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Charge Carrier Dynamics in Metals and Metal-Semiconductor Junctions Studied by  
Transient Absorption and Photoemission Spectroscopy

by

Bethany Rose de Roulet

A dissertation submitted in partial satisfaction of the  
requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Stephen R. Leone, Chair

Professor Naomi Ginsberg

Professor David Attwood

Spring 2022



Charge Carrier Dynamics in Metals and Metal-Semiconductor Junctions Studied by  
Transient Absorption and Photoemission Spectroscopy

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Bethany Rose de Roulet

## Abstract

### Charge Carrier Dynamics in Metals and Metal-Semiconductor Junctions

Studied by Transient Absorption and Photoemission Spectroscopy

by

Bethany Rose de Roulet

Doctor of Philosophy in Chemistry

University of California, Berkeley

Professor Stephen R. Leone, Chair

Transient spectroscopy enables the observation of fundamental processes that bring an out of equilibrium material back to its original, equilibrium state. In the most general terms, transient spectroscopy requires varying the time delay between two pulsed beams of light, where one beam perturbs the sample out of equilibrium and the other beam observes the material response. Through the discovery of high harmonic generation of extreme ultraviolet (XUV) light, transient spectroscopy gained the element specificity provided in the x-ray regime, while retaining the excellent time resolution afforded by fiber broadened, compressed laser light. Throughout the course of this thesis, the capabilities of transient XUV absorption and photoemission spectroscopy will be discussed. New insights into the charge carrier dynamics of metals and metal-semiconductor junctions will be gained through the employment of these techniques.

In chapter 1 the fundamental principles of absorption, photoemission, and high harmonic generation will be laid out. The transient XUV absorption and photoemission spectroscopy apparatuses will be shown in chapter 2 and 3, respectively. Thin film growth of metals and metal-oxide is discussed in chapter 4. Attosecond XUV transient absorption is then used to provide insight into the dependence electron thermalization rates on the band structure of metals in chapter 5. In chapter 6, transient XUV absorption spectroscopy is used to study electron transfer in a Pt/TiO<sub>2</sub> heterostructure. Finally, transient photoemission spectroscopy is used to study hole transport in Zn/GaP junction.

*to my God*  
*to my husband*  
*to my family*

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# Chapter 1. High harmonic generation of extreme ultraviolet photons for transient absorption and photoemission spectroscopy

## 1.1 Introduction

Transient spectroscopy provides the ability to observe a material's temporal response to non-equilibrium conditions. Practically this is accomplished by dividing a pulsed laser into a pump arm, which perturbs the system out of equilibrium, and a probe arm which reports on the material response. It is greatly advantageous to have a probing technique that provides clear information on the energetic state of the material. Probing techniques in the extreme ultraviolet (XUV) regime are an excellent method as they interrogate core levels which have a large energy separation between different elements, that ultimately leads to a clear transient response for various elements within a sample. Additionally, the high harmonic generation (HHG) process which creates the XUV photon has an attosecond temporal duration that is intrinsic to the generation process. The elemental sensitivity and the excellent time resolution give transient XUV spectroscopy the ability to clearly resolve complex dynamics within a single material, or inter-layer dynamics in heterostructures. Throughout the course of this thesis the use of transient XUV absorption spectroscopy and transient XUV photoelectron spectroscopy to study the response to photoexcitation in metals and metal-semiconductor junctions is presented. In this chapter an introduction to absorption spectroscopy and photoemission spectroscopy is given and the theory of HHG is presented in the context of its use in absorption and photoemission spectroscopy.

## 1.2 XUV Absorption Spectroscopy

Absorption occurs when a photon promotes an electron from an initial state into a final state. The probability of this process ( $W_{fi}$ ) is described by Fermi's golden rule.

$$W_{fi} = \frac{2\pi}{h} |\langle \phi_f | \hat{T} | \phi_i \rangle|^2 \delta(h\omega - \Delta E) \quad (1.1)$$

In equation 1.1  $\phi_i$  and  $\phi_f$  are the wavefunction of the initial and final states, respectively,  $\hat{T}$  is the transition matrix element,  $h\omega$  is the energy of the incident light, and  $\Delta E$  is the energy difference between the final and initial state.

In single photon absorption processes the transition matrix element,  $\hat{T}$ , is the electric dipole operator. Inserting the electric dipole operator into eq. 1.2

$$W_{fi} = \frac{e^2}{hc} \frac{4\omega^3}{3c^2} |\langle \phi_f | \vec{e} \cdot \vec{p} | \phi_i \rangle|^2 \delta(h\omega - \Delta E) \quad (1.2)$$

Here  $\vec{e}$  is the polarization vector of the absorbed light,  $\vec{p}$  is the momentum, and  $\omega$  is the frequency of the light.

The initial state is a bound core level. The final state depends on the type of material being studied. The lowest energy transitions possible, which give rise to the onset of XUV

absorption, involves transitions from core levels to the lowest unoccupied state in the material. For metals the onset corresponds to transitions between the core level and open states just above the Fermi level, while for band gap materials (semiconductors and insulators) the absorption onset arises from core level to valence band transitions. In either situation, the final state can be approximated as a Bloch wavefunction, which is a plane wave free electron state modulated by a periodic function accounting for the crystal lattice. This approximation is not necessarily true, as the core hole has been shown to strongly interact with the final state of the system, however some important insights arise from making this simplification [1].

With this we get the transition probability matrix element ( $M^2$ ) between the bound core level initial state,  $|b\rangle$ , and the final  $|\epsilon\rangle$  states just above the Fermi level in the case of a metal or valence band, for band gap materials.

$$M^2 = |\langle \epsilon | \vec{e} \cdot \vec{p} | b \rangle|^2 \quad (1.3)$$

Ultimately this leads to the XUV absorption cross section  $\sigma_{XUV}$  being equal to the density of final states probed ( $\rho$ ), either conduction band for band gap materials or states above the Fermi level for metals, scaled by the transition probability matrix element.

$$\sigma_{XUV} = \rho M^2 \quad (1.4)$$

As was stated earlier, this is heavily dependent on the assumption that the core hole does not interact with the system. Limitations of this are discussed in the introduction section of the chapter 5.

The selection rules for absorption can be seen by determining when  $M^2 \neq 0$ . In the case here, of the electric dipole operator,  $M$  is not zero when the angular momentum quantum number of the initial and final state differs by 1, and the spin quantum number does not change. In the context of the XUV light used in these studies, absorption from the  $M_{2,3}$ -edge corresponds to  $p \rightarrow s$  or  $d$  transitions, while absorption at the  $N_7$ -edge corresponds  $f \rightarrow d$  transitions.

The theory outlined above shows that, XUV absorption spectroscopy provides insight into the energy of the core levels relative to the lowest unoccupied states. When absorption is implemented as the probe in transient XUV absorption spectroscopy, in the most simplistic sense it reports on changes in the relationship between the core level and unoccupied density of states. For example, if the pump promotes an electron from the valence band to the conduction band of a semiconductor, and core hole interactions are ignored, then an absorption transition is now open in the valence band and a transition is blocked in the conduction band. This will be further explored in the context of attosecond XUV transient absorption measurements of Fe and Pt in the chapter 5 and a Pt/TiO<sub>2</sub> junction in the chapter 6.

### 1.3 XUV Photoemission Spectroscopy

Photoemission spectroscopy (PES) uses the photoelectric effect to reveal the electron distribution of a material. The photoelectric effect states that when the energy of light ( $E_{light}$ ) impinging on a material is larger than the binding energy that holds an electron in

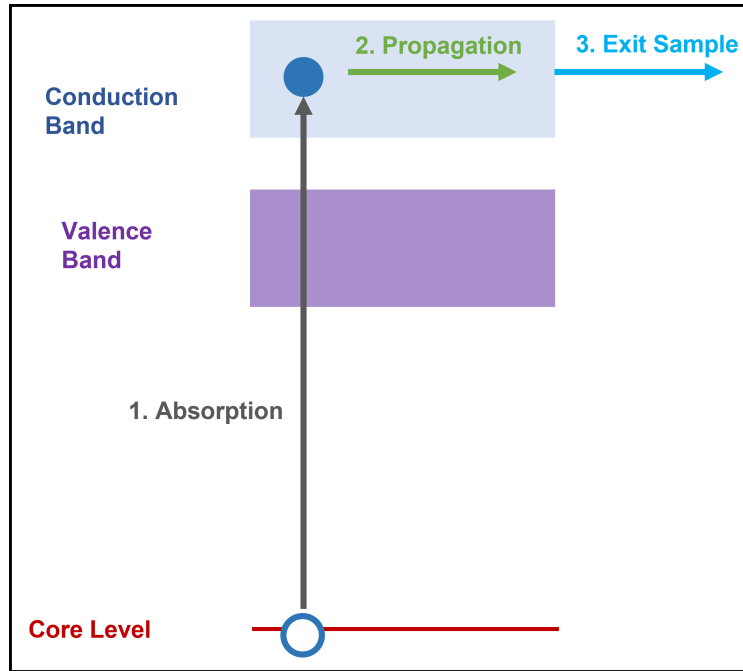


the material ( $\phi_{BE}$ ) then the electron will be ejected with a kinetic energy ( $E_{ke}$ ) equal to the energy difference between the photon energy and the binding energy of the electron.

$$E_{ke} = E_{light} - \phi_{BE} \quad (1.5)$$

In PES a sample is irradiated with a known energy of light and the kinetic energy of the photoelectrons is measured by the detector. From this the binding energy of the photoelectrons can be determined using the conservation of energy relationship shown in eq. 1.1. In this way, PES provides insight into the distribution of electrons in a material.

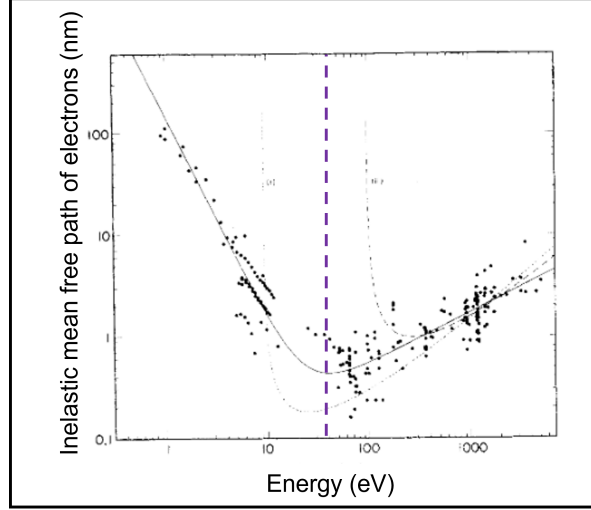
The photoemission process can be further broken down into 3 steps. In step one, an electron absorbs a photon. Then, the electron travels to the surface of the sample. In the third step, the electron escapes the sample. There are several insightful points introduced through this model.



**Fig. 1.1** Diagram of the three step model of photoemission spectroscopy depicted for a semiconductor. The first step is absorption of a photon, second step is propagation of the excited electron to the surface of the material and the third step is the electron escaping the surface of the material.

If only conservation of energy (eq. 1.1) is considered, then PES would directly reveal the electron occupation of the density of states of a material. The three step PES model reveals that the ejected electrons are dependent on the absorption of an XUV photon. In the previous section it was shown that the XUV absorption cross section is equal to the density of the final states scaled by the transition probability matrix (eq. 1.4). Inherently, this means that the photoelectrons generated from the light are not an exact copy of the electron filling of the density of states.

During the second step, an electron must propagate through the material. In this step electrons might collide inelastically with the lattice, impurities, or other electrons. These

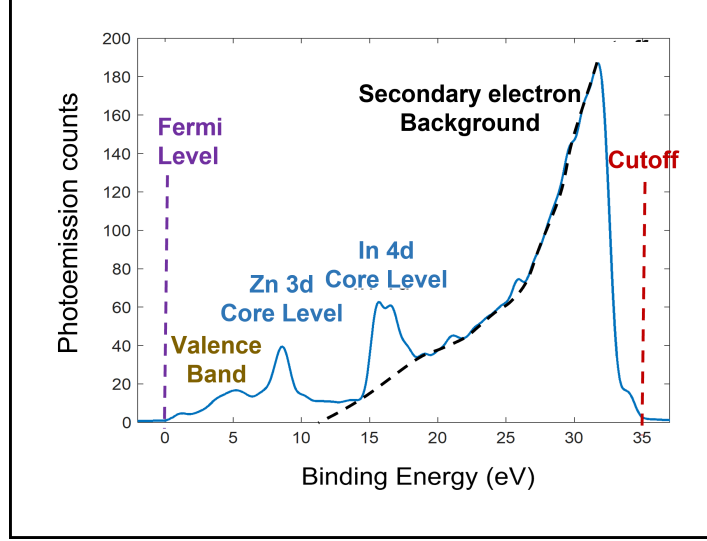


**Fig. 1.2** The inelastic mean free path of electrons in a material is plotted as a function of excitation energy is reprinted with permission from the publisher [2]. The dashed purple line shows that the 41.9 eV photon energy used in PES studies presented in the this thesis probes only the upper 0.5 nm of the sample being interrogated.

collisions lead to two important factors. First, the only photoelectrons that will be measured by the detector come from a depth smaller than the electron mean free path of the material (Fig. 1.2). This makes PES a surface sensitive technique. Second, due to inelastic collisions there will be more electrons ejected at lower kinetic energies than initially captured in equation 1.1. This gives the characteristic rising background to the photoelectron signal (Fig. 1.3).

The cut off energy for the secondary electrons shows the minimum amount of energy required for an electron to escape the material. In equation 1.1 this corresponds to  $E_{ke} = 0$ . For solids state samples the position of the secondary electron cutoff is equal to the work function of the material. For the example shown in figure 1.3, the incident photon energy was 38.75 eV, the cutoff energy was measured at 35.00 eV, making the work function of the material 3.75 eV.

