular diagnostics. Before every diffraction experiment the streak camera can be used to tune the timing system to ideal conditions. A second reason for using the streak camera rather than the ponderomotive measurement is that it is far less sensitive to the precise spatial positioning of the pump laser; a simple flip mount optic can be used to transfer back and forth between using the pump for a) streak camera measurements and b) specimen excitation. Although using a flip-mount to transfer between modes would be possible in the ponderomotive geometry as well, the time required to re-align the ponderomotive beam paths after a flip-mount error is significantly longer than for the streak camera. The streak camera has the added advantage of being able to characterize the IRF in a single exposure as \( \tau \) does not need to be scanned and so the time required
for a single measurement is much faster. The trade off is time resolution—the ponderomotive measurement is more sensitive to both the pulse duration and the jitter and thus was the appropriate technique for the initial characterization. Since we now know the IRF FWHM is limited to a value measurable with the streak camera, the convenience of the streak camera outweighs the accuracy of the ponderomotive measurement.

With the detailed understanding of the instrument gained from the measurements reported in this chapter, we are prepared to apply RF compressed UED to study laser-induced dynamic processes in materials with unprecedented beam brightnesses. The next chapter will present a detailed case study of the model system, femtosecond laser-induced structural dynamics in graphite, chosen to demonstrate the temporal and spatial resolution of the novel instrument.
References


CHAPTER 5

UED Study on the Structural Dynamics of Graphite Thin Films

5.1 Introduction

The performance of the radio-frequency compressed electron beamline presented in the previous chapter is a significant step forward in the development of ultrashort electron sources. The charge density now available per pulse opens up new avenues for studying structural dynamics of molecules and materials using ultrafast electron diffraction. This includes studies aimed at developing an understanding of mechanisms governing non-reversible processes or in those which attempt to measure very subtle changes of the position and intensity of Bragg peaks. The direct characterization of the instrument IRF using the ponderomotive scattering cross-correlations showed that fast (< 350 fs) processes can be studied in the high electron pulse charge (> 0.1 pC) regime. This chapter will detail a series of experiments performed on thin film graphite specimens, the results of which demonstrate the dramatic improvement to the instrument signal-to-noise and time resolution; the transient diffracted peak intensities exhibited a suppression of less than 1% on the 300 fs time scale with a relative error on the data points of less than $10^{-3}$.
The unique electronic properties of graphite, graphene and carbon nanotubes have inspired a great deal of attention for both fundamental and practical reasons with the hope that these materials will enable high performance carbon-based electronic devices [1, 2]. In graphite and graphene, these properties emerge from the nature of the electron-lattice interactions in the highly anisotropic crystal structure made up of strong, covalently bound hexagonal sheets of carbon atoms (graphene) that are each weakly bound together to form the layered structure of graphite (Fig. 5–2b). These interactions manifest most profoundly in the electronic bandstructure, notably the linear dispersion of the bands near the Fermi level and the point-like Fermi-surface at $K$ and $K'$ in the Brillouin zone. This linear dispersion results in the unique mass-less carrier transport properties and high electron mobilities for carriers near the Fermi level where the electron-phonon coupling is weak [3]. However, these interactions also manifest in other very important ways, in particular through the strongly anisotropic (momentum-dependent) electron-phonon interaction that results from the ineffective screening of the Coulomb interaction in these semimetals. The most conspicuous manifestation of this coupling is the strong electronic renormalization in the optical phonon bands (Kohn anomalies) at the $K$ and $\Gamma$ points [4]. The strong nonadiabatic coupling between electrons and phonons for these optical $K - A_1$ and $\Gamma - E_{2g2}$ modes makes them profoundly sensitive to carrier doping [5] and the micro/nanostructure (e.g. number of layers, level of disorder) in a way that can be exploited through Raman spectroscopy as a materials characterization tool (through the so called D and G peaks that report on these modes) [6]. Interaction with these specific strongly coupled optical modes (SCOP) has been implicated as the limiting factor in the high-field transport of carriers in graphene, graphite and carbon nanotubes [4,6–8].
The large body of work on this subject, both experimental and theoretical, speaks to the importance of understanding the electron-phonon interactions in graphene and graphite but also to its complexity. Our work is unusual in that it focuses on the electron-phonon coupling from the perspective of the lattice degrees of freedom, rather than the electronic system or an electronic response function as has been more commonly the case. Specifically, we probe the lattice responses to impulsive (35 fs, 800 nm) photoexcitation using radio-frequency compressed ultrafast electron diffraction. The 1.55 eV photons excite vertical $\pi - \pi^*$ transitions from the valence to conduction bands near the $K$ points to optically prepare a strongly non-equilibrium electron-hole plasma. Previous experimental investigations of the photodoped, non-equilibrium carrier dynamics using time-resolved THz spectroscopy [9] and photoemission spectroscopy [10] have demonstrated that the initial carrier relaxation is extremely rapid, with approximately 90% of the deposited electronic excitation energy leaving the electron sub-system within 500 fs. The strongly coupled $K - A_1'$ and $\Gamma - E_{2g2}$ modes were implicated as the reservoirs into which this energy preferentially flows, consistent with time-resolved Raman and vibrational spectroscopy studies of the $\Gamma - E_{2g2}$ mode [11, 12]. UED provides a complementary perspective on the electron-lattice coupling. It enables us to directly probe both incoherent and coherent aspects of the lattice response in graphite following photoexcitation. We are able to directly confirm that initial carrier relaxation is dominated by the interaction with the SCOP modes. In addition, we observe coherent lattice responses beyond the incoherent coupling associated with the carrier relaxation/cooling, unifying a number of previous observations.
This chapter is organized as follows. After describing how samples were prepared and characterized in Section 5.2.1, a model of the unit-cell of graphite and the pump-probe geometry used will be presented in Section 5.2.2 and Section 5.2.3, respectively. Section 5.3 will present a series of results which demonstrate both the excellent spatial and temporal resolutions of the instrument as it captures the dynamics of extremely fast electron-phonon coupling as well as a coherent 1.4 THz optical and 0.05 - 0.2 THz acoustic phonon.

5.2 Investigating graphite thin films with UED

5.2.1 Sample Characterization

Two types of graphite samples were studied in our instrument: highly oriented pyrolitic graphite (HOPG) of quality Grade SPI-1 and single crystal natural graphite (SCNG) provided by Naturally Graphite®. The samples begin as blocks with dimensions of approximately 1mm x 1mm x 1mm. The transverse dimensions of such a block are well suited to UED experiments, but in order for electrons to diffract kinematically (in the single-scattering limit) through a specimen in a transmission geometry, sample thicknesses are limited to approximately 100 nm for electron energies of 100 keV in order to minimize multiple scattering effects. In order to reduce the thickness of the 1 mm blocks of both HOPG or SCNG, the graphite samples were repeatedly exfoliated based on a technique that was first introduced by Novoselov et. al. [13]. A starting flake is peeled off the bulk graphite sample with scotch tape and glued to a 3 mm copper G200 square mesh TEM-grid, using clear color crystalbond 509 (a high bond strength adhesive). Starting with this thick graphite flake adhered to the TEM grid, layer after layer is peeled off using scotch tape until what remains is nearly transparent to visible radiation. At this point the crystalbond is carefully removed with acetone, leaving only the graphite behind on the TEM-grids. This
process has a high failure rate and often the final ‘peel’ removes the remainder of the sample. As a result many attempts were made before a high quality specimen with a uniform sub-100 nm thickness was successfully prepared. Fig. 5–1 shows the optical microscope and AFM images taken when characterizing the specimen thickness of semi-transparent flakes. Panel A and B highlights two flakes with slightly different greyscale intensities when viewed with a constant light source. These flakes were transferred off the TEM grid and were mounted onto a silicon wafer for AFM characterization, shown in Panel C. The measured thicknesses for samples A and B were found to be \(83.9 \pm 2.4\) nm and \(73.0 \pm 1.7\) nm, respectively. This indicates that the constant greyscale intensity observed by eye is a fairly good indicator of a uniform thickness of the sample.

### 5.2.2 Unit Cell and Reciprocal Lattice

A single crystalline sample of graphite has a microstructure that can be described entirely by the bravais lattice of graphene and a specific stacking sequence. The honeycomb graphene sheets stack in an ABAB arrangement, each sheet separated by 3.35 Å from the sheet above and below it, and shifted with respect to the surrounding...
sheets along the x-direction by the nearest neighbour distance of 1.42 Å, as shown in Fig. 5–2b and Fig. 5–2c. This microstructure can be represented by the direct bravais lattice vectors:

\[
\vec{a}_1 = a \left[\frac{3}{2}, \frac{\sqrt{3}}{2}, 0\right], \quad \vec{a}_2 = a \left[-\frac{3}{2}, \frac{\sqrt{3}}{2}, 0\right], \quad \vec{a}_3 = c [0, 0, 1] (5.1)
\]

where \(a\) is the nearest neighbour distance (1.42 Å) and \(c\) is twice the stacking distance (6.7 Å). This space-group alone doesn’t produce the honeycomb structure shown in Fig. 5–2b since the representation of all of the atoms in the honeycomb require that we additionally define the set of basis vectors:

\[
\vec{r}_1 = [0, 0, 0], \quad \vec{r}_2 = a \left[\frac{1}{2}, \frac{\sqrt{3}}{2}, 0\right], \quad \vec{r}_3 = c \left[0, 0, \frac{1}{2}\right], \quad \vec{r}_4 = \left[-\frac{a}{2}, \frac{\sqrt{3}a}{2}, c\right]. (5.2)
\]

At each bravais lattice centre defined by Eq. 5.1, four atoms are positioned according to Eq. 5.2. The reciprocal lattice which defines the diffraction pattern is constructed from the vectors:

\[
\vec{b}_1 = \frac{1}{a} \left[\frac{1}{3}, \frac{1}{\sqrt{3}}, 0\right], \quad \vec{b}_2 = \frac{1}{a} \left[-\frac{1}{3}, \frac{1}{\sqrt{3}}, 0\right], \quad \vec{b}_3 = \frac{1}{c} [0, 0, 1]. (5.3)
\]

### 5.2.3 Pump probe geometry

All data shown below was taken using SCNG samples. SCNG diffraction patterns have peaks separated in both radius and azimuth and are thus more easily analyzed compared to HOPG patterns since peaks do not overlap with one another. The microstructure of SCNG does not allow for diffraction from all the crystallographic planes to be simultaneously measured. For a particular crystal orientation only planes with a normal perpendicular to the electron beam direction satisfy the Laue condition in the ‘zero-order’ Laue zone closest to the transmitted beam. The thin film direction is the stacking direction perpendicular to the graphene layers (\(\vec{b}_3\)).
Figure 5-2: Ultrafast electron diffraction of single crystal graphite. (a) The specimen normal can be rotated by an angle $\phi$ relative to the transmitted electron beam direction. Transient diffraction patterns are captured at every time delay $\tau$. (b) Unit cell and Brillouin zone of graphite in the x-y plane. (c) Unit cell and Brillouin of graphite in the x-z plane. (d) Strongly coupled optical phonon modes ($E_{2g}$ and $A_{1}'$) of graphene and graphite. (e) Transverse interlayer shearing phonon modes of graphite, with different wavenumbers indicated by different colored arrows. (f) Lowest order longitudinal acoustic phonon mode (with open boundary conditions at both surfaces) of graphite quantized by the specimen thickness denoted by $L$. 
Fig. 5–2a shows the pump-probe geometry used to study the dynamics of the graphite films. The electron beam arrives at a delay \( \tau \) relative to the pump beam which excites the specimen at a 10\( ^\circ \) angle (the smallest angle achievable experimentally) with respect to the film normal in order to reduce the time-resolution broadening due to geometry (described in Section 2.4.3) as much as possible. The electron beam direction is fixed. The specimen is mounted on a tip-tilt rotation stage so that the angle of the film normal can be varied from 0\( ^\circ \) and 45\( ^\circ \) in the \( x-z \) plane, and the \( y-z \) angle can be varied between -2\( ^\circ \) to 2\( ^\circ \). In this way we can probe different diffraction planes by tuning the angle \( \phi \) in the \( x-z \) plane and we can use the \( y-z \) rotation to intersect all peaks on the pattern with approximately the same intensity. When \( \phi = 0 \) the electron beam direction is parallel to the surface normal and the \( c \) axis of the graphite lattice. Only Bragg reflections sensitive to in-plane structural dynamics (\( hkl = 0 \)) are observed in this orientation (Fig. 5–2b). For suitably chosen \( \phi \neq 0 \), however, reflections with \( l \neq 0 \) are observed and dynamics in both the stacking direction and graphene planes are probed (Fig. 5–2c). All the phonon modes relevant to this study are shown in panels (d)-(f). By performing experiments at two separate angles, we obtain information on both directions of relevance to the graphite unit cell. In order to satisfy the [0 0 \( l \)] peaks \( \phi \) would have to approach 90\( ^\circ \), which is how a reflection geometry measurement is made. We limited our maximum angle to less than 45\( ^\circ \) for reasons of time-resolution; a tilted specimen leads to a geometrical time-resolution broadening in the same way that having a non-zero angle between pump and probe does (see again Section 2.4.3). The \( c \) lattice constant is extracted by defining the \( a \) lattice constant dynamically and solving for \( c \) using the diffraction data taken at an angle.
5.2 Investigating graphite thin films with UED

The typical transverse size of a graphite film that could be exfoliated with a constant thickness was approximately 250 µm. Due to the electron optical configuration used, the beamsize at the specimen could not be made this small. In order to probe a uniform thickness required the use of an aperture. A 250 µm silver aperture was placed directly on top of the graphite specimen so that electrons outside this diameter would not be transmitted through the specimen. The pump laser spot at the specimen was sized a factor of two to three times larger than the aperture size to ensure homogeneous excitation. Pump probe spatial overlap was ensured by maximizing both the electron and laser flux through the aperture at the same specimen position. Due to the higher electron pulse charges used in the RF compressed geometry, the undiffracted transmitted electron beam saturates the CCD camera in 25-250 shots. To protect the CCD a beam-stop was used to block the main beam since the exposures used to collect time resolved data were in excess of 1000 shots.

The data presented below was post-processed to handle certain systematic errors that occur during a UED diffraction measurement. The fixed orientation of the specimen relative to the electron beam leads to very significant errors when extracting peak intensity and peak position dynamics (see Section 2.3). Appendix B discusses the degree to which these errors will influence the interpretation of the results presented below. Appendix C discusses the influence of the laser-induced surface charge at the graphite-vacuum interface on the spot positions in the time-resolved diffraction patterns. Appendix D presents the data post-processing algorithm implemented to correct for the time-zero synchronization drift discussed in Section 4.5.1. Where appropriate, a short summary of each appendix will be summarized in the text below.
5.3 Results and Discussion

Experiments performed at normal incidence ($\phi = 0$) reveal a bi-exponential behaviour of the $<110>$ peak intensity dynamics. Fig. 5–3 shows data collected after laser excitation for a total absorbed fluence per layer of 59 $\mu$J/cm$^2$. The normalized intensity suppression is determined to a statistical precision better than $7 \times 10^{-4}$ (approximately the size of the data markers) in 10 minutes of acquisition per time delay with RF compressed UED operating at 250 Hz. The dashed line is the result of fitting the function $I = I_0 + A_1 e^{-\tau/b_1} + A_2 e^{-\tau/b_2}$ to the data. The extracted time constants from the fitting procedure are $259 \pm 60$ fs and $6.5 \pm 0.6$ ps for $b_1$ and $b_2$, respectively, and the extracted normalized amplitudes of the suppressions are $0.013 \pm 0.001$ and $0.019 \pm 0.001$ for $A_1$ and $A_2$, respectively. The 259 fs time constant was
extracted after time-correcting the dataset as described in Appendix D. It should be viewed as an upper limit defined by the instrument IRF.

An increase in dynamic disorder resulting from incoherent lattice excitation attenuates the zero Kelvin intensity of a diffraction peak by the Debye-Waller factor $e^{-2M}$, where

$$M = 8\pi^2 <u_s^2> \frac{\sin^2 \theta}{\lambda^2},$$

and $<u_s^2>$ is the mean-square vibrational amplitude of atoms along the direction of the reciprocal lattice vector $\vec{g}_{hkl}$, where $|g_{hkl}|/2 = s = \sin \theta/\lambda$ [14]. Assuming that the phonon modes are populated/sampled incoherently, time averaging and two-dimensional isotropic averaging leads to the measured vibrational amplitude being related to the average vibrational amplitude, $a_P$, of any individual phonon by $<a_P^2> = 4 <u_s^2>$. Since the $K-A'_1$ and $\Gamma-E_2g$ SCOP modes are excited incoherently, increased population results in an observed Debye-Waller like suppression of the peak intensities rather than a coherent modulation of diffracted intensity like that shown subsequently. If we assume that relaxation of the initial photoexcitation occurs exclusively through the SCOP modes at times less than 1 ps, the energy per atom transferred to the SCOP modes from the electrons after excitation is

$$\Delta <E_{\text{vib}}>= \frac{1}{2}m\bar{\omega}^2\Delta <a_P^2 >,$$

where $m$ is the mass of a carbon atom and $\bar{\omega} = 280$ THz is the average SCOP angular frequency [15]. Based on the extracted $A_1$ and $b_1$ parameters and using $\Delta <E_{\text{vib}}>/E_A$ to calculate the energy transfer (where $E_A = 0.1$ eV is the amount of laser energy absorbed per atom), the observed suppression in diffracted intensity is consistent with the view that 84% of the laser deposited energy is stored.
in the SCOP modes by $\tau = 500$ fs. The bi-exponential behaviour of the UED data results from the closing of the SCOP relaxation channel once these specific modes reach thermal equilibrium with the electronic system [16]. The longer timescale dynamics result from a combination of further carrier cooling through electron-phonon interactions with more weakly coupled mid-low energy phonon modes and also the phonon-phonon scattering necessary for lattice thermalization (cooling of the hot SCOP modes).

When phonons are excited coherently, the instantaneous lattice distortions that arise due to coherent phonon motion modulate the electron structure factor (and by extension the diffracted intensity) and/or the Bragg spot positions. Coherent coupling of the photoexcitation to in-plane and out-of-plane lattice motions were observed in addition to incoherent coupling to SCOP modes in these studies. Fig. 5–4 shows the peak intensity dynamics measured in the $\langle 100 \rangle$ family for the same dataset shown in Fig. 5–3 (the blue and red data in Fig. 5–4 was extracted from the corresponding peaks shown in Fig. 5–3a). Superimposed on the intensity suppression is a modulation of intensity measured only in the $\langle 100 \rangle$ families. Notice that the $(1-1 0)$ peak is out of phase with the remaining $<100>$ peaks by precisely $\pi$. The extracted modulation frequency—for both the red and blue data—is 1.4 THz. This is consistent with the measured frequency of the shearing phonons in graphite [17]. The shear phonons listed in Fig. 5–2e affect peaks as a function of the indices $h$ and $k$ because their polarization vectors point in the transverse direction. Thus, experiments at $\phi = 0$ measure these modes. Whether the phonon is located near $\Gamma$ or $A$ is not clear from the frequency analysis alone, and so the out of phase relationship between the blue and red data was explored. Modelling the instantaneous structure factor of the $\Gamma$ shear phonon requires a 4 atom basis, where the phonons near $A$
5.3 Results and Discussion

Figure 5–4: Coherent transverse shearing optical phonon of graphite. As well as exhibiting peak suppressions, the \(<100>\) family of peaks have an oscillatory component to the intensity dynamics at early times. The \((1-10)\) peak is out of phase by \(\pi\) with respect to the other four measured peaks. The optical phonon begins approximately 250 fs after the onset of the suppression dynamics and is well explained by equation Eq. 5.6.

require an eight atom basis. The time-resolved structure factor for a \(\Gamma\) phonon is given by

\[
S(\tau) = 1 + e^{-i2\pi \frac{2h+k}{\delta}} + e^{-i2\pi \frac{h-k}{\delta}} A_f \sin \omega \tau \left[ 1 + e^{-i2\pi \frac{h+2k}{\delta}} \right],
\]

(5.6)

where \(A_f\) is the shear amplitude and \(\omega\) is the shear frequency. The results of equation Eq. 5.6 for selected reflections are shown in Fig. 5–4 as solid lines. Equation Eq. 5.6 produces the correct out of phase phase relationship between the aforemention peaks, while simultaneously predicting the lack of modulation of the \(<110>\) family (consistent with the data shown in Fig. 5–3). The shear amplitude \(A_f\) was chosen so that
Eq. 5.6 would lead to the same intensity modulations extracted from the data. The shear amplitude was found to be on the order of 0.06 pm. The eight atom basis of the \( A \) phonon mode was also modelled and compared to the data, but this mode does not explain the out of phase nature of the peak dynamics and also results in a much weaker modulation of peak intensities. All measurements therefore suggest the \( \Gamma \) phonon mode specifically was coherently excited. Transient reflectivity measurements by Mishina et. al. suggest that the coherent excitation of the interlayer shearing mode is generated by the \( \pi - \pi^* \) optical transition [18]. The intensities used to extract the electron-phonon coupling rates and the coherent shear motion were shown in Appendix B to be not significantly influenced by \( a \) lattice constant changes (a change in \( a \) would lead to a peak intensity error due to the fixed orientation of the specimen).