In the theory outline above, PES is examined in light of the information it provides for material analysis. Specifically, it gives insight into the electron occupation of the material, which is particularly useful for determining a materials elemental composition or work function. In the context of transient photoemission spectroscopy, PES reports on how a material responds to laser excitation. For example, changes to the Fermi level from electron heating or photo-induced occupation of gap states can be directly observed. Additionally, changes to the electron environment for different elements can also be observed. For example, considering the Zn/InP junction presented in figure 1.3, if there is an excess of negative charge accumulating around the Zn atoms, then the extra negative charge will accelerate electrons ejected from the Zn 3d core level, which will result in an observed shift toward lower binding energies for this peak. In this manner, transient photoemission reports on the light-induced changes to material properties as well as the accumulation of charge around elements within a material or junction. This will be further explored in the chapter 7.



**Fig. 1.3** PES measurements taken for Zn deposited on InP shows the Zn 3d, In 4d, the Fermi level (purple dashed line), the shape of the secondary electron background (black dashed line) and the secondary electron cutoff (red dashed line).

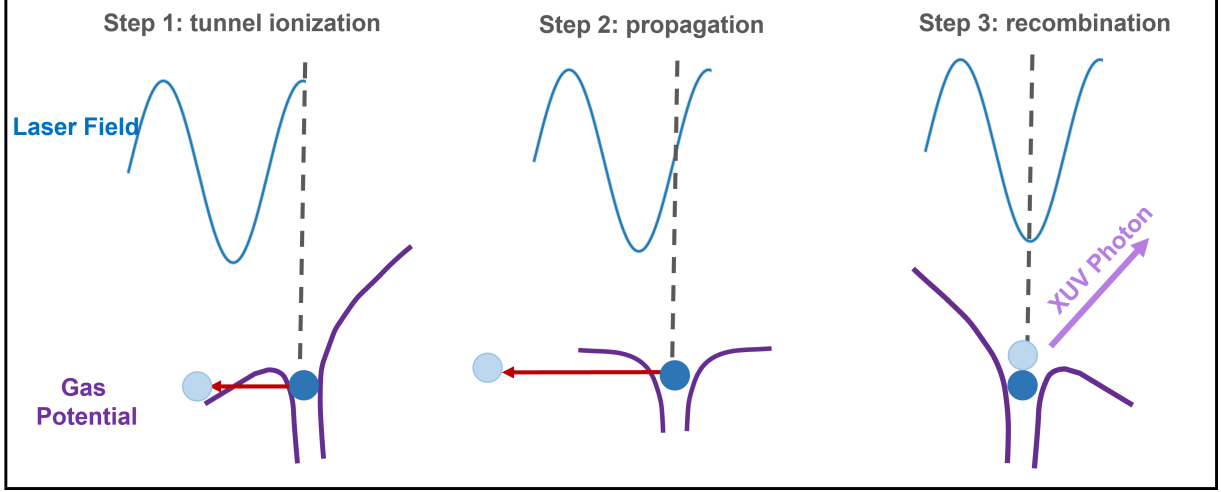
## 1.4 High Harmonic Generation

Broadly, HHG is a process where an intense laser field interacts with the potential of a material resulting in the release of an XUV photon. While harmonics can be generated in a gas or solid medium, the explanation here will focus on a rare gas as the generation medium, as that is what is used in the experiments presented in later chapters.

There are several properties of the generated XUV light that arise from the HHG process that are relevant to obtaining a suitable probe source for transient absorption and photoemission spectroscopy. For photoemission it is preferable to have a well-defined single energy of light, while for absorption spectroscopy a broad continuous XUV spectrum is desired. The three step model of HHG is a semi-classical model that captures the relevant fundamental characteristics of the emitted XUV light to understand the temporal duration of the XUV light and the available variables in the HHG process to generate either a narrow or broad XUV spectrum [3-6].

As the intense electric field from the driving laser bends the Coulomb potential of the gas, an electron wavepacket can tunnel out of the potential. The electron then propagates in the continuum during step 2. The propagation process is guided by the laser field and when the potential switches sign, half a period later, the electron passes the nucleus and has a non zero probability of recombining with the parent atom. If the electron recombines with the nucleus, the extra energy gained by the electron during propagation is released as an XUV photon.

The timing of the steps displayed in the three step model are locked to the phase of the driving laser field, with the emission of an XUV photon occurring every half cycle of the driving laser field (Fig. 1.4). This has several ramifications. First, in the context of pulsed lasers used in transient spectroscopy, the pulse train generated in one pulse of the driving field is temporally locked to the original driving field. This is a very beneficial factor



**Fig. 1.4** The three step model of HHG consists of tunnel ionization of an electron, propagation through the continuum, and finally an XUV photon is released if the electron recombines with the nucleus.

in transient spectroscopy as it means the pump and probe arm are inherently temporally locked. Second, the sign of the electric field switches every half cycle, which causes the emitted XUV burst to have a sign flip for every half cycle of the driving laser field. Lastly, the small time period for which an electron propagates in the continuum gives the XUV burst an attosecond time scale. Figure 1.5 demonstrates the relationship between the temporal profile of a pulsed driving laser field and the emitted XUV bursts.

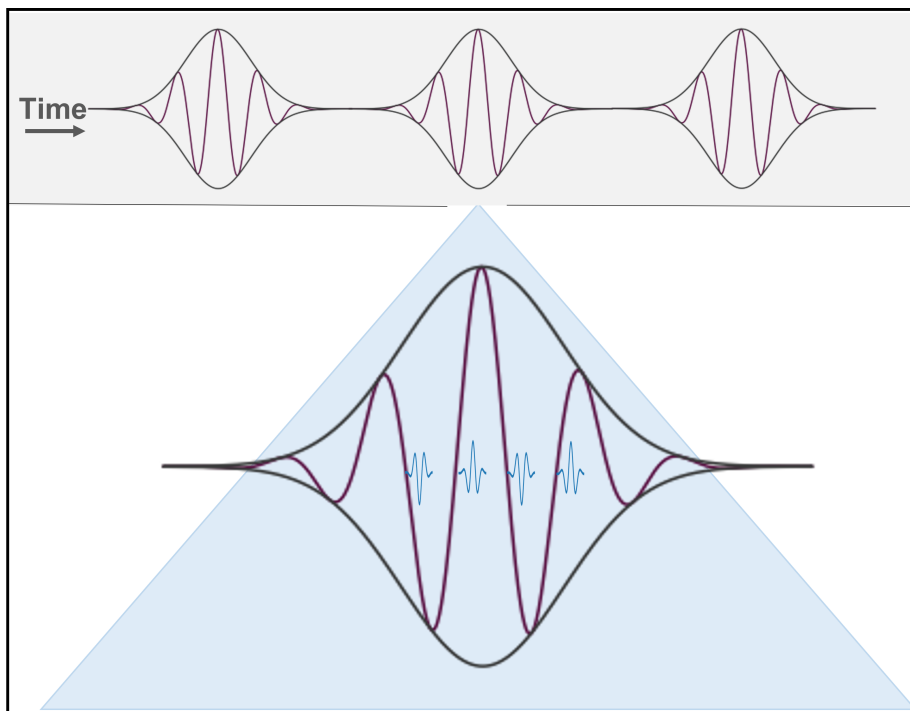
The HHG bursts can be modeled as a sinusoidal function with a Gaussian envelope which is then convoluted with a series of Dirac functions repeating every half cycle of the laser with opposite sign.

$$E(t) = G(t)e^{\omega_{XUV}(t_i+t)} * \sum_{n_0}^{n_p} (-1)^n \delta(t - n \frac{T}{2}) \quad (1.6)$$

In equation 1.6,  $G(t)$  is a Gaussian function describing the envelope of a single XUV burst and  $e^{\omega_{XUV}(t_i+t)}$  captures the sinusoidal aspect of the XUV burst. The summation, set for  $n_p$  half cycles, accounts for the sign flip with the  $(-1)^n$  factor, and the Dirac function is only non-zero at every half cycle of the driving laser field period with period  $T$ . By taking the Fourier transform the structure of the XUV light in frequency space can be seen.

$$E(\omega) = G(\omega - \omega_{XUV})e^{\omega_{XUV}t_i}e^{i(n_0 + \frac{n_p-1}{2})}(\omega \frac{T}{2} + \pi) \left[ \frac{\sin(n_p(\omega \frac{T}{4} + \frac{\pi}{2}))}{\sin(\omega \frac{T}{4} + \frac{\pi}{2})} \right] \quad (1.7)$$

There are two useful features to be highlighted from the frequency space expression of the XUV light. First, in frequency space  $G(\omega - \omega_{XUV})$  is a Gaussian envelope that is centered at the XUV frequency. This shows that the temporal duration of the initial XUV burst is proportional to the width of the frequency of the XUV spectrum. Second, the factor inside the brackets demonstrates that the XUV light is periodic in frequency space. Furthermore, the quantity  $\sin(n_p(\omega \frac{T}{4} + \frac{\pi}{2}))$  goes to zero when the harmonic order  $n_p$  is even. In other



**Fig. 1.5** XUV photons (blue line) are emitted every half cycled of the driving laser field with a sing flip corresponding to the change in direction of the field. Here the gray line indicating the envelope and of the field and the purple line showing the oscillations of the electric field for the driving laser.

words, only odd harmonics will be observed in an isotropic gas medium with a driving laser of a single wavelength.

For PES, where the generation of narrow odd harmonics is wanted, the driving laser should be closer to a single wavelength resulting in a temporally longer pulse. The single color results in a comb of odd harmonics to be produced and the longer pulse creates a longer XUV burst, which results in narrower spread of energies for each harmonic. The generation of narrow, odd harmonics provides an excellent XUV source that can be further refined to a single XUV energy through several methods. In the experimental apparatus presented in chapter 3 the driving laser field is a narrow 800 nm source and an XUV monochromator is employed to further select a single odd harmonic for the PES probe.

For absorption spectroscopy a broad XUV source is required. This is accomplished in the experimental apparatus presented in chapter 2 by using a broad (420 - 920 nm) driving laser field. From equation 1.7 it can be seen that many input frequencies  $\omega$  lead to the summation of many odd harmonics of different  $2\omega$  frequency spacing. This ultimately results in an observed continuum of XUV light.

## 1.5 Conclusion

Throughout the course of this chapter a fundamental understanding of absorption and photoemission spectroscopy was given. From these two sections it was shown that the XUV

source has opposite requirements. For absorption spectroscopy the source needed to be broad in energy and short in time, while the PES needed to be narrow in energy. In the final section of this chapter, HHG was explained in terms of the three step model. It was shown that a narrow comb of odd harmonics can be generated using a single frequency input laser with a longer pulse duration. It was also shown that a broad XUV spectrum can be generated by using a broad driving laser. The theory laid out in this chapter serves as a starting point to explore carrier relaxation dynamics in metals (chapter 5), charge transfer in the femtosecond timescale in a Pt/TiO<sub>2</sub> junction (chapter 6), and charge relaxation on the picosecond timescale in a Zn/GaP heterostructure (chapter 7).

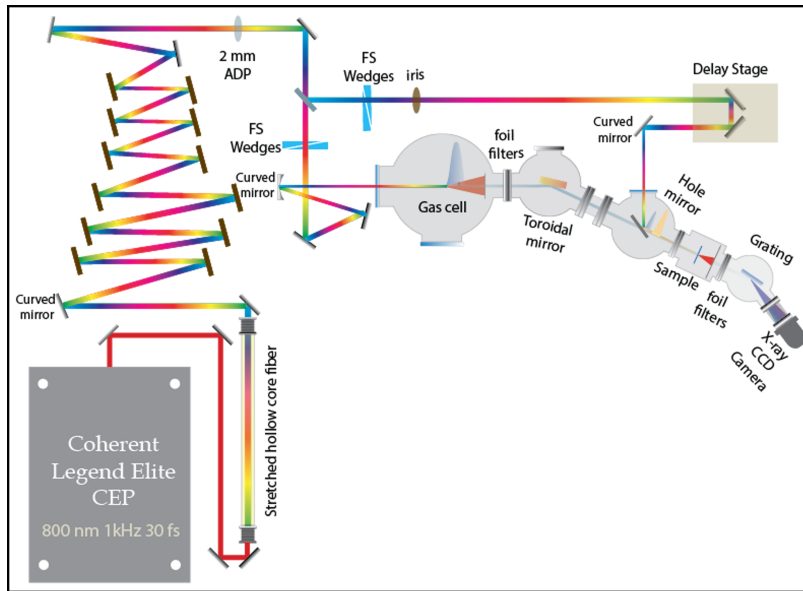
# Chapter 2. Attosecond transient extreme ultraviolet light absorption spectroscopy experimental apparatus

## 2.1 Introduction

This chapter details the experimental apparatus used in attosecond extreme ultraviolet (XUV) light transient absorption experiments. The optical alignment is outlined, theoretical and practical considerations of spectral broadening in the hollow-core fiber are discussed, methods of spatial and temporal overlap are provided, temporal characterization of the instrument is described, and camera calibration is shown.