Experiments performed at a larger angle (\( \pi/8 > \phi > \pi/4 \)) revealed statistically significant lattice expansion and coherent phonon signatures. Coherent vibrations and lattice expansion dynamics have previously been observed in UED and UXD experiments [19–22]. Fig. 5–5 shows the dynamics of the extracted \( c \) lattice constant following excitation. From experiments on different specimen thicknesses it was apparent that the frequency of the \( c \)-axis modulation depended strongly on the greyscale intensity (thickness) of the specimen when viewed through an optical microscope. The measured frequency is thus the lowest order longitudinal acoustic phonon mode quantized by the specimen thickness \( L \). Since the graphite is free standing, open boundary conditions were assumed and the specimen thickness is extracted using \( L = v/2f \), where \( v \) is the speed of sound and \( f \) is the extracted linear frequency. The vibration shown in Fig. 5–5 is 0.2 THz and using the speed of sound of graphite in the stacking direction [23], the specimen thickness is on the order of
5.3 Results and Discussion

Figure 5–5: Lattice dynamics along the stacking direction. The $c$ lattice constant exhibits an oscillatory behaviour during the photoinduced expansion that is best explained by the lowest order longitudinal acoustic phonon quantized by the sample thickness. The measured frequency of 0.2 THz corresponds to a sample thickness of 10 nm.

10 nm. The specimen used to collect the data shown in Fig. 5–3 and Fig. 5–4 had a frequency suggesting a thickness of 30 nm. The systematic errors due to both the fixed orientation of the specimen and the transient surface charge at the graphite-vacuum interface significantly affect the absolute value of the extracted change in $c$ lattice constant. Appendix B demonstrates that the measured $\Delta c$ should be approximately 54% larger than the actual value for the orientation of the specimen relevant to the data shown in Fig. 5–5. The absolute values reported in the inset have been corrected by this amount. The measured oscillation frequency and the linear trend of the expansion dynamics, on the other hand, were shown to not depend on the peak position errors. Due to the TEF effect described in Appendix C, the dynamical
value of $a$ is unclear. This may add additional error to the reported $\Delta c$ values, since $a$ was assumed to be constant in order to extract $c(t)$.

### 5.4 Conclusions

We have directly determined the incoherent and coherent electron-lattice couplings in graphite following femtosecond laser excitation using UED. Within 500 fs, most of the initial electronic excitation energy has flowed out of the electron system into two specific SCOP modes, ie. $\Gamma - E_{2g}$ and $K - A'_{1}$. The result is a unique non-equilibrium state with the electron subsystem in thermal equilibrium with only very a small subset of the lattice degrees of freedom. The coherent shear excitation also described here demonstrates the sensitivity of UED when capturing subtle lattice distortions; not only can we extract vibrational periods, but we can localize the driven oscillation in $k$-space (to a specific wavenumber) while simultaneously extracting vibrational amplitudes approximately sixty times the diameter of a proton. More generally, these results highlight the ability of UED to directly probe the fastest and most fundamental structural changes in material systems.

The exceptional improvement to the signal to noise per pulse demonstrated here should inspire the field to continue to push the limits of charge density and time resolution. It is very likely that UED will break the 100 fs barrier within the next 5 years and there is a great deal of research to suggest that charge densities will continue to increase at the specimen. The following chapter will be devoted to exploring how space-charge fields resulting from such elevated charge density at the specimen can influence the interpretation of a diffraction pattern.
References


CHAPTER 6

Post-Specimen Space-charge effects on UED Diffraction Patterns

6.1 Introduction

ULTRAFAST ELECTRON DIFFRACTION and Dynamic Transmission Electron Microscopy (DTEM) are complementary techniques for studying structural dynamics in molecules and materials. DTEM operates very similarly to UED, except that it attempts to resolve structure in an imaging or real-space mode rather than in reciprocal space, allowing it to study phenomena such as reaction front motion in reactive multilayer foils as well as the nucleation and growth rates during the laser-driven crystallization of amorphous germanium [1, 2]. Just as in UED, Coulomb repulsion between electrons plays the determining role in DTEM, providing the practical limits to instrument performance. As has been described in previous chapters, research efforts to date have primarily focussed on understanding the effect that Coulomb interactions have on the specimen-illumination end of these instruments, where space-charge forces lead to electron pulse broadening and a dramatic increase in the kinetic energy spread in the beam [3–5]. Stochastic electron-electron scattering appears to be relatively unimportant in the illumination end of
the instrument, but does influence the spatial resolution of DTEM experiments in the post-specimen to detector region [6]. There has not, however, been a systematic study of electron-electron interactions in the post-specimen region of a UED instrument or the diffraction plane of DTEM instruments. Such a study is particularly important based on the extremely high charge densities accessible with the use of electron pulse compression technology, as was described in Chapter 3. Since bunch compression technology has now been implemented in several research groups [7–12], the limits to charge density at the specimen may soon be realized. The results of Chapter 3 showed that the charge density at the specimen can be as high as it was at the electron pulse source—under such conditions space-charge interactions have a known, dramatic influence on the electron beam. The impact of these interactions in the post-specimen region - where the structural information is carried - is unknown. In addition, there are proposals for ultra-cold photoelectron sources that could lead to even further enhancements in on-sample brightness [13,14]. Given these developments there are a number of important questions to be addressed: What effect do space-charge interactions in the post-specimen region have on UED patterns? How do these effects depend on important parameters like electron pulse charge, pulse duration, beam energy and energy spread? At what level do these interactions impact on the interpretation of UED data? Which experimental conditions and geometries are likely to make the best use of the enhancements in electron beam brightness offered by ultra-cold photoelectron sources? This chapter will address these questions by modelling the electron beam dynamics in the post-specimen region of a typical UED instrument. The influence of total electron pulse-charge, electron energy and detector distance on the process of diffraction pattern formation that takes place between a single-crystal specimen and the detector camera will be investigated. It
will be shown that significant distortions of the electron diffraction pattern can occur at currently available on-specimen current densities and that these distortions are well described by space-charge interactions between the diffracted ‘beamlets’ and the main (unscattered) beam.

This chapter is organized as follows: Section 6.2 describes the methods that were used to investigate space-charge interactions in the post-specimen region of UED instruments. In Section 6.3 the results of a systematic set of simulations that cover the parameter space relevant to UED and DTEM experiments is presented. In Section 6.4 a summary of the important findings of this study and their relevance in providing direction for future developments in UED and DTEM instrumentation is given.

### 6.2 Simulation methods

A schematic of the electron optical system typical of most current UED instruments in the immediately pre and post specimen region is shown in Fig. 6–1. The optical system consists of at least one pre-specimen focussing lens as well as a temporal lens, which prepares weakly convergent illumination of a spot on the order of 100 microns in diameter and 100 fs in duration at the specimen. The specimen is followed by an appropriately chosen free flight distance and the detector camera at which the illumination beam comes to a focus. Since our focus is on the effects of Coulomb repulsion in the post-specimen region of UED instruments, we do not simulate beam dynamics in the specimen illumination stage of the instrument, as this has already been done in Chapter 3. Instead, the starting point taken here is that ultrashort electron pulses of variable total bunch charge, diameter, convergence angle, and energy can be made incident on a single crystal specimen. Simulations of the electron beam dynamics begin in the plane immediately post-specimen, making use
6.2 Simulation methods

Figure 6–1: Typical UED geometry and the electron optical model used in the simulations presented

of the General Particle Tracer code (GPT) [15] to take account of electron-electron interactions between the specimen and detector.

6.2.1 Initial conditions

As described in Chapter 3, GPT is a classical code for simulating the dynamical evolution of a system of interacting charged particles under the influence of externally applied EM fields. Thus, it is necessary to define an initial position and momentum for each particle in the simulation. We define a distribution of \( N \) macroparticles, each carrying a charge of \( q = \frac{Q}{N} \), where \( Q \) is the total bunch charge. Each macroparticle has kinetic energy \( U = (\gamma_v - 1)mc^2 \) where \( \gamma_v \) is the relativistic Lorentz factor corresponding to the velocity, \( v \). At non-relativistic velocities the kinetic energy reduces to \( U = \frac{1}{2}mv^2 \). For all simulations presented in this chapter the initial position distributions are randomly sampled from normal distributions, with FWHM width \( \sigma_x = 200 \mu m \) in the transverse direction and FWHM duration \( \sigma_t = 50 \) fs in the direction of propagation unless otherwise indicated. The initial momentum distribution
depends on both the prepared illumination conditions (beam convergence angle) and
diffraction from the specimen and is described below.

**Beam convergence**

The beam convergence angle is modeled using a thin lens approximation to the
paraxial ray equation for focussing with a magnetic solenoid lens [16]. Let $L$ be
the distance from the specimen plane to the detector plane. Such a lens focuses a
monochromatic beam perfectly, so that each electron crosses the longitudinal axis at
exactly the same position, which we define to be the detector position $L$. Assuming
$v_z \approx v$, the amount of time that passes in the lab frame of reference between the
sample and the detector is $\Delta t = \frac{L}{v}$. Since we require that all macroparticles focus
to the origin in the transverse plane at $L$, we solve $x_i(\Delta t) = x_i(0) + v_{x,i}\Delta t = 0$
substituting $\Delta t$ above:

\[
\begin{align*}
  v_{x,i} &= -\frac{x_i}{L} \\
  v_{y,i} &= -\frac{y_i}{L} \\
  v_{z,i} &= \sqrt{v^2 - v_{x,i}^2 - v_{y,i}^2}
\end{align*}
\]

where $v_{z,i}$ is defined so to conserve kinetic energy.

**Diffraction**

The aim of the work is to model distortions in ultrafast electron diffraction pat-
terns due to electron-electron interactions in the post-specimen region, so we make
no effort to rigorously model the electron/specimen interaction or to quantitatively
model diffraction intensities. Here we take our specimen to be a simple cubic lat-
tice with lattice constant $d = 0.6$ nm oriented in the $(100)$ direction and we define
the transmission constant $T$ to randomly separate the $N$ macroparticles into two
subpopulations:

\[ \begin{align*}
N_m & = NT \\
N_s & = N(1 - T)
\end{align*} \quad (6.2) \]

where \( N_m \) is the number of main beam (unscattered) macroparticles, and \( N_s \) is the number of scattered macroparticles. A transmission constant \( T = 0.7 \) is used in all the simulations presented here unless otherwise stated. Particles that fall into the main beam subpopulation have their momentum unaltered by diffraction, so that their initial momenta are defined by Eq. 6.1 above. Scattered macroparticles have their initial position unchanged but their momenta adjusted in accordance with the Bragg condition. For a specimen in which atomic positions are given by \([x, y, z] = d[a, b, c]\), where \( a, b, \) and \( c \) are integers, the reciprocal lattice vectors are simply:

\[ \vec{G}_{hkl} = \frac{1}{d}[h, k, l] \]

where \( h, k, \) and \( l \) are also integers. A scattered macroparticle with incident unit direction \( \vec{s}_0 = \frac{1}{q}[v_{x,i}, v_{y,i}, v_{z,i}] \) will have an exit unit direction defined by the relation

\[ \frac{1}{\lambda} \vec{s} = \frac{1}{\lambda} \vec{s}_0 + \vec{G}_{hkl} \quad (6.3) \]

where \( \lambda \) is the wavelength of the electrons defined by \( U \). For each scattered particle, \( \vec{s} \) is determined by the reciprocal lattice vector. In these simulations we randomly distribute (with equal weighting) the scattered macroparticles over \([h, k]\) ranging from \([-h_{max} : h_{max}, -k_{max} : k_{max}]\); i.e. we ignore the decrease in scattering at larger wave-vector due to the atomic-form factor. This artificially increases diffracted intensity in the higher order reflections, making the distortions that result from electron-electron interactions more evident. Truncating at \( h_{max} = k_{max} = 3 \) mimics the effect of the Ewald sphere curvature in eliminating diffraction features at high...
orders. Combining Eq. 6.1 and Eq. 6.3 we solve for the momenta of the scattered particles:

\[ v_{x,i,scat} = v_{x,i} + \frac{v\lambda h}{d} \]
\[ v_{y,i,scat} = v_{y,i} + \frac{v\lambda k}{d} \]
\[ v_{z,i,scat} = \sqrt{v^2 - v_{x,i,scat}^2 - v_{y,i,scat}^2} \]  \hspace{1cm} (6.4)

where \( v_{z,i,scat} \) is once again defined in order to conserve kinetic energy. Together with the particles in the main beam, these scattered particles complete the set of initial conditions necessary to perform the simulations.

**Emittance Considerations**

The formulation of Eq. 6.1 and Eq. 6.4 ensures that - in the absence of electron-electron interactions - all diffraction orders focus to infinitely small points in the focal plane at \( L \). This is shown in Fig. 6–2, panel A. The beam so defined has zero transverse emittance and zero energy spread (or longitudinal emittance) [17]. The remainder of this chapter is devoted to exploring how space-charge distorts the diffraction pattern from this non-interacting reference, and the choice of zero beam emittance for most of this work makes it possible to isolate electron-electron effects from the influence of electron ‘beam quality’. Where appropriate, however, we do compare the magnitude of electron-electron induced diffraction spot broadening to that expected from beam emittance considerations. In addition, we perform a systematic study of the impact of electron beam energy spread on the magnitude of these electron-electron effects. Thus, we provide a brief description of the essential features of emittance as an electron beam quality measure that are necessary for understanding the results that follow.
6.2 Simulation methods

Transverse emittance

At a beam waist (or focal plane) the product of the standard deviation of the spot size, $\sigma_x$, and the momentum spread, $\sigma_{px}$ depends on the normalized transverse emittance of the beam in the following way:

$$\varepsilon_{n,x} = \frac{1}{mc} \sigma_x \sigma_{px}. \quad (6.5)$$

This expression shows that the effect of non-zero transverse emittance is to limit the focusability of the beam; a finite spot size at the detector is expected even in the absence of electron-electron interactions. Using Eq. 6.1 and the definition of relativistic momentum $p_x = \gamma v m x$, the initial momentum standard deviation in our simulations is the following:

$$\sigma_{px} = \frac{\gamma v m x \sigma_s}{L}, \quad (6.6)$$

where $\sigma_s$ is the electron spot size at the sample. Assuming the convergence angle in the detector plane is the same as in the sample plane, we can sub Eq. 6.6 into Eq. 6.5 and solve for the spot size at the detector in the absence of space-charge:

$$\sigma_x = \frac{cL \varepsilon_{n,x}}{\gamma v \sigma_s}. \quad (6.7)$$

Where appropriate we indicate this ‘emittance limited’ spot size for $\varepsilon_{n,x} \leq 0.02$ mm mrad, a value that is typical of photoactivated electron sources used in UED experiments [18]. This provides a reference level against which the magnitude of any electron-electron induced spot blurring effects can be appreciated.
Longitudinal emittance

Longitudinal emittance, $\varepsilon_{n,z}$, is defined as the product of the standard deviation of the uncorrelated part of the energy spread, $\sigma_U$, and the pulse duration, $\sigma_t$:

$$\varepsilon_{n,z} = \frac{1}{mc} \sigma_U \sigma_t. \quad (6.8)$$

As described above, most simulations in this work were performed with a monoenergetic electron beam; $\varepsilon_{n,z} = 0$. However, in order to investigate the influence of energy spread on the results presented, we also perform simulations at constant pulse duration and a normal distribution of electron energies. This was accomplished by defining initial conditions in which macroparticle energies are assigned at random according to a normal distribution with standard deviation $\sigma_U$. Since an energy spread necessarily adds chromatic aberrations to the focus quality of electron beams, we define here also how the convergence angles of Section 6.2.1 are handled for different energies. We assume the solenoid magnetic lens defined will focus electrons with mean energy $U_0$ at $L = L_0$. The focal length of a thin magnetic lens is proportional to $(\beta \gamma v)^2$ [16], where $\beta = v/c$. Thus for the $i^{th}$ macro particle simulated with random energy $U_i$, the focal length of that macro particle is defined by:

$$L_i = L_0 \left( \frac{\beta_i \gamma v,i}{\beta_0 \gamma v,0} \right)^2, \quad (6.9)$$

where $\beta_i$ and $\gamma v,i$ are defined by $U_i$ in the usual way. The results of these simulations are presented as a function of the magnitude of the energy spread in Section 6.3.4.

6.2.2 Electron-electron interactions

The effect of electron-electron interactions on the beam dynamics in the post-specimen region were modelled at various levels of accuracy in GPT. Before these details are addressed, however, we present results which capture the qualitative way
in which electron-electron interactions affect the x-y electron positions as the bunch travels from the sample to the detector (i.e. during the process of diffraction pattern formation), motivating the work that follows.

**Diffraction pattern distortion**

Fig. 6–2 shows this x-y phase space evolution for a $Q = 0.1$ pC beam at $U = 100$ keV simulated for an initial convergence angle defined by $L = 3.0$ cm. Panel A of this figure show the results of a simulation performed with electron-electron interactions ‘turned off’ and panel B with electron-electron interactions ‘turned on’. The distortions resulting from these interactions can be clearly appreciated. Close to the sample there is no apparent difference between the two simulations. The diffracted
‘beamlets’ are all spatially overlapped with the undiffracted beam and each other. Towards the detector when the scattered beamlets are spatially separated, however, the effect of the electron-electron interactions becomes evident. As beamlets begin to emerge it is obvious that the electron-electron interactions have caused broadening of the beamlet widths, and that the initial normal distributions have been distorted so that the beamlets have charge concentrations that are not distributed about a center of symmetry and have shapes that point radially outwards. The results at the far right show the diffraction pattern in the detector plane. Here the distortion is the most dramatic, the pattern with electron interactions included deviating significantly from the well ordered and infinitesimal reference. Although the degree to which electron-electron interactions distort the reference pattern depends on many parameters, (which will be explored in detail in Section 6.3), it is clear that these interactions have a significant effect on UED diffraction patterns at current experimentally feasible bunch charges and beam energies.

Space-charge model

GPT is a full 3-dimensional particle tracking tool that allows for efficient and accurate simulation of charged particle accelerators and beam lines. Several different 3D models are available for computing the forces due to electron-electron interactions. The most accurate solves all pair-wise interactions from first-principles and converges on the order of $N^2$. The computational costs of this approach are such that on the order of 1000 macroparticles can be simulated on a PC. This is far too restrictive given the requirements of this study, and so two other models were explored. The first method uses a Barnes-Hut (BH) algorithm to compute the electron-electron interactions and converges on the order of $N\log(N)$ [19]. Barnes-Hut still solves pair-wise interaction in local cells, so that pair-wise interactions between neighbouring
macroparticles are still included. To dramatically improve performance compared to an all-pairs algorithm, the Barnes Hut scheme clusters Coulomb interactions based on an overall accuracy parameter $\theta$. The core of the algorithm takes only center-of-mass and quadrupole moments into considerations for clusters of particles if $L_c/d_c < \theta$, where $L_c$ is the distance to the cluster and $d_c$ the size of the cluster. The second approximation model was a Particle-In-Cell (PIC) solver and converges on the order of $N$ [20]. The PIC method is by far the most efficient to use and allows for a large parameter space to be explored at reasonable computational expense. The approximation in PIC is the most severe however, as it ignores pair-wise interactions and only allows macroparticles to experience forces due to the average charge density of the bunch.

Figure 6–3: Influence of the space-charge model. Results of simulations for the $[h, k] = [2, 2]$ reflection at $z = L$. A: Results solved using the BH algorithm. B: Results solved using PIC algorithm. Simulation parameters used were $Q = 0.1$ pC, $U = 100$ keV, $L = 3.0$ cm, $\sigma_t = 50$ fs (FWHM), $\sigma_x = 200$ $\mu$m (FWHM), $T = 0.7$, $\sigma_U = 0$ and $N = 625 000$. Color indicates the local electron density.
To ensure that distortions observed in the electron diffraction pattern were not simply an artifact of a particular model, simulations using the PIC and BH algorithms under identical conditions were performed. The test simulation was performed at $U=100$ keV, $Q=0.1$ pC, $L=3.0$ cm, $N = 625 000$, and $\sigma_t = 50$ fs. Note that here $q = \frac{Q}{N} = e$ so that each macroparticle represents a single electron. Note also that for sufficient accuracy, the BH test simulation was performed with the BH simulation parameter $\theta = 0.5$. A GPT custom element that measures the transverse position of each electron as it reaches $z = L$ was used to simulate a perfectly thin detector. The results of this test simulation are shown in Fig. 6–3. It is clear from this test simulation that the PIC and BH simulations are in excellent agreement qualitatively, but that the magnitude of distortion is underestimated when the PIC model is used. This is due to the fact that local pair-wise interactions do not contribute to peak broadening in the PIC model. For the test peak shown, the measured standard deviations differ by 26% and the absolute mean radial positions differ by 2%. Furthermore, for all 48 peaks measured, (not including the $[h,k] = [0,0]$ reflection), the average difference in measured standard deviation was $25\% \pm 2\%$ and the average difference in measured radial position was $2\% \pm 0.25\%$. For the main beam, the difference in standard deviation was only $13\%$. Given the excellent qualitative agreement between the results computed with the two models it is clear that space-charge interactions (rather than stochastic interactions) are dominant in the post-specimen region at the beam conditions used in this study. Given this fact, and the order of magnitude larger computational cost associated with the BH simulations, the remainder of the simulations presented in this chapter use the PIC algorithm. This approximation means that it was possible to investigate the effects of electron-electron interactions
over broad ranges of the relevant parameter space, but that the results presented should be seen as a lower limit on the expected distortions.