## 2.2 Optical Alignment

Briefly, the transient absorption is accomplished by broadening and temporally compressing the 25 fs, 795 nm laser output to a broadband, 420 nm - 920 nm, 4 fs light. The broadband light is then split into a probe arm, which generates XUV light used for x-ray absorption, and a pump arm, which is used to perturb the sample through optical absorption. Time dependent dynamics are measured by physically changing the path length of the pump arm, which results in a controllable, variable time delay between the pump and probe arm. Upon leaving the laser, the light is broadened from  $\sim 100$  nm bandwidth to  $\sim 500$  nm



**Fig. 2.1** The diagram of the transient absorption experimental setup shows a schematic of the components in the pump and probe optical path.

bandwidth in a 2 m silica, stretched hollow core fiber (Polymicro Technologies 1068150029) with an  $704 \mu\text{m}$  inner diameter and  $849.8 \mu\text{m}$  outer diameter. The broadening process is described in section *Hollow Core Fiber*. The beam is collimated with a curved mirror and routed through nine pairs of double-angle, broadband compression mirrors (Ultrafast Innovations PC1332, PC70). Next, 2 mm of ammonium dihydrogen phosphate (ADP) is used to

compensate for higher order dispersion [7]. A broadband beam splitter reflects 30% of the beam to be used as the optical pump, while the remaining, transmitted portion is used to generate the extreme ultraviolet (XUV) light probe.

After the beam splitter, the probe arm passes through a pair of anti-reflective (AR) coated, fused silica wedges. The second wedge in the pair is on a translation stage that travels perpendicular to the beam path, which allows for active tuning of the second order, group delay velocity compensation. A 1 m curved mirror focuses the beam into a gas nozzle where the XUV light is generated. The driving laser light is filtered out with a thin, metal foil filter, either 100 nm thick Al or 150 nm thick Zr. The expanding XUV light is re-imaged at the sample position using a gold-coated toroidal mirror. The distance between the gas cell and toroidal mirror and the distance from the toroidal mirror to the sample is 1 m. This 1:1 ratio between the second image and the first image, also known as a Rowland configuration, creates the minimal amount of aberrations [8]. After the toroidal mirror, the focusing XUV light passes through a hole mirror and then is partially absorbed by the sample. Finally, the remaining, transmitted, XUV light passes through another metal foil filter and is then reflected by a curved grating (Hitachi 001-0640). Finally, the separated light is collected on an XUV camera (PIXIS-ZO: 400B).

The path for the optical pump arm also passes through a pair of AR coated fused silica wedges, where the second wedge is on a translation stage perpendicular to the beam path to allow for active adjustment of the second order dispersion. An iris is used to control the power of the optical pump. The pump then passes through a delay stage that controls the relative timing between the pump and probe arms. The delay stage is composed of a longer delay stage (50 mm range) and a piezo controlled delay stage with a 50  $\mu\text{m}$  range. The pump beam is then reflected by a curved mirror (focal length, 1 m), and then the surface of a the hole mirror, where the pump and probe co-propagate to the sample. Lastly, any residual pump beam that is transmitted through the sample is blocked by a metal foil filter, either 150 nm thick Al or 250 nm thick Zr.

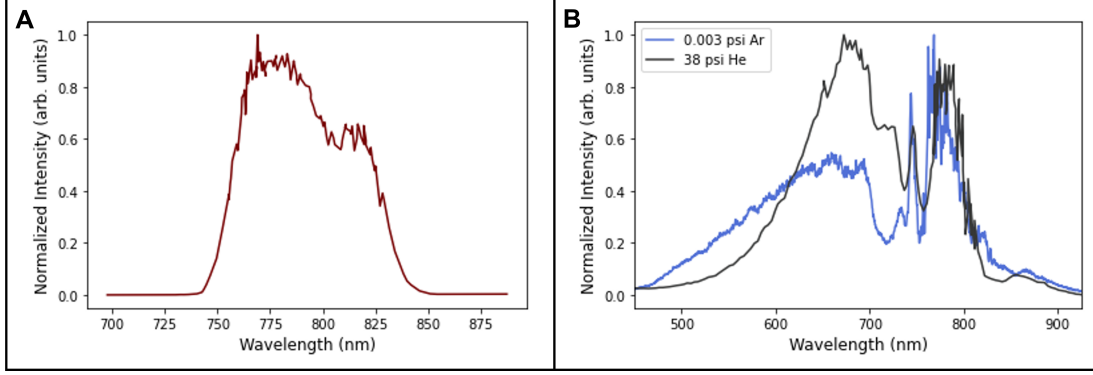
## 2.3 Hollow Core Fiber

In order to perform these transient absorption experiments, the temporal duration of the light from the laser needs to be shortened, while retaining as much power as possible. The process of self-phase modulation (SPM) in a stretched, hollow core-fiber is employed to convert the 25 fs, 795 nm light from the output of the laser to 4 fs light spanning from 420 nm - 920 nm (Fig. 2.2).

Theoretically understanding the process of SPM provides guidance for optimizing the contributing factors in the pursuit of the broadest possible spectrum, with a centralized mode, and highest possible power. SPM is an optical process that occurs when an intense light field interacts with the non-linear index of refraction and produces a phase shift of the driving light field. The phase shift produced, also known as the B-integral, is mathematically described in equation 2.1.

$$\Delta\phi = \frac{-w_0}{c} \int_0^L n_2(x) \frac{\partial I(x,t)}{\partial t} dx \quad (2.1)$$





**Fig. 2.2** The amplifier output (A) gets broadened by self-phase modulation with either Ar or He as the non-linear medium (B).

where  $\Delta\phi$  is the phase shift,  $w_0$  is driving field frequency,  $c$  is the speed of light,  $L$  is the length of the interaction medium (i.e. the fiber length),  $n_2$  is the non-linear index of refraction,  $I(x, t)$  is the field intensity as a function of time ( $t$ ) moving along the fiber axis,  $x$ . The amount of broadening ( $F$ ) possible for the non-linear refractive index of the broadening medium ( $n_2$ ), laser field intensity ( $I(x, t)$ ), and fiber length ( $L$ ) is shown in equation 2.2.

$$F = \sqrt{1 + \frac{4}{3\sqrt{3}} \left| \frac{-w_0}{c} \int_0^L n_2(x) \frac{\partial I(x, t)}{\partial t} dx \right|^2} \quad (2.2)$$

The largest broadening occurs when the B-integral is maximized [9].

|           | non-linear index of<br>refraction ( $\times 10^{-20}$<br>$\text{cm}^2 \text{W}^{-1} \text{atm}^{-1}$ ) | ionization potential<br>(eV) |
|-----------|--------------------------------------------------------------------------------------------------------|------------------------------|
| <b>He</b> | <b>0.4</b>                                                                                             | <b>24.59</b>                 |
| <b>Ne</b> | <b>1.8</b>                                                                                             | <b>21.56</b>                 |
| <b>Ar</b> | <b>15</b>                                                                                              | <b>15.76</b>                 |
| <b>Kr</b> | <b>28</b>                                                                                              | <b>14.00</b>                 |
| <b>Xe</b> | <b>70</b>                                                                                              | <b>12.13</b>                 |

**Table 1.** The nonlinear index of refraction divided by the pressure and the ionization potential for the noble gases are key factors in the self-phase modulation of intense laser fields.

There are three variables available to increase the broadening factor,  $F$ ; fiber length, the non-linear index of refraction, and the intensity of the driving field. Theoretically, propagation losses set the upper limit for the fiber length, however it is often practical means, such as table length and difficulty aligning longer fibers, that limit the fiber length. The ionization threshold sets the upper limit for the non-linear index of refraction, and the intensity is capped by ionization effects and self-focusing.

To limit the ionization effect, noble gases, which have a high ionization threshold from their fully filled valence orbitals, are selected as the broadening medium in the experimental apparatus presented here. Table 1 lists the ionization threshold and non-linear index of refraction divided by pressure for the noble gases.

Self-focusing limits ( $P_{sf}$ ) the driving laser field power to a critical value.

$$P_{sf} = \frac{\lambda_0^2}{2\kappa_2 P} \quad (2.3)$$

where  $\lambda_0$  is the wavelength of the driving laser field,  $\kappa_2$  is the non-linear index of refraction divided by gas pressure, and  $P$  is the gas pressure. As the pressure at the entrance of the fiber is minimized,  $P_{sf}$  goes to infinity. Both the ionization limitation and the critical power for self-focusing naturally lead to the benefits of using a gradient pressure in the fiber, which has been shown to reduce these effects at the fiber entrance, while still producing good coupling into the hollow-core fiber [10].

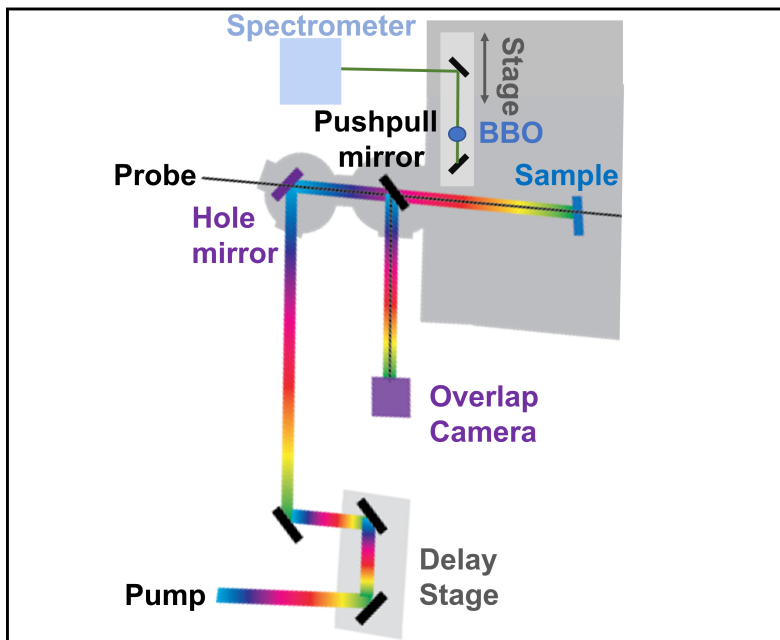
In the experimental apparatus outlined here, both He and Ar were used as the broadening medium, operated at gradient pressure, in the 2 m fiber. The nonlinear index of refraction is  $\sim 38$  times larger for Ar than He. Additionally, the ionization potential is 1.56 times smaller for Ar than He. The higher degree of non-linearity for Ar and lower ionization potential leads to a  $\sim 10^4$  reduction in gas pressure to attain the comparable broadening (Fig. 2.2).

Lastly, the maximum power output of the fiber has been shown to correspond to the condition when the beam diameter is equal to 64% inner diameter of the fiber [11]. In the experiment here, the fiber diameter is 704  $\mu\text{m}$  and the beam size, which makes the optimal  $\frac{1}{e^2}$  beam diameter at the fiber entrance 450  $\mu\text{m}$ .

## 2.4 Spatial and Temporal Overlap

Experimentally determining the delay stage position where the pump and probe beams coincide in time is central to the design of transient spectroscopy experiments. Spatially overlapping the two beams is a prerequisite for obtaining temporal overlap. In this setup, a silver mirror on a push pull located between the hole mirror and the experimental chamber redirects the broadband light that generates the XUV probe and the pump beam through a 0.5 mm AR coated window and onto a camera that images visible light with a semiconductor CMOS sensor (IC Capture DMK 72BUC02) outside of the vacuum chambers. The camera is located the same distance from the push-pull mounted mirror as the sample and, therefore, it images the sample position. Because the XUV probe propagates collinearly with the broadband driving laser beam used to generate the XUV light through high harmonic generation in the gas cell, spatial overlap is accomplished by overlapping the XUV driving laser and the pump beam outside of the vacuum chamber on the overlap camera (Fig. 2.4).

Once spatial overlap is established, temporal overlap can be found in several ways. If it is expected that overlap has changed by several millimeters, a set of mirrors on a transnational stage can be used to redirect the pump and probe beam into a spectrometer (Ocean Optics HR4000) where the two beams interfere to create spectral fringes. When the two beams are temporally overlapped the spectral fringes are infinitely spaced apart. While this method



**Fig. 2.3** Diagram of the tools available to accomplish spatial and temporal overlap.

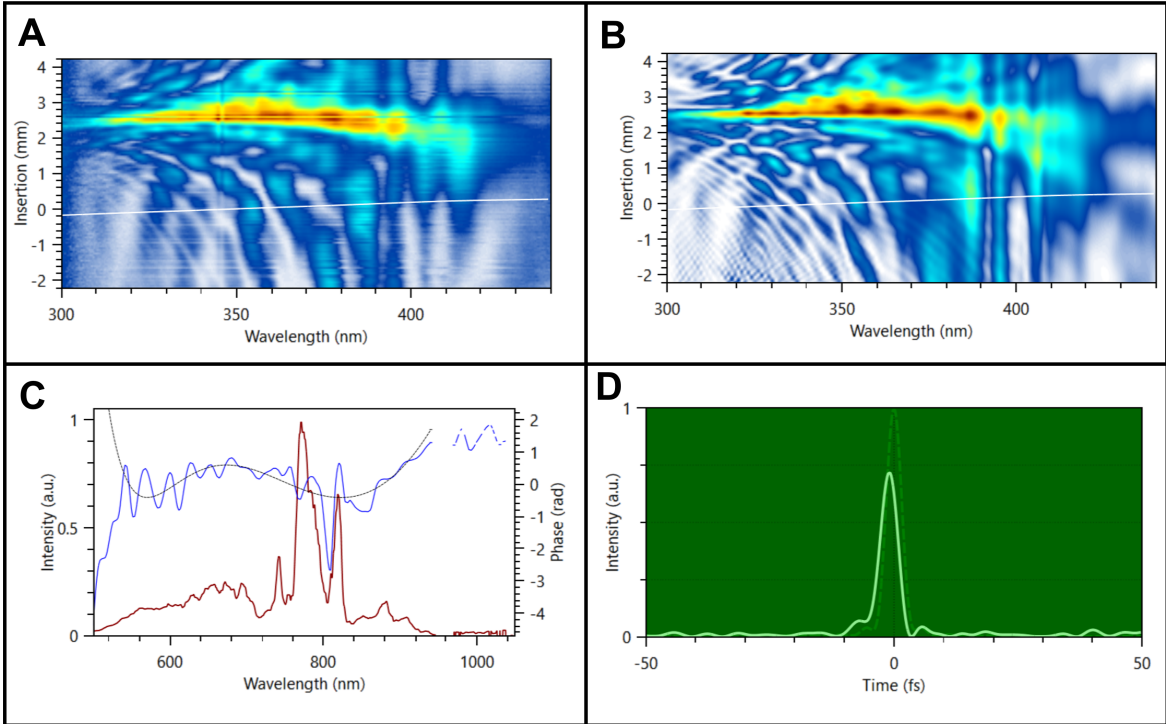
allows for the identification of temporal overlap over a larger range of the delay stage, it can be difficult to determine the maximal spacing between spectral fringes within  $\sim 0.5$  mm. In order to get a more accurate position for temporal overlap the lineshape change of Ne from NIR coupling to the ionization continuum is observed. In brief, temporal overlap corresponds to the delay position for which the Fano shape of the Ne  $2s^1 2p^6 3p$  line recovers. This is also used to measure the temporal duration of the instrument and is discussed in greater detail in the next section.

## 2.5 Temporal Characterization

By the nature of high harmonics generation, the probe pulse is composed of an attosecond pulse train. The temporal resolution of the transient absorption experiment is then set by the temporal duration of the pump pulse, which has a lower bound set by the Fourier transform limit. Optimizing the glass insertion of the pump arm for the broadest second harmonic generation (SHG) spectrum, dispersion scanning and fitting the lineshape change of Ne autoionization states are methods that have been used to optimize the compression of the pump pulse to determine the temporal resolution of the instrument. All of these methods have a trade off between the amount of information obtained by the method, the accuracy of the information, and the time it takes to perform the technique. Therefore it is beneficial to use a combination of the methods in order to get the shortest possible pulses that are well-characterized.

The most basic method for optimizing the pump pulse compression is accomplished by tuning the amount of glass in the beam path to obtain the broadest SHG spectrum. For the

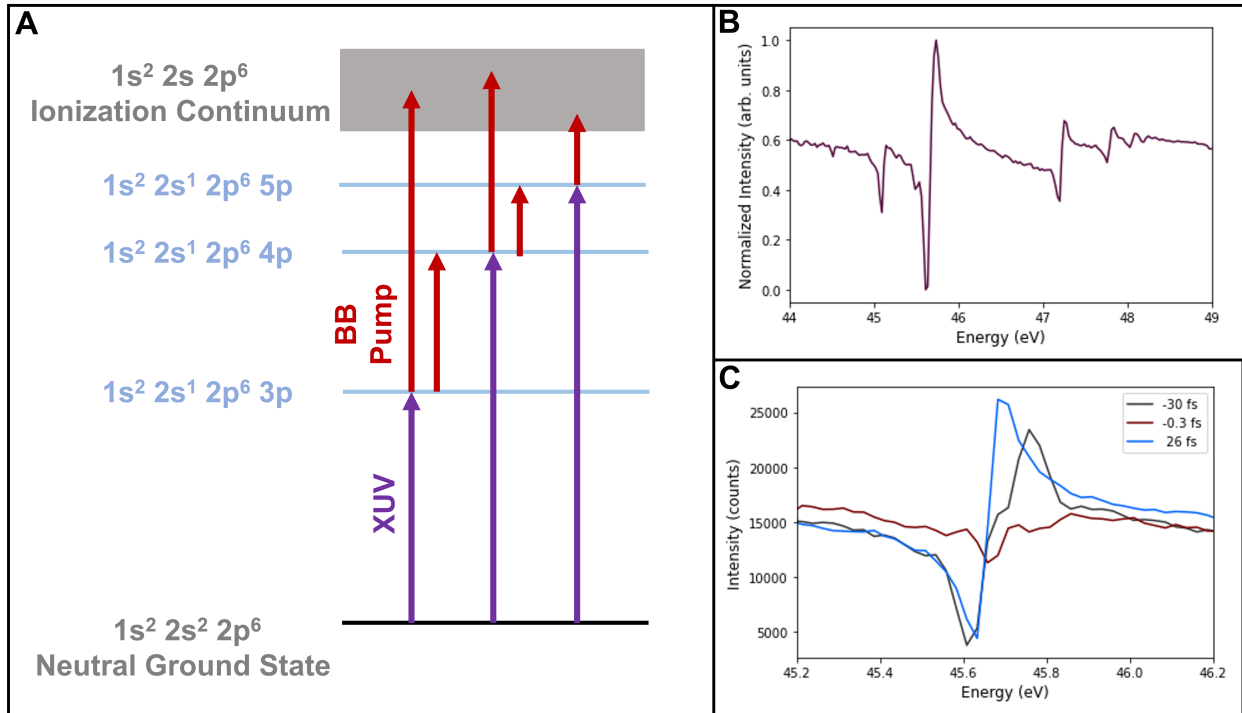
pump powers used in our experiments, the sum frequency generated spectrum is proportional to the square of the peak power. Additionally, the broadest SHG spectrum occurs at the highest peak power, which corresponds to the most temporally compressed pulse. In this specific experimental technique a set of mirrors on a delay stage inside of the experimental chamber can be inserted into the beam path to redirect the pump to a spectrometer outside of the chamber (Fig. 2.4). The benefit of this technique is the ability to directly observe the SHG spectrum while actively tuning the wedge insertion. This method of finding the optimal compression of the pump pulse lacks the exact temporal duration and phase information. It is also not directly reporting on the pulse at the sample position, as it is optimized after the beam passes through an additional 0.5 mm glass window while exiting the experimental chamber.



**Fig. 2.4** The dispersion scan of the fiber output provides the measured second harmonic generation spectrum (A), reconstructed second harmonic generation spectrum (B), measured input spectrum with constructed phase (C), and constructed temporal profile (D).

The most information about the pulse in this experimental configuration can be determined from dispersion scanning. Dispersion scanning is a measurement technique where the fundamental and second harmonic generation (SHG) spectrum for increasing amounts of glass insertion is used to obtain the temporal and phase characteristics of the light [12, 13]. The dispersion scan results presented here are taken with the Sphere Ultrafast Photonics d-scan B, which uses the measured fundamental spectrum and reconstructs the SHG spectrum, minimizing to the measured SHG spectrum for increasing amounts of glass using a downhill simplex algorithm with multiple basis sets (Fig. 2.5) [14]. Additionally, these measurements are taken just before the delay stage (Fig. 2.4), which results in the pump path having an

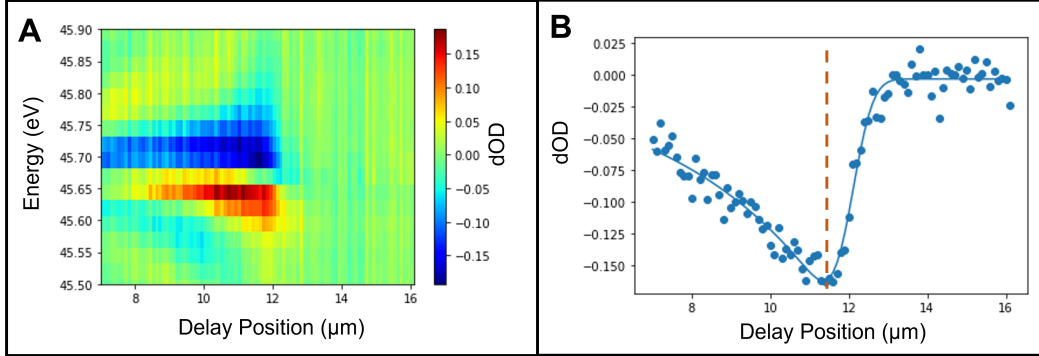
additional 1 m path length in air and 0.5 mm of AR (anti-reflective) coated glass (from the vacuum chamber entrance window) during transient absorption measurements. While the software accounts for the difference in path length and glass in the reconstruction algorithm, it should be noted that it is not a direct measurement at the sample position. Additionally, the pump power is limited by the saturation limit of the spectrometer and therefore an iris used to modulate the pump power selects the very center of the pump beam, which does not always accurately represent the pump beam (Fig. 2.5). The main strength of this technique is the phase retrieval and the reconstruction of the temporal profile, which gives insight into the structure of the pulses. Because this is not an in-situ technique, and therefore does not necessarily accurately report the temporal duration or location of temporal overlap at the sample, it should be viewed as a lower bound for the temporal resolution of the instrument.



**Fig. 2.5** The single electron autoionization states in Ne are probed by XUV light, purple arrows, and promoted into the ionization continuum with the broad band pump, red arrows (A). The measured static XUV spectrum shows a clear Fano profile arising from the interference between the autoionization states and the first ionization continuum (B). Evolution of the Ne autoionization lineshape from the broadband pump (C).

While dispersion scanning is the only technique to provide phase and temporal structure information about the pulse, fitting the temporal lineshape changes in autoionization states of Ne directly measures the location and temporal duration of the instrument at the sample position. The one electron excited states in Ne correspond to the transition from the ground state to the  $1s^2 2s^1 2p^6 np$ , where  $n = 3, 4, 5, \dots$ . The Fano profile arises from a coupling between the discrete one electron states and the first ionization continuum ( $1s^2 2s^1 2p^6$ ) (Fig. 2.6B) [15]. The broad band pump excites the one electron states into the second ionization

continuum ( $1s^2 2s^2 p^6$ ), which results in the Fano profile being destroyed (Fig. 2.6C). As the delay between the XUV pulse and the broad band pump increases, the lineshape recovers.



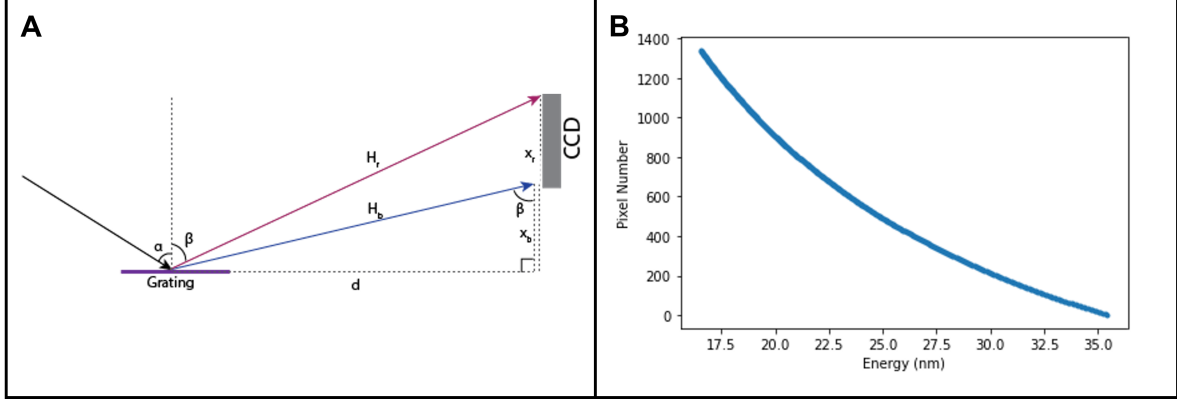
**Fig. 2.6** The heat map of the lineshape change in the Ne single electron  $3p$  autoionization state is shown in panel A. The temporal evolution of the lineshape is fit with a Gaussian broadened error function (B) to get the position of temporal overlap and temporal resolution of the instrument.

The simplicity of the physical process behind the lineshape suppression in autoionizing states of Ne allows for the direct measurement of the temporal duration of the instrument as well as a precise location of temporal overlap on the pump delay stage. Temporal overlap occurs at the delay position for which the lineshape of Ne is destroyed (Fig. 2.7A). For an infinitely short pump pulse the recovery of the lineshape would be instantaneous (i.e. perfectly fit by an error function), so any additional broadening in the rise of the transient signal in Ne is due to the temporal resolution of the instrument [16]. Fitting the lineshape change in Ne with a Gaussian broadened error function followed by an exponential decay provides the position of temporal overlap (dashed orange line) and the time duration of the instrument, which is equal to the full width half maximum of the fit Gaussian component (Fig. 2.7B). For the example shown in figure 2.7, the position of temporal overlap is located at 11.9  $\mu\text{m}$  on the delay stage and the temporal resolution is 5.19 fs.

Overall there is a benefit to using these techniques in various situations. If the wedge insertion is far from the position of highest compression, the “real-time” feedback of optimizing the SHG spectrum provides a practical way for determining the approximate wedge insertion for optimal pulse compression. When it is necessary to characterize the fiber output, dispersion scanning accurately assesses the character of the light by retrieving phase information and temporal pulse profile. Fitting the lineshape change in the autoionization state of Ne characterizes the pulse duration at the sample position and gives an exact position of temporal overlap, however it does not provide phase information or the temporal profile of the pulse.

## 2.6 Camera Calibration

X-ray absorption is measured by the collection of dispersed XUV photons on a charge coupled device (CCD). Here, dispersion is accomplished with a curved, reflective grating that has 1200 grooves per mm, an input angle of  $85.4^\circ$ , and a radius of curvature of 5649



**Fig. 2.7** A graphical depiction of the grating equation in the context of this experimental equipment is shown in panel A. The energy vs pixel distribution as detailed in the text is displayed in panel B.

mm that focuses the reflected light 0.25 m after the grating. The relationship between the pixels of the CCD and the energy of light can be determined by solving the grating equation (eq. 2.4).

$$\sin(\alpha) + \sin(\beta_i) = Nm\lambda_i \quad (2.4)$$

$\alpha$  is the angle between the grating normal and the incident light,  $N$  is the groove density of the grating,  $m$  is the diffraction order,  $\lambda$  is the wavelength of incident light, and the subscript  $i$  denotes a specific wavelength. Figure 2.7A schematically shows the dispersion of longer and shorter wavelengths, marked with subscript  $r$  and  $b$  for red and blue, respectively. The grating equation is solved for the first order diffraction with the distances and grating specifications listed above and setting the distance between red and blue wavelengths to be the 26.8 mm chip length of the CCD in figure 2.7B.