6.3 Results and Discussion

We have explored the effect of space-charge interactions on the UED patterns from single crystal specimens over a wide range of the experimentally relevant parameter space; $Q$, $U$, $L$, and $\sigma_t$ (with zero emittance electron pulses unless otherwise indicated). The convergence and numerical stability of all simulations were first checked by scaling the number of macroparticles, and results were found to converge after $N \approx 25000$ macroparticles. While experimental feasibility was a consideration in the range of parameters studied, beam parameters well outside of that which can currently be produced were also investigated due to the exploratory nature of this work. One aim of this study was to determine the thresholds at which space-charge interactions have a significant impact on UED patterns. To quantify the impact, two simulations were performed for each parameter set; one with space-charge interactions “turned off”, and a second simulation (with identical initial conditions) was performed with space-charge “turned on”. We quantify the position and width of each Bragg spot in the diffraction patterns ‘with space-charge’ as follows:

$$r_{hk}(z_n) = \sqrt{\bar{x}_{hk}^2(z_n) + \bar{y}_{hk}^2(z_n)}$$
$$\sigma_{hk}(z_n) = \sqrt{\sigma_{x,hk}^2(z_n) + \sigma_{y,hk}^2(z_n)},$$

where $\bar{x}_{hk}(z_n)$, $\bar{y}_{hk}(z_n)$, $\sigma_{x,hk}(z_n)$, $\sigma_{y,hk}(z_n)$ are the respective measured mean $x$, $y$ positions and widths for the $[h,k]$ reflection at position $z_n = z/L$. The quantities $\hat{r}_{hk}$ and $\hat{\sigma}_{hk}$ are defined in the same way, but refer to the non-interacting reference simulation. Note that, based on the initial conditions defined, diffraction spots will be separated by $\hat{r}_{10} = (\lambda L z_n)/d$ in the absence of space-charge interactions. These
Figure 6–4: Width and position measures of diffraction reflections for various $h^2 + k^2$ values as a function of $z_n$. Simulation parameters used were $Q = 0.1$ pC, $U = 100$ keV, $L = 3.0$ cm, $\sigma_t = 50$ fs (FWHM), $\sigma_x = 200$ µm (FWHM), $T = 0.7$, $\sigma_U = 0$ and $N = 100 000$. The solid lines in Panel B show the fits to data using the model presented in Section 6.3.1 definitions allow us to construct two simple measures for the impact of space-charge on the position and width of each diffraction spot:

\[
\text{Position} = \frac{(r_{hk} - \hat{r}_{hk})}{\hat{r}_{10}}
\]

\[
\text{Width} = \frac{(\sigma_{hk} - \hat{\sigma}_{hk})}{\hat{r}_{10}}. \tag{6.11}
\]

The position measure indicates the space-charge induced displacement of the spot position from the non interacting case as a fraction of the inter-spot spacing. The width measure indicates the space-charge induced increase in spot width from the non interacting case, again as a fraction of the inter-spot spacing.

Fig. 6–4 plots these measures for the simulation data shown in Fig. 6–2 as a function of $z_n$. The data has been averaged over like orders, that is, all reflections with equivalent scattering angles defined by $h^2 + k^2$ have been averaged. Panel A in Fig. 6–4 shows the relative broadening of each diffraction order experiences as
the bunch propagates towards the detector at \( z_n = 1 \). Panel B shows the impact of space-charge interactions on spot position for several \( h^2 + k^2 \) values as a function of \( z_n \). It is clear from both the spot-position and spot-width results that the space charge distortions have a \( \vec{s} \) dependence; spots close to the main beam are deflected and broadened the most severely. This is expected, since the lower order reflections spend a longer time overlapped with the undiffracted beam.

### 6.3.1 Simplified space charge model: A mechanistic view of the distortion

A simple space-charge model was explored to explain the results in Fig. 6–4. We assume here that the electron pulse charge distribution, from sample to detector, can be approximated as a uniformly charged spheroid bunch. The spheroid charge distribution is defined by:

\[
\rho(\vec{r}) = \rho_0 \Theta \left( 1 - \left( \frac{r}{R} \right)^2 - \left( \frac{\zeta}{L_z} \right)^2 \right),
\]

(6.12)

where \( \Theta(x) \) is the Heavyside step function, \( \rho_0 = (3Q)/(4\pi R^2 L_z) \) is the charge density inside the bunch, \( R \) is the bunch radius and \( L_z \) is the bunch half length. Here \( \zeta \) is the longitudinal coordinate travelling with the bunch, so that \( \zeta(t) = z(t) - \bar{z}(t) \). Inside the spheroid the electrostatic potential is given by [21]:

\[
V(r, \zeta) = \frac{\rho_0}{2\epsilon_0} (M R^2 - M_r r^2 - M_\zeta \zeta^2),
\]

(6.13)

where \( M = \arctan(\Gamma)/\Gamma \), \( M_r = (1/2)(1 - M_\zeta) \), \( M_\zeta = (1 + \Gamma^2)(\Gamma - \arctan \Gamma)/\Gamma^3 \), and \( \Gamma = \sqrt{R^2/L_z^2 - 1} \). The electric field inside the spheroid can be solved analytically using \( \vec{E} = -\nabla V \). The radial fields inside the spheroid are:

\[
\vec{E}_r(r) = \frac{\rho_0}{\epsilon_0} M_r r, \quad r \leq R.
\]

(6.14)
An analytical solution for the fields outside the spheroid could not be found, so the fields in this region \((r > R)\) were determined directly from the GPT simulations. For our model, we assume macro particles belonging to a scattered beamlet defined by [h,k] may be considered test charges interacting with the mean field of the transmitted beam defined by Eq. 6.14 and the measured GPT fields for \(r > R\). We assume the test charges to be located at the centre of the bunch longitudinally, ie. \(\zeta = 0\).

The equations of motion for \(r(t)\) were solved numerically using the initial conditions \(r(0) = r_0\) and \(v_r(0) = \sqrt{v_x^2 + v_y^2}\), where \(v_x\) and \(v_y\) are defined by Eq. 6.1 and Eq. 6.4. Because the simulated bunch is focussing and under the influence of space-charge, \(R\) and \(L_z\) were parameterized as \(R(t)\) and \(L_z(t)\) using the measured dimensions from the transmitted beam simulation results. Initial positions were chosen to vary from \(r_0 = -R(0)\) to \(r_0 = R(0)\), and the results were averaged for \(r(t)\), so that the results can be compared to the previously defined quantity \(r\) of Eq. 6.10. The results are shown as the solid lines in Fig. 6–4, panel B. The simplified model is in excellent agreement with the simulations provided that an ‘effective charge’ \((Q_{eff} = 0.039 \text{ pC})\) approximately half that of the simulated transmitted bunch charge \((QT = 0.07 \text{ pC})\) is used in the model. The reduced effective charge is necessary in the 1D model since a test charge placed at \(\zeta = 0\) (the model initial conditions) is positioned to experience the maximum deflection due to the bunch space charge forces, not the average deflection. Thus, to bring the model into agreement with the average displacement obtained in the 3D simulations an effective charge smaller than the total bunch charge is required.

With this physical picture in mind, it may seem reasonable that an effective way to reduce these space-charge distortions would be to introduce a beam-block that removes the main-beam. This was explored but was found to be ineffective; only a
1% reduction was evident. This clearly indicates that these distortions result from the accumulated influence of space-charge interactions while the beams overlap. Once the beams become spatially separated, space-charge interactions have less influence, thus beam-blocking is ineffective at mitigating the observed distortions.

6.3.2 Diffraction pattern resolvability

In addition to the above, we also define a measure for diffraction pattern resolvability as was done in Chapter 3. From Fig. 6–2 and Fig. 6–4 it is clear that space-charge distortions are most severe for the 1st order reflections and that these reflections will be the first to overlap with neighbouring peaks for sufficiently high $Q$. Thus we define a quantity that measures the amount of overlap between the main beam and the 1st order peaks:

$$\Omega = \frac{\sigma_{00} + \sigma_{10}}{r_{10}}.$$  \hspace{1cm} \text{(6.15)}

We define ‘overlap’ between the main beam and 1st order peaks to be the point at which diffraction peaks begin to overlap at the 1 $\sigma$ level; i.e. $\sigma_{00} + \sigma_{10} = r_{10}$. This leads to a limit of resolvability of $\Omega < 1$.

It was found through this work that beam convergence has a significant impact on resolvability. To first order, space charge effects act to simply defocus the diffraction pattern at the detection plane. Thus, if the free-flight distance between specimen and detector is made too large (i.e. the main beam is too weakly focused), space-charge defocus dominates and the diffraction pattern cannot be resolved at the detector. Space-charge defocus can be overcome - to some degree - by ‘overfocusing’ the electron beam through the sample sufficiently. The practical limit to this approach is determined by the minimum specimen/detector distance that must
be maintained in the instrument (which will be determined by purely technical considerations and the resolution of the detector). Fig. 6–5 shows the effect of $L$ on resolvability at various beam energies. Note that the trend here is opposite as to that determined in Chapter 3–there it was found that as $L$ is made smaller the pattern becomes less resolvable. The apparent contradiction is due to the fact that in Chapter 3 we were actually adjusting the beam illumination conditions pre-specimen and were thus changing the amount of charge density at the specimen for each $L$. In the present example, the initial charge density at the sample is fixed for a given colour in Fig. 6–5 and are thus only investigating the influence of space-charge. Notice that for larger $Q$ (and thus higher initial charge density) the resolvability does become worse, consistent with the results of Chapter 3.
6.3 Results and Discussion

![Figure 6–6: Width and position measures at z_n = 1 for the h^2 + k^2 = 2 reflection as a function of Q at various energies. Dashed line in panel A shows a reference spot-width due to a 0.02 mm mrad normalized transverse emittance. Simulation parameters used were L = \hat{r}_{10}d/\lambda, \hat{r}_{10} = 200 \mu m, \sigma_t = 50 fs (FWHM), \sigma_x = 200 \mu m (FWHM), T = 0.7, \sigma_U = 0 and N = 100 000.]