To enable measurement across a broad range of energies, the camera is mounted on a horizontal translation stage. The camera is then calibrated by fitting a second degree polynomial to the relationship between the energy and pixel position of the standard. Typical standards are listed in table 2.2.

|                                | Energy (eV)  |              |              |              |
|--------------------------------|--------------|--------------|--------------|--------------|
| <b>Ne 2s2p<sup>6</sup> np</b>  | <b>45.54</b> | <b>47.12</b> | <b>47.70</b> | <b>47.97</b> |
| <b>He 2s2p<sup>6</sup> np</b>  | <b>60.0</b>  | <b>63.6</b>  | <b>64.5</b>  | <b>64.8</b>  |
| <b>Ar 3s3p<sup>6</sup> np</b>  | <b>26.6</b>  | <b>28.0</b>  | <b>28.5</b>  |              |
| <b>Kr 4s4p<sup>6</sup> np</b>  | <b>91.23</b> | <b>92.45</b> |              |              |
| <b>Si L<sub>2,3</sub>-edge</b> | <b>100.0</b> |              |              |              |
| <b>Al L<sub>2,3</sub>-edge</b> | <b>72.72</b> |              |              |              |

**Table 2.2.** The known energy of elements with transitions in the x-ray regime commonly are used for calibrating the CCD camera.

## 2.7 Conclusion

Overall, this experimental design provides for a standardized way of measuring attosecond transient absorption in solid-state samples. The systematic methods of characterizing the absorption energy, spatial and temporal overlap results in a robust experimental apparatus, which leads to reproducibility of the measurements. Additionally, the stability of the equipment allows for the accumulation of data for hours, which ultimately enables the measurement of smaller signals.

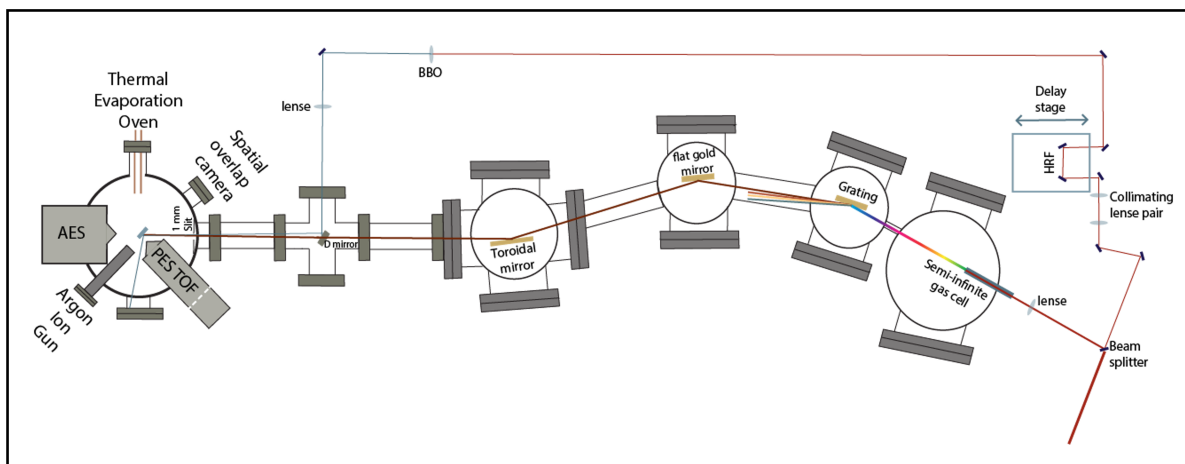


# Chapter 3. Transient extreme ultraviolet light photoemission spectroscopy experimental apparatus

## 3.1 Introduction

As was described in the *XUV Photoemission Spectroscopy* section of chapter 1, precisely knowing the energy of the incident light that creates photo-ejected electrons is crucial in determining the binding energy of detected electrons. A precise input energy is achieved in this experimental setup by passing odd XUV harmonics through a monochromator, where the generated light is separated, selected, and focused before impinging on the sample. The monochromator style design provides a very narrow energy spread and allows for easy adjustment of the photoemission probe energy. The following chapter details the optical setup, how a narrow energy is selected for the PES source, as well as how spatial and temporal overlap of pump and probe are achieved.

## 3.2 Optical Alignment



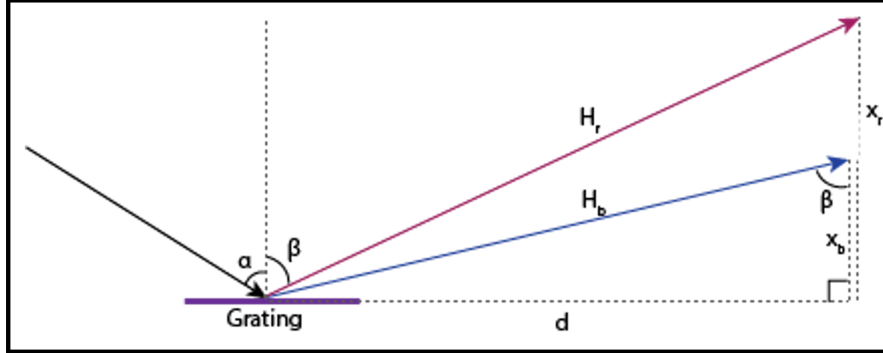
**Fig. 3.1** The diagram of the transient photoemission experimental setup shows a schematic of the components in the pump and probe optical path. In the experimental chamber, the PES TOF detector, thermal evaporation oven and instruments available to monitor and calibrate sample growth can be seen.

Figure 3.1 shows an overview of the photoemission experiment. The laser source is a Spectra Physics, Tsunami oscillator coupled to a Spitfire chirped pulse amplifier which gives a 2.7 W, 1 KHz, 35 fs, 800 nm output. Directly after the laser amplifier a beam splitter is used to direct 70% of the light to the probe arm, for the production of XUV pulses by the process of high harmonic generation (HHG), while allowing the remaining 30% of the light to go into the pump arm, for sample excitation [3]. Following the probe arm, the light is then focused with a 75 cm lens to the end of a semi-infinite gas cell, which is capped with a

150  $\mu\text{m}$  thick stainless steel foil, in which the XUV light is generated [17]. The XUV light and the driving laser field are then spatially separated with a flat grating with 600 grooves per mm and  $3.4^\circ$  incident angle. A single harmonic is then directed with a flat mirror onto the toroidal mirror, which focuses the beam onto the sample. Any stray light is blocked by a 1 mm slit at the entrance of the experimental chamber. Additionally, the grating, flat mirror, and toroidal mirror are all gold coated and used at a grazing incidence angle to maximize reflection in XUV energy range.

Considering to the pump arm, the first two mirrors are used to ensure the beam is pointing straight through a set of collimating lenses and a hollow retroreflector on a delay stage. The collimating lenses shrinks the beam diameter from  $\sim 22$  mm to  $\sim 5$  mm. Optionally, the beam can be frequency doubled through a  $\beta\text{-BaB}_2\text{O}_4$  (BBO) crystal. Next, an anti-reflective coated, 1 m lens is used to focus the pump beam on the sample. Finally, the beam is reflected off a motorized D shaped mirror, before hitting the sample. The narrow crossing angle ( $\sim 1^\circ$  in the vertical direction) allows for the beams to have the longest possible spatial overlap region and the shortest pump-probe timing.

### 3.3 Energy Resolution of the Monochromator



**Fig. 3.2** The nature by which light interacts with a grating is visually represented in the above figure. Additionally, the geometric relationship between the outgoing light and the degree of separation is also shown.

The resolution of the monochromator is set by the degree of spatial separation for adjacent energies at the slit and the slit width. Figure 3.2 depicts incoming light (black arrow) reflecting off a grooved grating. Note that  $x_r$  and  $x_b$  are horizontally displaced in figure 3.2 for clarity, however as  $d$  is a set distance, in reality these quantities overlap vertically. The separation between adjacent energies at the slit entrance is described in equation 3.1.

$$S = x_r - x_b \quad (3.1)$$

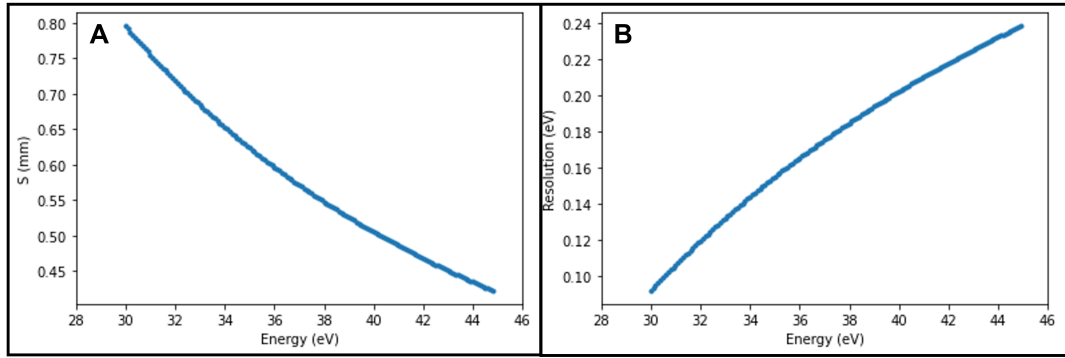
where  $S$  is the spatial separation,  $x_r$  and  $x_b$  is the vertical displacement from the grating for the red and blue light, respectively. Using trigonometric relationships equation 3.1 becomes:

$$x_i = H_i \cos(\beta_i) \quad H_i = \frac{d}{\sin(\beta_i)} \quad (3.2)$$

Here the subscript  $i$  indicates the wavelength of light,  $H$  is the distance of the light of wavelength  $i$  traverses,  $\beta$  is the angle between the diffracted light and the grating normal, and  $d$  is the distance between the grating and slit. As  $d$  is a set distance of 2.08 m,  $\beta$  is the only unknown quantity left in this relationship. The grating equation (eq. 3.3) is used to calculate  $\beta$ .

$$\sin(\alpha) + \sin(\beta_i) = Nm\lambda_i \quad (3.3)$$

where  $\alpha$  is the angle between the grating normal and the incident light,  $N$  is the groove density of the grating,  $m$  is the diffraction order, and  $\lambda$  is the wavelength of incident light. Figure 3.3 shows  $S$ , the spatial separation of adjacent energies, in mm, from 30 eV to 45 eV for a grazing incident angle ( $\alpha$  is 87 ° with respect to normal), the first order diffraction, and a groove density of 600 grooves per millimeter.



**Fig. 3.3** The spread of the energy 2.08 m after the grating (where the slit is), is shown in panel A. The instrument resolution, according to the distance spatial separation of adjacent energies is shown in panel B.

Finally, the resolution is calculated by the spread of energies (sum of  $S$ ) accepted through the 1 mm slit. For example the sum of  $S$  for 30 eV to 30.1 eV 1 mm, therefore the resolution at  $\sim 30$  eV is 0.1 eV. On the high energy side, the light is less separated. The sum of  $S$  values from 44.76 eV to 45 eV is 1 mm, giving a 0.24 eV resolution at  $\sim 45$  eV. Most experiments were conducted at the 27<sup>th</sup> harmonic ( 41.9 eV), which has an energy resolution of  $\sim 0.20$  eV.

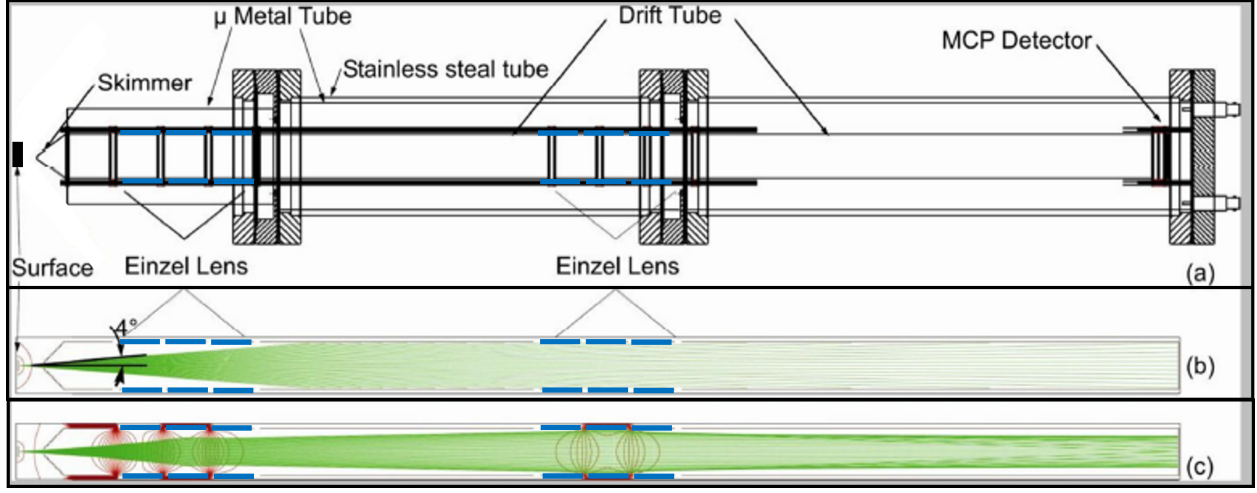
### 3.4 Time-of-Flight Detector

The Energy resolution of the instrument is set by both the energy spread of the incident XUV light and the resolution of the photoelectron detector. As was shown in the *XUV Photoemission Spectroscopy* section of chapter 1, by having a monochromatic light source and measuring the kinetic energy of photo-ejected electrons, the binding energy of electrons can be calculated. Here, a Time-of-Flight (TOF) detector is used to determine the electron kinetic energy, and therefore subsequently calculate the electron binding energy, of photo-ejected electrons. In this method the arrival time of electrons is measured at a fixed distance,

which allows for the electron kinetic energy to be directly calculated.

$$KE = \frac{1}{2}mv^2 = \frac{1}{2}m \left( \frac{d}{t} \right)^2 \quad (3.4)$$

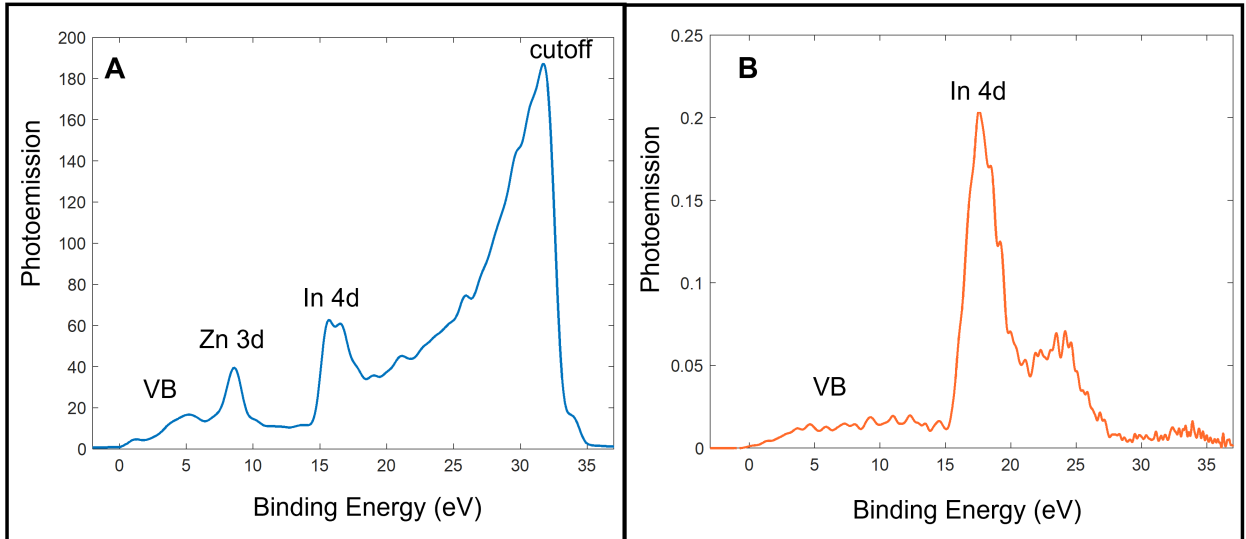
here  $KE$  is the kinetic energy of the electrons,  $m$  is the electron mass,  $v$  is the electron velocity,  $d$  is the distance from the photoelectron source (i.e. the sample being investigated) to the detection point, and  $t$  is the measured time it takes for the electron to move from the source to the detection point.



**Fig. 3.4** A schematic of the main components in the TOF detector are shown in panel A. To demonstrate the effect of the einzel lenses SIMION simulations are run with the lenses ‘off’ in panel B and ‘on’ in panel C.

In the experimental apparatus, the home-built TOF is composed of 1 m long tube, with a 2.5 mm opening, and  $\mu$ -metal shielding to ensure the drift tube is free from magnetic fields that might deflect the electrons (Fig. 3.4A). Furthermore, a set of two einzel lenses are used collimate the photoelectrons to allow for a more efficient detection of high kinetic energy electrons (Fig. 3.4B,C). Each einzel lens is made up of three cylindrical electrodes, depicted in blue in figure 3.4. A symmetric electric field is created by holding the outer electrodes at the same voltage (Fig. 3.4C), while the strength of the electric field is determined by the amount of voltage applied to the center electrode. This tunability allows for a 0.01 eV - 0.250 eV energy resolution, which is on the same order as the energy resolution of the incident light acquired from the grating. Once the photoelectrons are focused at the back of the TOF drift tube, two stacked, chevron style microchannel plates (MCP) measure the incident electrons. This signal is then further increased by  $10^6 - 10^7$  by an MCP amplifier and then read by a fast 5 GHz multichannel scalar electronics unit (FAST P7887).

While the detector settings are another main factor effecting the theoretical instrument resolution, in practice the geometry between the sample and TOF can have a profound effect on the measured spectra. Figure 3.5 demonstrates that the alignment between the sample surface and TOF plays a crucial role in ensuring that photo-ejected electrons are accepted

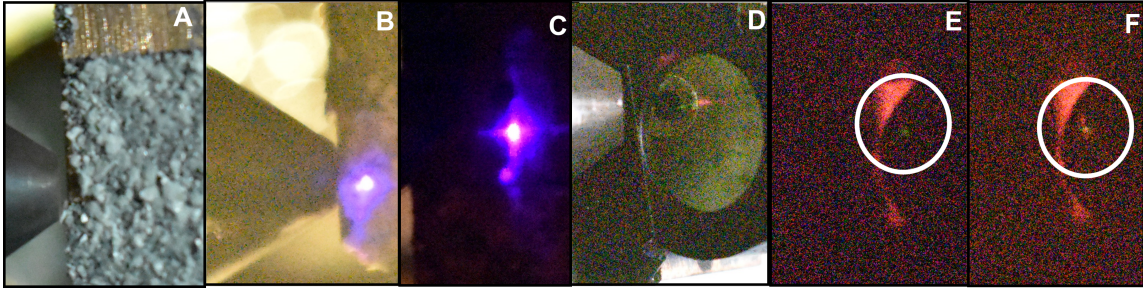


**Fig. 3.5** Photoemission spectrum of Zn on InP for a 45° angle between the sample normal and the TOF (A) and for a non-45 °angle between the sample normal and the TOF (B).

into the TOF at the correct angle to be focused by the einzel lenses and successfully measured by the MCP. Figure 3.5 shows the photoemission spectrum of a zinc, indium phosphide junction, where in panel A the normal of the sample surface is in line with the TOF opening (as shown in Fig. 3.1) and in panel B the sample surface is rotated to no longer be perfectly in line with the TOF. There are several spectral features which are general to all photoemission spectra, as discussed in the *XUV Photoemission Spectroscopy* section of chapter 1, that are missing from Fig. 3.5B and the overall intensity is much lower and the cutoff is obscured. The dramatic improvement in intensity from having the sample normal in line with the TOF follows previous findings that showed that the ejection cone of photoelectrons expands in line with the normal of the sample surface [18]. Furthermore, it was also shown that slower electrons, like electrons with higher binding energy or inelastically scattered secondary electrons, show more angular dependence than faster electrons [18], which explains why the secondary electron cutoff vanishes in panel B.

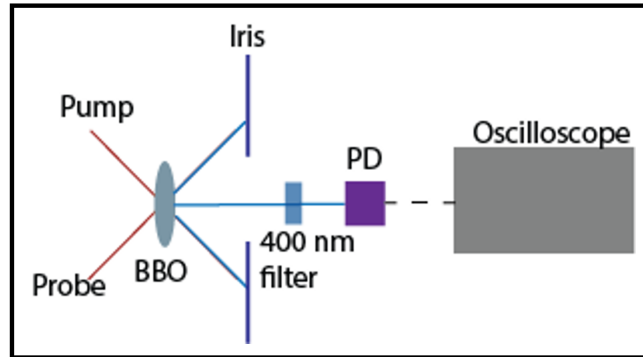
### 3.5 Spatial and Temporal Overlap

In order for transient dynamics to be measured, the two beams must be spatially overlapped and the point of temporal overlap between the beams (time zero) must be well-defined. While the monochromator design used in the photoemission arm provides excellent energy resolution it necessitates imaging light in the XUV range. To visualize the XUV beam a fluorescent material must be moved into the beam path. Additionally, because the spot size of the XUV is small ( $\sim 70 \mu\text{m}$ ) and the emitted light is weak, a camera with high magnification (Nikon D3400) and a long exposure time is set up to image the sample region through a window in the experimental chamber (Fig. 3.1).



**Fig. 3.6** Camera images of determining spatial overlap with sodium salicylate (A-C) and a cerium doped yttrium aluminum garnet scintillation plate (D-F) are shown. Panels A and C respectively show sodium salicylate and the scintillation plate without the pump or probe beam. Panels B and E show the XUV light on respective the imaging mediums and panels C and F show the pump and probe beams after spatial overlap has been achieved.

Figure 3.6 contrasts two XUV imaging methods that were tested. In the first method a slurry is made by combining sodium salicylate (ss) powder with a few drops of deionized water. The paste is then packed onto the sample holder and allowed to dry (Fig. 3.6A). In the second method a cerium doped yttrium aluminum garnet (Ce:YAG) scintillation plate was used to image the beam (Fig. 3.6D). Figure 3.6 shows the imaging region (Fig. 3.6A, D), XUV beam (Fig. 3.6B, E), and the overlap of pump and probe beams (Fig. 3.6C, F) for the ss and Ce:YAG plate methods, respectively. While the fluorescence efficiency is higher in the ss it has lower spatial resolution due to the surface roughness and the crystal size, which both smear the image by scattering the emitted light [19].



**Fig. 3.7** A schematic of the optical set up that was used to determine the position on the delay stage that corresponds to temporal overlap between the pump and the probe is shown above.

Temporal overlap is obtained by performing a cross-correlation in a BBO crystal. To achieve the optical setup outlined in figure 3.7 the bellow connecting the experimental chamber and the recombination chamber is removed and a mirror is placed to redirect the beams.

The IR pump and the zero order of the probe are directed into a BBO crystal at a crossing angle of  $\sim 2^\circ$ . The crossing angle ensures that the input beams are spatially separated, thereby enabling the main IR and frequency doubled beams to be separated by blocking the 800 nm beams with an iris. After the input beams are focused into the BBO, the angle of the BBO crystal is varied until the greatest amount of SHG output for the pump and probe beams is attained. This process of rotating the angle of the BBO minimizes dispersion within the crystal and maximizes type-I phase matching. Once this is done, the cross-correlation can be collected.

Cross-correlation via frequency doubling relies upon the physical phenomenon that near temporal overlap a third beam is generated from the addition of one photon from the pump arm and one photon from the probe arm [20]. The efficiency of this third beam reaches its maximum when the two input beams arrive in the crystal at the same time, given that type-I phase matching conditions are met. Because the third SHG beam is created by a photon from each input beam it accurately and directly shows the location of time zero. Typically the temporal resolution of the instrument can also be determined from the width of the cross-correlation, however in this optical design the temporal resolution is limited by the grating, which is more thoroughly discussed at the end of this section. The temporal shape of the cross-correlation signal (i.e. the SHG intensity) is defined in equation 3.5 .

$$I_{corr}(\tau) = \int_{-\infty}^{\infty} I_{probe}(t) I_{pump}(t - \tau) dt \quad (3.5)$$

where  $I_{corr}(\tau)$  is the cross-correlation signal,  $I_{pump}$  is the intensity of the pump beam,  $I_{probe}$  is the intensity of the probe beam, and  $\tau$  is the time delay between the pump and probe. When both the pump and probe are Gaussian profiles the measured SHG intensity will also be a Gaussian, where the center is time zero and the time duration is found in equation 3.6.

$$W = 0.67 \text{ fwhm} = 0.67 \sqrt{2 \ln(2)} \sigma \quad (3.6)$$

where  $W$  is the temporal duration and  $\sigma^2$  is the variance of the Gaussian fit. A typical cross-correlation is shown in figure 3.8. The Gaussian fit shows time zero is located at  $11.250 \pm 0.014$  cm.

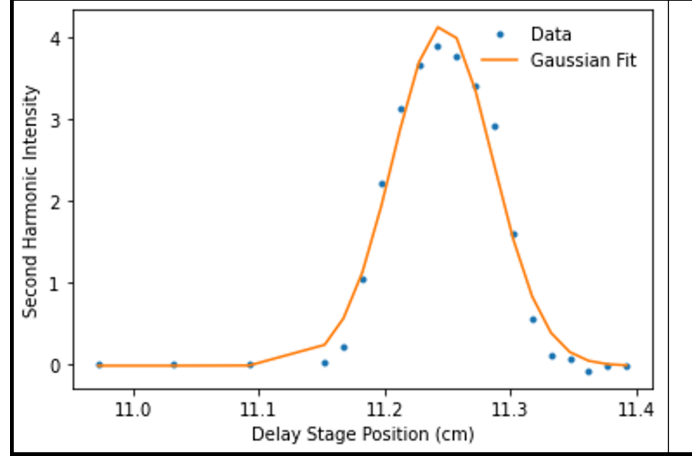
In most cases the time duration of the XUV arm is composed of an attosecond pulse train, which makes the pump pulse duration the limiting factor in the overall instrument response. However, in this case, the addition of a dispersive element (ie gratings, prisms, etc.) causes a pulse-front tilt, which temporally broadens the dispersed XUV light. Furthermore, the pulse-front tilt is not captured in the cross-correlation because the zero order of the grating is used in this measurement. Figure 3.9 graphically depicts a beam with no pulse-front tilt (Fig. 3.9A) and with a  $20^\circ$  pulse-front tilt (Fig. 3.9B).

The amount of tilt induced by a grating can be calculated in equation 3.7.