In order to compare results at different energies in the subsequent sections, we define L such that the inter-spot spacing \hat{r}_{10} = 200 \mu m for all energies simulated, which requires that L = \hat{r}_{10}d/\lambda. This inter-spot spacing is on the order of 10 pixels for typical detectors. We then explore the influence of electron pulse charge, beam energy, pulse duration, energy spread and sample transmission on UED patterns from single crystals. The measures defined above facilitate the comparison of these results using a minimum number of figures.

6.3.3 Bunch charge and energy

Total bunch charge (or bunch fluence, Q/A) and electron energy are critical considerations in any UED or DTEM experiment, and these parameters have the most dramatic influence on the space-charge distortion. Fig. 6–6 shows results for the second order reflection (i.e. h^2 + k^2 = 2) as a function of Q and U. In this figure
6.3 Results and Discussion

Figure 6–7: Upper limit on $Q$ for different bunch energies and initial FWHM pulse durations measured at $z_n = 1$. Simulation parameters used were $L = \hat{r}_{10} d/\lambda$, $\hat{r}_{10} = 200 \, \mu m$, $\sigma_x = 200 \, \mu m$ (FWHM), $T = 0.7$, $\sigma_U = 0$ and $N = 25000$.

The width and position measures given are for a detector position at $z_n = 1$. At 100 keV (0.1 MeV) and $Q > 80$ fC (other beam conditions described in the caption), space-charge interactions are the determining factor in the observed width of the second order reflection; spot widths are more than double the emittance limited spot size under these conditions. The second order spot position is also shifted by more than 10 percent of the inter-Bragg spot spacing for $Q > 80$ fC under these conditions.

It is clear from Fig. 6–6 that electron energy has a dampening effect on both spot broadening and spot shifts. Despite the smaller diffraction angles that increase the overlap between beams, higher beam energy allows for larger bunch charges to be used. A threshold for the bunch charge, $Q_{\text{max}}$, at which space-charge distortions become so severe that diffraction peaks begin to overlap can be determined using the
6.3 Results and Discussion

Figure 6–8: Width and position measures at \( z_n = 1 \) as a function of \( \sigma_U \) at various \( h^2 + k^2 \) values. Dashed line in panel A shows a reference spot-width due to a 0.02 mm mrad normalized transverse emittance. Simulation parameters used were \( Q = 0.1 \) pC, \( U = 100 \) keV, \( L = 3.0 \) cm, \( \sigma_t = 50 \) fs (FWHM), \( \sigma_x = 200 \) µm (FWHM), \( T = 0.7 \) and \( N = 100 \) 000.

resolvability condition described above. \( Q_{max} \) was determined for various energies and pulse durations. The results are shown in Fig. 6–7.

6.3.4 Beam energy spread

In practice electron pulses do not have a zero energy spread at the specimen, and so it is necessary to address how a finite longitudinal emittance affects the space-charge effects. A finite energy spread was modelled as described in Section 6.2.1. Fig. 6–8 shows the results of this simulation for a mean energy \( U = 100 \) keV and bunch charge \( Q = 0.1 \) pC. From the width measure shown in panel A, it is clear that energy spread causes a dampening of the space-charge induced broadening as compared to a zero energy spread reference. This is due to the fact that the energy distribution causes the pulse to spread, reducing the local charge density and the space-charge fields more rapidly than would be the case without the energy distribution. The position measure shown in panel B indicates that space-charge induced
peak shifting is also dampened by energy spread. Panel B also suggests that after a sufficient energy spread, low order reflections are deflected by a smaller amount than the higher order reflections. This can be explained by observing Fig. 6–4 and noticing that higher order reflections separate from the main beam and begin to feel a deflecting force earlier than low order reflections. For a low energy spread, the charge density stays concentrated for a relatively long time, and so even though it takes longer for the inner peaks to separate, once they are separated they experience greater forces for longer times than outer peaks. For high energy spread, however, by the time inner peaks have separated, the main beam has already diffused and the space-charge forces are small, causing the inner peaks to deflect less.

There can be significant peak broadening effects that occur from the energy spread alone. Chromatic aberrations of the magnetic focussing lens and a scattering angle spread results from the spread in energy in the bunch. This means the standard deviations $\hat{\sigma}_{hk}$ will be non-zero when there is an energy spread. Thus the width measure in panel A does not represent an increase from ‘infinitesimal’ spots as it has in all other figures. The practical limitation to how much energy spread can be used to reduce space-charge effects will thus depend on the amount of chromatic aberrations present in the focussing element and the degree to which higher order reflections broaden due to the resultant spread in scattering angles.

6.3.5 Sample transmission

Up until now, simulation results have been shown for transmission constants $T = 0.7$. Using a 0.1 pC bunch as an example, this level of transmission partitions approximately 440,000 electrons into the main beam and only 4,000 electrons into each of the 48 diffracted beamlets. Under these conditions, it is not surprising that the interaction between the main beam seems to be the dominant force at play. In
order to gain further insight into the nature of the main beam and beamlet interactions, the effect of sample transmission on space-charge distortions was modelled by performing simulations under an identical set of beam parameters while varying $T$ in Eq. 6.2 from 0.1 to 0.9. Fig. 6–9 shows the spot width and displacement as a function of $T$ for these simulations. For all reflections the spot broadening depends linearly on the transmission coefficient, as was determined by the linear least-squares fits shown. Two distinct broadening and displacement mechanisms can be distinguished in this figure. First, space-charge interactions between individual scattered beamlets and the main beam. Second, space-charge interactions between all the scattered beamlets. The strength of the first is proportional to $T$ and the strength of the second is proportional to $(1 - T)$. Thus, a positive slope in Fig. 6–9 is strong evidence that the primary mechanism for the spot-width broadening and spot-position shifts are main beam-beamlet interactions. A negative slope is evidence that the primary mechanism for the spot-width broadening and spot-position shifts is space-charge interaction.
beamlet-beamlet interactions. Note that the high index reflection, \( h^2 + k^2 = 18 \), has a negative slope. This reflection is at the greatest angle with respect to the main beam and interacts most weakly with it. Under these conditions, spot-width broadening and spot-position shifts appear to be dominated by beamlet-beamlet interactions. The width and position of the lower order reflections, however, are dominated by beamlet-main beam interactions.

6.4 Conclusions

This chapter has revealed that electron-electron interactions in the post-specimen region have a detrimental impact on UED patterns at currently realizable electron beam illumination conditions and that these impacts increase in severity with beam brightness and are reduced with increasing (relativistic) beam energies. The distortions in the electron diffraction pattern, which include displacement and distortion/broadening of the Bragg spots, are well described by space-charge interactions between the diffracted beamlets and the main unscattered electron beam; stochastic electron-electron scattering effects are not important over the electron beam parameter range investigated. Lower order reflections, which interact/overlap with the unscattered beam for a longer period of time, are impacted more severely by space charge interactions than higher order reflections which become spatially separated from the main beam more rapidly. Space-charge distortions under all beam energy/beam brightness conditions can be minimized by using large convergence angles, small transmission constants (i.e. relatively thick specimens) and moderate electron beam energy spreads. Since these effects are rather straightforward to model, UED data can be corrected for space-charge induced distortions by off-line processing if required. This work identifies two avenues for exploiting future enhancements in electron beam brightness in UED experiments. The first avenue is to scale UED
systems to higher energy as is currently being pursued by several groups internationally [22–24]. Based on the current work, we note that these advances in MeV UED must proceed in parallel with developments in high sensitivity, high resolution detectors for these systems in order for such developments to have the greatest impact. The second avenue, at lower beam energy, is to move away from UED instrument geometries with large free-flight specimen to detector distances that is the current standard. The post-specimen region of UED instruments has not been an area of active research and development, and this work suggest that creative experimentation in post-specimen electron optical design is essential to manage space-charge distortions of UED patterns and make use of any future dramatic enhancements in electron source brightness in UED experiments.
References


CHAPTER 7

Conclusions and Future Outlook

Ultrafast electron diffraction is now in an excellent position to provide very subtle atomic information on the femtosecond time scale. The barriers formerly insisted upon the field by space-charge are gone and the limits to instrument performance are now rooted in the femtosecond synchronization of microwave oscillators. Due to the extremely promising beginnings upon using RF compression technology, it is the opinion of the author that future generations will overcome the jitter limitations reported in this thesis. Upon doing so, it is extremely likely that the sub-100 fs barrier will be crossed, allowing UED to access the most fundamental time scales of lattice vibrations and atomic motions. The future direction of UED research should be thus broken into two streams. The first and most important effort is of course to continue to perform investigations into the fundamental properties of material systems. The 300 fs instrument response function possible today allow for a rich variety of systems to be studied without being limited by time resolution. The smaller subset of systems that require better time resolution in order to answer fundamental questions motivate the second important research effort: to continue to improve upon the instrument performance of UED diffractometers. This effort can be broken down again into smaller research goals. The limits to the time resolution of RF compressed
Figure 7–1: Compact specimen chamber. The propagation distance through the chamber is 7 cm and will allow for approximately 2 orders of magnitude improvements to the charge density at the specimen.

instruments are not completely understood due to the fact that the IRF measured is a convolution between pulse duration and synchronization jitter. The first step to improving the IRF is thus to detangle these two terms and identify to what degree jitter is actually limiting the system. A rigorous understanding of the jitter will help to design better synchronization systems. Once the jitter is reduced down to the 10 fs level the remaining limits to the IRF must be systematic in nature and the results of chapter 3 should help in identifying problem areas of the apparatus. The Siwick group has begun a research program devoted to diagnosing the jitter. The efforts will include a combination of RF phase diagnostics and high time-resolution streak camera design. The ability to access the pulse-to-pulse arrival time and pulse duration simultaneously will allow for an unambiguous characterization of the machine
and allow for a much deeper insight into the parameter space affecting performance. The second avenue of instrument design being sought out in the Siwick lab is to build a much more compact instrument capable of much higher charge densities as a result of significantly reduced transverse beam size. The new specimen chamber is shown in Fig. 7–1. The results of chapter 3 and 6 will aid in building such a compact system, since both the temporal properties at the sample as well as the resolvability of the diffraction pattern depend on the careful choice of length scales. It is possible the new system will approach the limit for which space charge leads to peak position errors and so a calibration may be required to post-process the time-resolved patterns for the accurate determination of lattice constants.