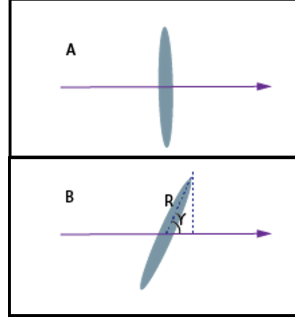
$$\tan \gamma = \frac{\lambda}{c (90^\circ - \beta) N} \quad (3.7)$$

where  $\gamma$  is the tilt angle,  $c$  is the speed of light, and  $N$  is the groove spacing [21]. The amount of temporal stretching created by the grating by the pulse-front tilt can then be





**Fig. 3.8** The second harmonic signal generated in the set up described above as a function of delay stage position allows one to determine the position of temporal overlap and the time resolution of the instrument.



**Fig. 3.9** Panel A demonstrates a pulse for which there is no pulse-front tilt. Here the purple arrow denotes the direction the light is traveling and the blue circle demonstrates a pulse. Panel B demonstrates a pulse with a 20 ° front tilt. here *gamma* is the degree of the pulse-front tilt and *R* shows the broadening of the tilted pulse.

calculated as:

$$T = \frac{2 \cos(\gamma) R}{c} \quad (3.8)$$

where *T* is the temporal stretching and *R* is the beam radius. Using equation 3.8 it was found that from 30 eV to 45 eV there is a 670 fs temporal broadening from the phase-front tilt induced by the grating. For reference, the cross-correlation gives a temporal resolution of  $320.0 \pm 1.4$  fs. While the amount of pulse-front tilt is energy dependent in this case, because the change in  $\beta$  is small (less than 0.04 radian, 0.0007 °), the amount of temporal stretching is the same for all energies from 30 eV - 45 eV.

### 3.6 Conclusion

In conclusion, the optical alignment of both the pump and probe path was discussed. It was found that a Ce:YAG scintillation plate yielded better imaging of the XUV beam,



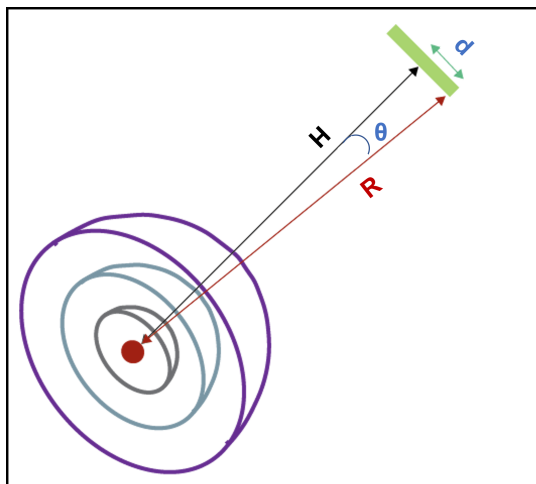
which is a necessary step to achieving spatial overlap. Furthermore it was also shown that while the use of a monochromator gives excellent energy resolution, (0.1 eV - 0.24 eV ), it also induces a pulse front tilt which gives the XUV beam a temporal spread of 320 fs, twice that of what was measured for the pump pulse. In the future there are several ways to remove the temporal broadening induced by the grating. One option is to introduce a second grating to compensate the temporal stretching. This solution allows for the energy resolution to remain while the pulse duration is maintained, however it greatly complicates optical alignment [22, 23]. A second option is to remove the grating and, instead, pass the odd XUV harmonics through thin, metal foil filters to select a single harmonic as the PES light source. Although this solution does not temporally broaden the beam and simplifies the beam path, it also decreases the energy resolution [24]. A third option would be to use a pair of multilayer mirrors after XUV generation to select a specific harmonic order, much like the filtering option, this would reduce the energy resolution to the width of the harmonic, but would tilt the pulse [25].

## Chapter 4. Thermal evaporation of metals and metal oxide thin films

### 4.1 Introduction

Thermal evaporation (TE) is a physical vapor deposition technique for sample growth. In brief, the desired deposition material is heated, under vacuum, to a specified vapor pressure. Everything in the vacuum chamber gets coated with the material, including the substrate located at some distance from the evaporation source. The direct control over the growth rate by temperature of the deposition material allows this technique to range from growing sub-monolayer thicknesses over the course of minutes to 500 nm per minute. The versatility and simple physics behind TE make it appealing for many solid state sample applications. In this chapter I will outline the theory of thermal evaporation, contextualize this for the specific geometry of the growth chamber used to grow samples, provide examples of sample growth and characterization for photoemission and absorption experiments, and, finally, describe the capability for metal oxide growth.

### 4.2 Theory of Thermal Evaporation



**Fig. 4.1** A visual representation of thermal evaporation from a point source (red solid sphere). The concentric spheres graphically depict surfaces of uniform atomic flux.  $H$  is the distance from the source to the substrate,  $d$  is the distance from the center of the substrate to the edge of the substrate. Finally,  $R$  is the distance from the source to the edge of the substrate.

In its most simplistic geometry, the evaporation process can be visualized as concentric spheres radiating from the evaporation point source. The density of the evaporated atoms (i.e. atomic flux) is the same for every point within a particular sphere. Spheres closer to the evaporation source have a higher density of atoms than spheres farther from the source (Fig. 4.1).

The thickness at any point along the surface of the substrate is equal to the dot product of the atomic flux for sphere of radius  $r$  and normal of the sample surface. Since the flux is a constant value over the entire surface area of the sphere, the dot product becomes just a multiplication factor of the flux and the surface area of the sphere. For the spherical point source shown in figure 4.1, the thickness ( $T$ ) at any point on the substrate can be found by the equation 4.1.

$$T = F4\pi \frac{H}{(H^2 + d^2)^{\frac{3}{2}}} \quad (4.1)$$

here  $F$  is the atomic flux (i.e. atoms per second through the surface area of a sphere),  $d$  is the distance between the vector representing the center of the source to the center of the substrate,  $H$ , and any vector,  $R$ , pointing from the center of the source to any position on the substrate.

Obtaining a homogeneous thickness of material over the sample area is a requirement for samples being studied by spectroscopic techniques. The geometric requirements to achieve a sample of even thickness can be found by considering the ratio of the thickness  $T$  to the point of maximum thickness. The maximum thickness occurs at the point of the substrate that is aligned with the evaporation source, which occurs when  $d = 0$ .

$$T_{max} = F4\pi \frac{1}{H^2} \quad (4.2)$$

Now taking  $T$  over the  $T_{max}$

$$\frac{T}{T_{max}} = \frac{H^3}{(H^2 + d^2)^{\frac{3}{2}}} \quad (4.3)$$

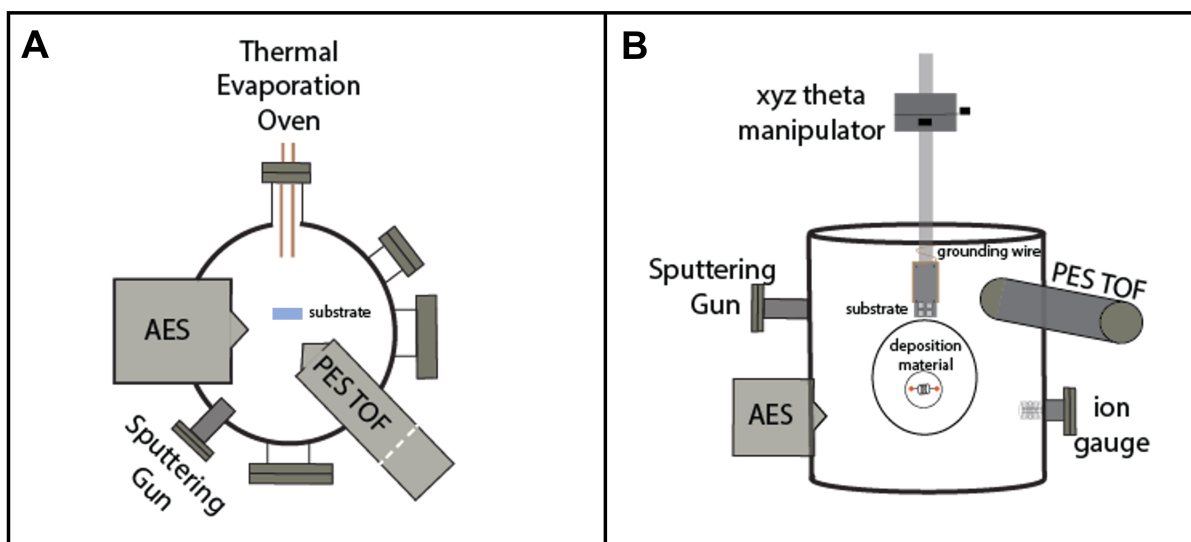
When  $\frac{T}{T_{max}}$  is small there is a large spatial disparity in thickness across the substrate. In other words, the sample will be uneven. Conversely, when  $\frac{T}{T_{max}}$  equals 1 there is no difference in thickness across the length scale of the substrate and the sample thickness will be even. In the limit that  $d \gg H$  then  $\frac{T}{T_{max}} = \frac{1}{d^3}$ , which is a very small number, representing a large variance in thickness across the sample. This gives the condition that when  $d \gg H$  the sample will be uneven. On the other hand, when  $H \gg d$   $\frac{T}{T_{max} = \frac{H^3}{(H^2)^{\frac{3}{2}}}} = 1$ . In this case

there is no difference in thickness between the center and outer edges of the sample. In this limit, the sample thickness will be even when  $H \gg d$ . These conditions provide geometric constraints to grow even samples and will be applied in the next section, *Growth Chamber Components*, which outlines the geometry and tools available during sample growth in the absorption and photoemission studies presented in this thesis.

### 4.3 Growth Chamber Components

The vacuum chamber where samples are grown features several key instruments that enable samples to be prepared by TE.

A top down view (Fig. 4.2A) and side view (Fig 4.2B) show the tools available to grow samples through TE. On the lower level of the deposition chamber there is a home-built TE



**Fig. 4.2** A schematic of the sample chamber shows the relative position of the tools available to grow samples and monitor the progress of growth. Panel A shows a top down view and panel B shows a side view of the growth chamber.

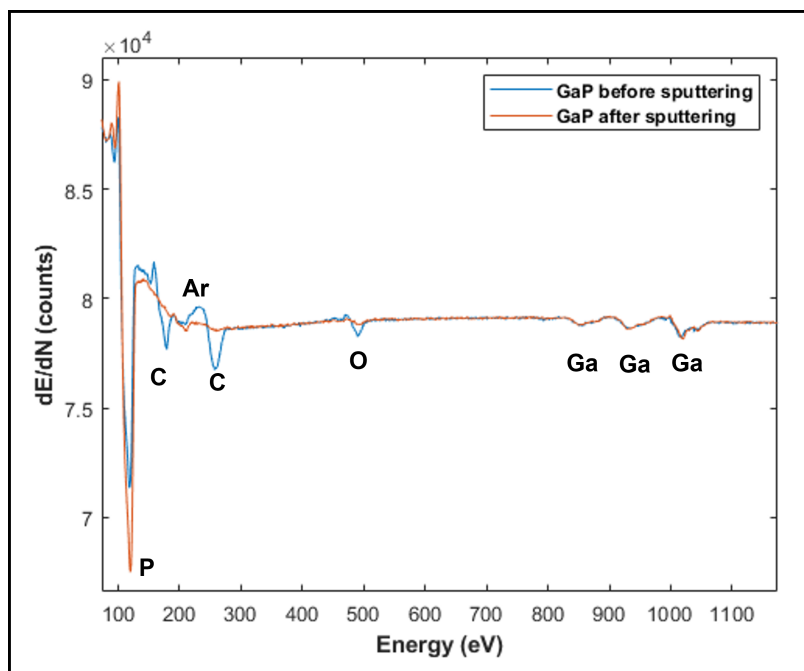
oven, an ion gauge, an Auger Electron Spectrometer (Perkin-Elmer Auger 11-500A), and a view port directly across from the oven, which allows for viewing of the oven or temperature measurements using a pyrometer. On the upper level there is an argon ion sputtering gun and a home-built electron time of flight (PES TOF), which is further outlined in chapter 3. The sample holder, which accommodates both wafer and x-ray microscopy substrates, is attached with screws that sit on sapphire spacers. There is a sapphire plate spacer behind the copper sample holder in order to electrically isolated the samples from the vacuum chamber and manipulator rod. An insulated copper grounding wire is attached to an external port located near the top of the manipulator rod and then sandwiched between the sapphire plate and the front of the sample holder to electrically ground the sample. Grounding the sample is essential to eliminate surface charging during Auger electron spectroscopy (AES) and photoemission spectroscopy (PES) measurements. In order to access the tools in the growth chamber, the sample holder is on an xyz- $\theta$  manipulator. The sample holder can be cryogenically cooled by filling the hollow manipulator rod with liquid nitrogen.

To achieve even film thicknesses the atomic flux from the evaporation source must be the same across all spatial locations of the substrate area. The substrate area for a typical wafer used in the photoemission experiments measures 0.5 in. x 0.5 in. and a batch of x-ray membranes measures 0.8 in. x 0.6 in. The importance of having the samples at a sufficient distance to get even coverage was shown in section *Theory of Thermal Evaporation*. In this configuration presented here the substrate is kept at the maximum distance from the evaporation oven (4 in.).

## 4.4 Monolayer Deposition for Photoemission Studies

For the energy used in the photoemission studies presented in this thesis, namely 41.9 eV, the mean free path of electrons escaping a sample is  $\sim 0.5$  nm. In order to measure layered materials, the overlay must be kept very thin. Additionally, any surface contamination must be removed from the base wafer. This leads to a general procedure of cleaning the wafer substrate by Ar ion sputtering and then depositing the overlayer material at a very low rate, in order to observe photoemission signal from both layers of the heterostructure. The details of this procedure will be discussed for the deposition of Zn on to n-GaP wafer, as an example, however this can be generalized for any metal-semiconductor system.