The work presented here has shown that UED is an exceptional technique for probing the lattice response of materials after laser excitation. When combined with time-resolved spectroscopies that are sensitive to electronic signatures a complete picture of atomic level dynamics can be achieved. Just as the world has become smaller with the advent of communication and transportation technologies, the microscopic world has become somewhat larger and less mysterious with the advent of pump-probe techniques.
APPENDIX A

Estimation of Ponderomotive Measurement Noise

The statistical analysis of the RF cavity phase jitter presented in Chapter 4 required an estimation of the upper limit on the contribution to the total measured standard deviation due to the ponderomotive measurement itself. This upper limit allowed for an estimation of both the RF compressed electron pulse duration \( \sigma_t \) and the rms phase jitter \( \sigma_\tau \). This appendix will present supplementary details on how the ponderomotive measurement noise was estimated.

For any given laser delay setting \( \tau \), the total uncertainty of the measured ponderomotive signal \( < I(\tau) > \) is due to three contributing factors:

\[
\sigma_T^2 = \sigma_B^2 + \sigma_{PM}^2 + \sigma_J^2, \tag{A.1}
\]

where \( \sigma_B \) are fluctuations measured at the baseline of the IRF, \( \sigma_{PM} \) are fluctuations due to energy/pointing fluctuations of the laser beams and \( \sigma_J \) are fluctuations due to phase error of the RF cavity. The baseline noise \( \sigma_B \) arises due to electron beam pointing/charge fluctuations, counting noise, and CCD readout noise. For \( \tau \) values sufficiently far away from the peak of the impulse response function, there is no
interaction between the laser and electron beams, and $\sigma_T = \sigma_B$. Fig. A–1 shows IRF measurements performed under two different settings. Panel A shows the IRF measured with the RF cavity turned off and approximately 10000 electrons per pulse. Panel B shows the IRF with 0.1 pC of charge and the RF cavity operating under optimal compression settings. Both measurements were performed using the same laser conditions and thus the degree to which laser energy and pointing fluctuations contribute to the total standard deviation can be assumed to be the same. The electron beam arrival time fluctuations with RF cavity turned off were shown to be negligible in chapter 2 and we assume that $\sigma_J = 0$ in this setting. Notice that in panel A the error bars are roughly the same size for all $\tau$ values but in panel B they
increase dramatically as $\tau$ moves from the baseline to the peak. This can only be due to the significant contribution from $\sigma_J$ when the RF cavity is turned on. In order to put an upper limit on $\sigma_M = \sqrt{\sigma_B^2 + \sigma_{PM}^2}$ we use the data of panel A (since $\sigma_J = 0$). The baseline standard deviation measured was $\sigma_B = 0.062$ and the total standard deviation at the peak was $\sigma_M = 0.066$. From this we solve for the contribution due to laser fluctuations and find $\sigma_{PM} = 0.023$. Normalized to the baseline subtracted peak intensity this puts an upper limit on the relative error of $\sigma_{PM}$ of 8%. Applying this relative upper limit to the data discussed in chapter 4, the upper limit on the absolute value of $\sigma_M$ for the RF compressed data must be 0.19.
APPENDIX B

Errors due to a fixed specimen orientation

The Ewald sphere peak position and intensity errors described in Section 2.3 are significant for a single crystal experiment such as the one discussed in Chapter 5. One way to handle such errors is by performing ‘rocking curves’ with repeated measurements at a fixed $\tau$ over a calibrated range of beam film normal orientations. This technique will be implemented in the next generation upgrade to the Siwick diffractometer. Rocking curves do not need to be performed when: a) the time-scale of interest is fast compared to any change in lattice-constant, b) the change in lattice constant is sufficiently small and one is interested in time-scale rather than absolute value, c) an exact structural solution is not sought and one is more interested in relative changes. The reasons for these statements become clear by calculating the amount of peak position and intensity error that arises from taking data a fixed orientation.

B.1 Deviation vector analysis

We will formulate the errors in the reference frame for which the sample is fixed in space and the electron beam direction is free to rotate in order to satisfy the Laue
condition. The reciprocal lattice points are broadened by crystal shape transform factors (described in Section 2.3) only in the $z$ direction since the transverse size of the film is large and transverse reciprocal lattice broadening is negligible. Conservation of kinetic energy requires the Laue condition to be expressed as:

$$\vec{k}_{\text{out}} = \vec{k}_{\text{in}} + h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3 + \xi \hat{z},$$  

where $\xi$ is the distance away from the centre of the reciprocal lattice point required to intersect the Ewald sphere. Working in spherical coordinates, where $\phi$ is the angle between the $z$ axis and the transverse plane, the incident-wave vector is $\vec{k}_{\text{in}} = \frac{1}{\lambda} [\sin \phi \cos \theta, \sin \phi \sin \theta, \cos \phi]$, and after substituting the reciprocal lattice vectors for graphite we have:

$$k_{x,\text{out}} = \frac{1}{\lambda} \sin \phi \cos \theta + \frac{h - k}{3a}$$
$$k_{y,\text{out}} = \frac{1}{\lambda} \sin \phi \sin \theta + \frac{h + k}{\sqrt{3}a}$$
$$k_{z,\text{out}} = \frac{1}{\lambda} \cos \phi + \frac{l}{c} + \xi.$$  

$\xi$ can then be solved for explicitly by using conservation of energy ($|\vec{k}_{\text{out}}| = |\vec{k}_{\text{in}}|$):

$$\xi = -\frac{1}{\lambda} \cos \phi - \frac{l}{c} \pm \sqrt{\frac{1}{\lambda^2} - (k_{x,\text{out}}^2 + k_{y,\text{out}}^2)}.$$  

The electron beam does not have a perfectly fixed orientation, however, since there is a spread in convergence angles ($\phi$ and $\theta$) as well as a spread in energy defined by $\sigma_\lambda$. These spreads define a spectrum of $\xi(t)$ for each $t$. Using Eq. 2.12, the shape factor contribution to the intensity is:

$$I(\xi) = \frac{\sin^2(\pi(l + \xi c)N)}{\sin^2(\pi(l + \xi c))}.$$  

(B.1)

(B.2)

(B.3)

(B.4)
where $N$ is the number of unit cells along the $z$ direction. Eq. B.3 - Eq. B.4 define the intensity distribution (minus the contribution due to the structure factor) for each diffraction peak.

### B.2 Errors when $\phi = 0$

Experiments performed on SCNG graphite specimens at normal incidence are not affected by $c$ lattice constant changes since only $(h k 0)$ peaks are measured in this geometry. The errors due to fixed orientation will thus depend only on dynamical changes to the $a$ lattice constant. If there are changes to the $a$ lattice constant, they must be very small, since it was not possible to measure peak position changes at normal incidence that were distinct from the shifts due to the transient electric field effect discussed in Appendix C (a short discussion on the possibility of a transient $a$ lattice contraction is found there). If we assume the timescale associated with a change in lattice constant is related to the lowest order acoustic phonon mode it is possible to put an upper limit on the possible change in $a$. The period of the acoustic mode is quantized by the transverse dimension of the film, which is on the order of 250 $\mu$m. Since there are open boundary conditions, the period of oscillation is just $T = 2L/v$, where $L$ is the diameter and $v$ is the speed of sound along the direction of oscillation. The speed of sound is 22 km/s in the basal plane of graphite [1], and so the acoustic phonon period is approximately 21 ns for the specimens studied. Assuming the maximum possible change in lattice constant of 20% occurs after one quarter period, the amount of lattice constant change after 100 ps has passed is on the order of 8 $\text{m\AA}$.

Experiments at normal incidence were set-up by fine tuning the rotation and tip-tilt stages iteratively until the $(h k 0)$ peaks of the same family of reflections had as uniform intensity as possible. The acceptance angle of the streak camera ($< 1^\circ$)
B.2 Errors when $\phi = 0$

and the manual nature of the tip-tilt stage did not allow for the peak intensities to be perfectly uniform and there was approximately 10-40% variation amongst the peaks. The peak intensity errors discussed in Section B.1 depend significantly on the exact orientation of the specimen. This section will present the method used to determine the specimen orientation and quantify the peak intensity errors when $\phi \approx 0$.

The distribution of electron trajectories was modelled by defining a Gaussian spread in $\phi$ (the angle between the $z$ axis and the transverse plane) and a uniform distribution of $0 < \theta < 2\pi$ for each $\phi$. This distribution was then rotated so that it was aligned in a direction defined by the mean orientation angles $\bar{\phi}$ and $\bar{\theta}$. The convergence angle $\sigma_\phi$ was determined experimentally to be 0.02°. For each electron

Figure B–1: Simulated intensity distributions of diffraction peak. A: Simulation result for $[h,k] = [1,0]$, $\bar{\phi} = 0$, $\bar{\theta} = 0$, $N = 50$, $\lambda = 4.18$ pm and $\sigma_\phi = 0.5°$. B: Simulation result for the same parameters and $\sigma_\phi = 0.02°$. 

trajectory in the distribution, the error $\xi$ was calculated by Eq. B.3 and the intensity was calculated by Eq. B.4. Fig. B–1 shows simulation results of the intensity distribution for a normal incident orientation and a specimen that is 50 layers thick. When there is a large spread in angles in the electron beam, the intensity distribution represents the entire reciprocal lattice point and the integrated intensity will not depend strongly on the lattice constant (panel A). With a realistic angular spread, however, only a part of the reciprocal lattice point is sampled and the integrated intensity depends much more strongly on the lattice constant and beam orientation (panel B). Fig. B–2 shows the integrated intensity for two centro-symmetric diffraction peaks as a function of the mean orientation angle $\bar{\phi}$. The intensity of the two peaks are equivalent only at angles within $\pm 0.02^\circ$ and remain within 30% of each other until $\pm 0.15^\circ$. This level of tolerance made it very difficult to align all 6 peaks of a given family to the same intensity with the manual stage used to orient the specimen. A characteristic diffraction pattern of the normal incidence data presented in Chapter 5 is shown in Fig. B–3. The measured intensities in the diffraction pattern were used in a least-squares fitting routine to extract the orientation angles $\bar{\phi}$ and $\bar{\theta}$. The fitting algorithm also let float $\sigma_\phi$, $N$, and the azimuthal orientation of the specimen. Fig. B–3 shows a comparison of the simulated and measured diffracted intensity. The average residual between the data and simulation measured for the best fit was 6%. The extracted parameters are $\bar{\phi} = 0.09^\circ$, $\bar{\theta} = -96^\circ$, $\sigma_\phi = 0.025^\circ$ and $N = 47$.

These extracted parameters were used to constrain a simulation on the expected peak intensity error that accompanies a change in lattice constant in the graphene sheets. Assuming an acoustic phonon period of 21 ns, the lattice constant was modelled by $a(t) = a_0 + \Delta a \sin \omega t$ and the peak intensities were simulated for the
B.2 Errors when $\phi = 0$

![Figure B–2: Influence of beam orientation on the uniformity of a family of peaks. Simulation performed for variable $\phi$, $\bar{\theta} = 0$, $N = 50$, $\lambda = 4.18$ pm and $\sigma_{\phi} = 0.02^\circ$](image)

[1,0] family of peaks. The result of these simulations are shown in Fig. B–4. Within 1 ps there is no significant peak intensity error, even for the maximum possible lattice change of $\Delta a/a_0 = 0.2$. At 100 ps, there are significant errors measured per peak, but the trend is opposite for centro-symmetric peaks; one of the pairing goes up in intensity, where the other goes down. This leads to the average intensity error of the family being significantly lower than the errors on each peak. For the example of a 20% lattice change, the average error at 100 ps is only 0.8%. It is thus not expected that lattice constant changes in the graphene sheets will lead to peak
B.2 Errors when $\phi = 0$

**Figure B–3:** Determination of specimen orientation.
B.3 Errors when $\phi > 0$

We will next assume that $c$ changes dynamically but $a$ stays constant. In this case, the only term which will lead to a time-dependant error is $l/c$. If we assume the $(h k l)$ peak is originally aligned so that $\xi = \xi_0$, then the time-dependant error $\xi$ can be expressed as:

$$\xi(t) = \frac{l}{c_0} - \frac{l}{c(t)} + \xi_0(\phi, \theta, \lambda, h, k, l, a).$$  \hspace{1cm} (B.5)
B.3 Errors when $\phi > 0$

Figure B–5: Simulated error on diffraction data due to lattice expansions along the stacking direction. A: Simulated lattice constant with and without error due to $\xi$. B: Simulated diffraction intensity. Simulated for $(h k l) = (1 0 -3)$, $\theta_0 = 0$, $\phi_0 = -33.25^\circ$, $\sigma_\phi = 0.02^\circ$, $\sigma_\lambda = 1\%$, $\lambda_0 = 4.18$ pm and $\Delta c = 0.15$ Å.

The mean error $<\xi(t)>$ can be determined by taking the first moment of the $I(\xi(t))$ distribution. This error defines the lattice constant that will be extracted from the data:

$$\bar{c}(t, \xi) = \frac{3al}{\sqrt{9a^2|g\xi(t)| + <\xi(t)>^2} - 4(h^2 + hk + k^2)}, \quad (B.6)$$

where $g = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ is the reciprocal lattice vector.

The spread in convergence angles was obtained directly by measuring the FWHM spot size of transmitted beam through the aperture when there was no graphite specimen in place. Using $\sigma_\phi = 0.02^\circ$ and assuming a spread on $\lambda$ of $1\%$, the intensity distribution for the $(1 0 -3)$ peak was calculated for various degrees of lattice constant changes defined by $c(t)$. Fig. B–5 shows the simulated error in the lattice constant and intensity for a total expansion of 0.15 Å. The time dependance of the simulated (zero error) lattice constant was $c(t) = c_0 + A_1(1 - e^{-t/b}) + A_2 \sin \omega t$. 

B.3 Errors when $\phi > 0$

Observing panel A, the simulated lattice constant (with error) $\tilde{c}(t, \xi)$ measured the same time-dependance as $c(t)$ and was consistent with the qualitative trend. The fitted value of $A_1$ for $\tilde{c}(t, \xi)$ was 33% larger, however, and over a range of 1 mÅ - 0.5 Å the error on $A_1$ was bounded by 32.4-35.7%. The error depended much more significantly on the orientation angle; for example, for $\phi_0 = -38.55^\circ$ the error was 54%, 20% larger than for the orientation of $\phi_0 = -33.25^\circ$ used in Fig. B–5. The simulated integrated intensity measured very significant errors as is clear in Fig. B–5 (panel B). There should be no time-dependance on the intensity as a result of a lattice constant change but due to the intersection with the Ewald sphere there is only one lattice constant (for a given set of orientation/wavelength parameters) that the intensity is maximum. In fact, depending on the initial error $\xi_0$, it is possible the lattice constant change will lead to an intensity increase, (as is the case for the orientation used in Fig. B–5 up until $\approx 100$ ps). For $A_1$ values above 0.5 Å (not shown in the figure), the peak completely walks off of the Ewald sphere and the measured intensity is zero. From this result, it is clear that for lattice constant changes on the order of 0.1 Å, the error on the intensity will be on the order of 5%-100%. The errors on the peak intensities due to $c$ lattice constant changes are therefore on the same order as the expected intensity suppressions caused by lattice heating. For this reason, we will make no attempt to analyze the peak intensity for peaks with a $l$ component. Peak position data, however, yields qualitatively consistent results and over-estimates the lattice constant by a fairly consistent amount. We can therefore extract lattice constant dynamics with complete confidence in timescale as well as the measured trend. Furthermore, by using the static (un-pumped) diffraction patterns to extract the specimen orientation angle, we can simulate the expected ‘over-estimation’ of the measured expansion dynamics using the equations in this appendix. For the data
shown in Fig. 5–5, the orientation of the specimen was -38.5° and the expected error is approximately 54%.
References

Transient electric field at the graphite-vacuum interface

One aspect of studying thin graphite films that must be handled correctly is the laser-induced transient electric field (TEF) that develops on the surface quickly after excitation [1,2]. Laser-excited electrons are emitted from surfaces by two mechanisms: emission due to quantum-mechanical multiphoton photoemission (MPPE) and also by thermionic emission that occurs after the hot electron gas has thermalized [3, 4]. It has been shown that for metals excited by femtosecond pulses, thermionic emission dominates over MPPE at fluences in excess of 1 mJ/cm\(^2\) [3–6]. UED experiments on graphite have shown that the likely mechanism is also thermionic above 1 mJ/cm\(^2\) due to the linear dependance on the surface potential as a function of excitation fluence [1,7].

Early work on graphite performed by Carbone et. al. [8] in a RHEED geometry has been criticized [9] for not taking account of the electric fields present at the surface of the graphite film when interpreting their time-resolved data. Park et. al. showed that transient electric fields present at the surface of a silicon specimen lead to a significant deflection of an electron beam if it passes close by the surface within...
Figure C–1: Deflection of diffraction pattern due to transient electric fields. The measured $x$ and $y$ coordinates of all diffraction peaks in the pattern exhibited a time-dependant deflection after laser-excitation that relaxed at long time scale.

Picoseconds after femtosecond excitation [2]. Although Carbone et al. presented evidence that their extracted lattice dynamics were not dominated by TEF effects [10], a deflection of the diffraction pattern due to TEF’s has been measured in two subsequent UED graphite studies [1,11] and so it is pertinent to separate the impact of TEF induced diffraction results from those caused by lattice changes.

Fig. C–1 shows data taken on a SCNG sample when there is a small ($\sim 0.1^\circ$) angle $\phi$ between the specimen and electron beam. After excitation with an incident
fluence of 12.4 mJ/cm$^2$, the average shift of the diffraction peaks was measured in both the $x$ and $y$ directions. The quantities $\Delta x$ and $\Delta y$ are defined to be the change in Bragg peak position relative to the value measured at negative $\tau$ values. The Bragg peak positions were calculated from the raw data by taking the first moment of the intensity distribution in both directions. Each individual peak in the diffraction pattern showed the same behaviour: the peaks moved towards $-x$ and towards $+y$, at a critical $\tau$ the deflections are maximum, and then the peaks relax back towards the equilibrium positions. This behaviour is consistent with the measurements presented by Park et. al [2] and is due to the combined interactions of the positive surface charge, the TEF induced by the travelling distribution of surface-emitted electrons and the electron pulse. The time-dependance of the deflections were fit with exponential decay functions and the $1/e$ time constants for the initial decay was extracted. The initial deflection of the pattern occurs with a time constant of $5.2 \pm 0.8$ ps.

The TEF effect is handled by post-processing the diffraction data. At each time delay $\tau$ the centre of the diffraction pattern is calculated based on the symmetry of the diffraction peaks and the diffraction angles are measured relative to this dynamically determined centre. If the $x$ deflection of each Bragg peak on the pattern has the same amplitude and time scale--and the same is the case for the $y$ deflections--tracking the diffraction pattern centre in this way would completely remove the TEF effect from the diffraction data. The deflections shown in Fig. C–1 is the average of 11 diffraction peaks which each showed the same qualitative trend. Fits to the amplitude of the deflection, however, showed variation amongst the peaks, such that the maximum deflection in the $x$ direction is $5.3 \pm 1.5$ µm and the deflection in $y$ is $6.6 \pm 3.1$ µm. Since a pixel width on the CCD is 14 µm, this variation corresponds to a fraction
of a pixel. It is possible that the variation amongst the peaks is due to a real $a$ lattice constant change, and that due to the fixed orientation errors discussed in Appendix B, each peak moves by a different amount. However, since the variation is less than a pixel and is on the same order as the global shift due to the TEF, a lattice constant change in $a$ could not be extracted with confidence. The future generation of the UED diffractometer, which will be equipped with the ability to perform rocking curves, will overcome this limitation since it will be possible to take data that does not suffer from peak position errors due to fixed orientation.
References

APPENDIX D

Post-processing time correction of the slow RF synchronization drift

The RF synchronization drift discussed in Section 4.5.1 (a drift in the mean arrival time of the electron pulses relative to the laser excitation pulse) will cause temporal information in the raw diffraction data to be broadened in proportion to the magnitude of the drift. Time-resolved diffraction measurements proceed by setting the delay $\tau$ between the electron and laser pulses and then collecting diffraction patterns. At each delay $\tau$ many diffraction patterns are acquired and averaged together until the signal to noise is sufficient to resolve the transient change of interest. For the dataset shown in Fig. 5–3 approximately 10 minutes of integration per data point was required. In order to track and correct for the time-zero drift, data was taken by scanning all time delays in a linear fashion (one 6 second acquisition per time delay), and once all delays were acquired, a new scan begins.

The scan by scan intensity dynamics collected for the Fig. 5–3 dataset is shown in Fig. D–1. The intensity dynamics of each scan was fit using an exponential decay to define the instantaneous time zeros. The dynamically determined time zero is represented by the black solid line in panel A. The FWHM spread on the fitted time
zeros for all runs shown was 600 fs. The drift was corrected by subtracting the $\tau$ values of each scan by the time zero values. The corrected intensity data is shown in Fig. D–1, panel B. The corrected data was binned into discrete time windows and averaged together. The binned data was then used to extract the dynamical information presented in Fig. 5–3.