A single crystal, n-GaP(100) wafer, purchased from MTI corporation was sputtering with an argon ion gun. The filament emission current used was 20 mA and the beam voltage was 3 kV. Sputtering was performed at these conditions for 10 min per side at a  $45^\circ$  angle from the sputtering gun to reduce Ar ion implantation into the wafer. After each 20 min. round was complete and Auger spectrum was taken to asses the progress of cleaning. Once residual carbon and oxygen Auger peaks were eliminated (Fig. 4.3) sputtering was finished.

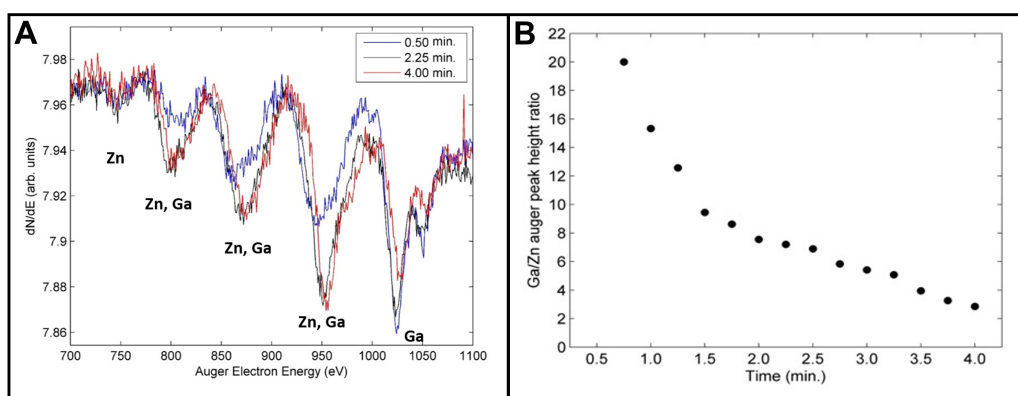


**Fig. 4.3** The Auger spectrum before argon sputtering shows prominent carbon and oxygen peaks. Both the carbon and oxygen peaks form a doublet denoting compounds that are surface adsorbed, lower energy, and surface bound, higher energy (blue line). After sputtering these peaks are eliminated and the phosphorus peaks is more intense (orange line).

The oven for the Zn deposition consisted of a 4 cm long Ta wire (0.5 mm diameter) wrapped around a Zn pellet. Typically measuring the temperature of the deposition material is done with a pyrometer, which senses the amount of thermal radiation an object is emitting. However the temperature corresponding to a vapor pressure of  $10^{-7}$  Torr of Zn ( $\sim 150^\circ\text{C}$ ) is below the  $650^\circ\text{C}$  detection limit of the pyrometer. Additionally, direct measurement

of the temperature with a thermocouple would require an insulating barrier between the thermocouple and the material to keep Zn from being deposited on the weld point of the thermocouple. However, an insulating barrier would also makes the temperature reading not a direct measurement of the Zn metal. Small variations in the temperature become important when slow deposition rates are required. Given these constraints, the deposition rate was set by measuring the elemental composition of the n-GaP surface through AES for increasing oven currents. A 5 min. equilibration time was taken between every 0.2 A increase of the oven current. Once Zn peaks began to appear the deposition rate was calibrated through observing changes in the AES spectrum as a function of deposition time.

Because AES is a surface sensitive technique, it is possible to track the accumulation of material on the surface of a substrate by taking the ratio of substrate peak height to the deposition material peak height. It was shown by Biberian and Somorjai when the ratio of the substrate peak height to the deposited material peak height is plotted as a function of time the formation of the first monolayer is observed as a distinct change in slope [26].



**Fig. 4.4** Panel A displays the Auger spectrum of increasing Zn coverage on n-GaP. The LMM region of the AES spectra for Zn/n-GaP films at increasing exposure times to the Zn oven (where a longer time indicates more Zn has been deposited) was used to determine the growth mode of the Zn/n-GaP film. The 5 spectral features correspond to a distinct Zn peak, a distinct Ga peak, and 3 peaks that have both Zn and Ga Auger electron contributions. The peak height of the Ga LMM peak centered at 1025 eV and Zn LMM peak at 745 eV were used in the Auger electron peak ratio, which was then used in the determination of the growth mode. Panel B shows the ratio of the peak height for the Ga LMM over the peak height for the Zn LMM plotted as function of deposition time shows a linear downward trend followed by oscillating peak ratio. Note the break at 1.4 minutes, indicating completion of the first monolayer.

Here, the Ga LMM peak, at  $\sim 1,025$  eV, and the Zn LMM peak, at  $\sim 745$  eV, were chosen as the substrate and deposited material peak, respectively, to avoid peaks with contributions from both the substrate and deposition material (Fig. 4.4A). The peak heights used in the ratio plot were determined by subtracting the peak minimum (1,025 eV for Ga, 745 eV for Zn) from the leading edge of the peak (1,002 eV for Ga, 728 eV for Zn). In order to determine the time for which a monolayer of material is deposited, a linear trend was fit to the data from 0-1.25 min and a second linear trend was fit for data from 1.5-4 min. The

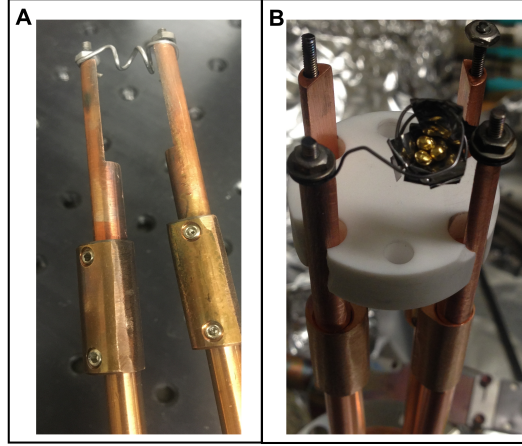
intersection of these two lines, which corresponds to a monolayer of Zn being deposited, was found to be 1.4 min. By using the same evaporation conditions as presented here, a sample composed of only a few monolayers of Zn on n-GaP can be made for study by photoemission. It should be noted that this method is no longer accurate in the case there is island formation of the deposited materials. The corresponding transient photoemission study on the Zn/n-GaP(100) sample is presented in the chapter 7.

## 4.5 Nanometer Thick Films for Absorption Studies

In absorption experiments samples need to be thin enough so that the incident XUV light is not completely blocked, but thick enough so that a measurable change is observed between the XUV light before and after the sample. For the apparatus presented in the chapter 2, the desired thickness of deposited materials can range from 5 nm - 150 nm, depending on if the sample is intended as a single material study or part of a junction and the magnitude of the extinction coefficient in the XUV energy range. The material vapor pressures corresponding to nm per hour or  $\mu\text{m}$  per hour deposition rates require higher temperatures than the monolayer per hour rates presented in the *Monolayer Deposition for Photoemission Studies* section. Additionally, the base substrate itself is no longer a wafer, but thin x-ray microscopy windows. Typically 30 nm - 50 nm thick  $\text{SiN}_x$  is used to limit the amount of light absorbed by the substrate, however in some cases 100 nm - 200 nm thick Si membranes are used for direct study as part of a heterostructure sample.

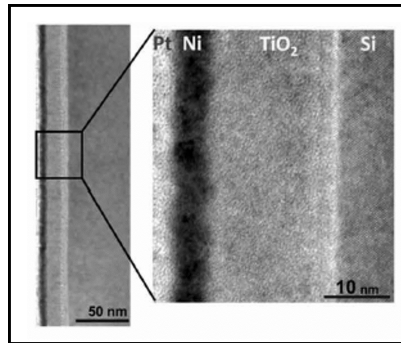
For the growth chamber geometry presented in section *Growth Chamber Components*, a deposition material vapor pressure of  $\sim 10^{-7}$  Torr yields  $\sim 1$  nm/hr growth rate. For many metals, such as Ti, Ni, Pt, Mn, or Co, the temperature corresponding to a  $\sim 10^{-7}$  Torr vapor pressure is well below the melting point of the material and the metals are ductile enough for high purity wires to be readily available. This allows for the simplest oven construction, a wire connected to two copper rods. A direct control and measurement of the wire temperature, using a pyrometer, and the simple oven design are the major benefits of this style of oven. It also requires less power, and it is therefore less strenuous on the conductive vacuum feedthroughs, which can crack and then leak from expansion and contraction due to current induced temperature changes on the insulating material between the copper rods and vacuum flange. The main drawback of this design is the deposition material is an integral part of the electrical circuit of the oven. As the material heats and eventually deposits the resistance of the wire changes so constant monitoring of the oven is required.

The other type of oven used to thermally evaporate materials here, is a direct contact heating oven. This design is preferred when the deposition material has a small extinction coefficient requiring a large amount of material to be deposited, or when the deposition temperature is close ( $\sim 100^\circ\text{C}$ ) to the melting point of the material. In this design, a wire is wrapped around the deposition material. The main wire is resistively heated. This heat is then transferred to the deposition material through contact. The resistively heated wire must be composed of a material with a deposition temperature much higher than the temperature required to deposit the desired material, preferably at least  $1000^\circ\text{C}$  larger, and the resistive wire and deposition material must not alloy to ensure that the heating wire is not co-deposited with the deposition material.



**Fig. 4.5** Panel A shows a resistive heating oven used to deposit Ni. A Ni wire is used to connect two copper rods. A current is then passed through the circuit to heat the Ni wire. Panel B shows the contact heating oven used to deposit gold. A low deposition rate was achieved by applying 25 A, 1.7 v to the tungsten wire surrounding the gold pellets.

A resistive heating style oven, shown in figure 4.5A, was successfully used to deposit Ni. The oven was constructed by connecting two copper rods with a Ni wire (Fig. 4.5A). The wire was then heated  $995^{\circ}\text{C}$  -  $1,005^{\circ}\text{C}$  by applying 6.2 A and 1.2 V. This resulted in a  $\sim 1.2$  nm per hour growth rate. Figure 4.5B shows an example of a direct contact heating oven used to deposit gold. The melting point of gold is within  $50^{\circ}\text{C}$  of the desired deposition temperature and it does not alloy with tungsten, making it a perfect candidate for direct heating. Here, a gold pellet was placed in a double stranded tungsten boat. The boat was then heated by applying 25 A and 1.7 V, to a temperature of  $\sim 850^{\circ}\text{C}$ .

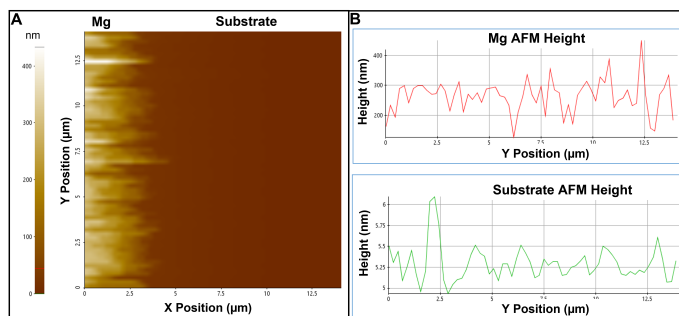


**Fig. 4.6** TEM measurement of the thickness of the  $\text{TiO}_2$  and Ni, which are  $19 \pm 0.6$  nm and  $5.6 \pm 0.6$  nm, respectively. The  $\text{TiO}_2$  is amorphous [27].

Once the materials are grown there are several methods that have been successfully used to characterize the thickness of the samples grown. Namely, cross-section transmission electron microscopy (TEM), atomic force microscopy (AFM) and x-ray absorption measurements have all been used to characterize the sample thickness. Cross-sectional TEM provides a direct measurement of the thickness of layers. In this method a section of the x-ray microscopy frame is cut away with a focused ion beam and then the thickness of the layers is measured

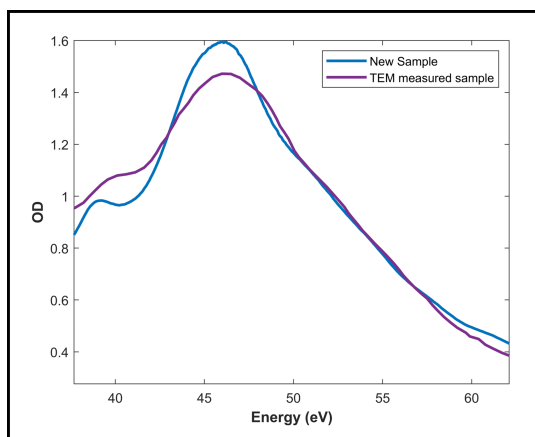


with TEM. This technique was used to measure the thickness of  $\text{TiO}_2$  and Ni layers that were sequentially deposited on a 200 nm thick Si membrane. Note that a Pt layer was added after the study by transient absorption to reduce the sample charging during TEM measurements (Fig. 4.6) [27]. It was found that the Ni layer was 5.6 nm and the  $\text{TiO}_2$  layer was 19 nm [27].



**Fig. 4.7** AFM measurement taken over the step height for a magnesium film is shown in panel A. The thickness of the Mg film is found to be 245 nm by subtracting the average height from  $X = 0-1 \mu\text{m}$ , top of panel B, from the average height from  $X = 10-13 \mu\text{m}$ .

It is also possible to measure the sample thickness through atomic force microscopy. In this case, a sharp line between the substrate and the deposited material is created by physically blocking a portion of the x-ray microscopy frame during the deposition (Fig. 4.8). Then an AFM measurement is taken across the step, allowing for the thickness of the deposited material to be determined. For example, AFM measurements of Mg show a step height (i.e. Mg thickness) of 250 nm (Fig. 4.7).



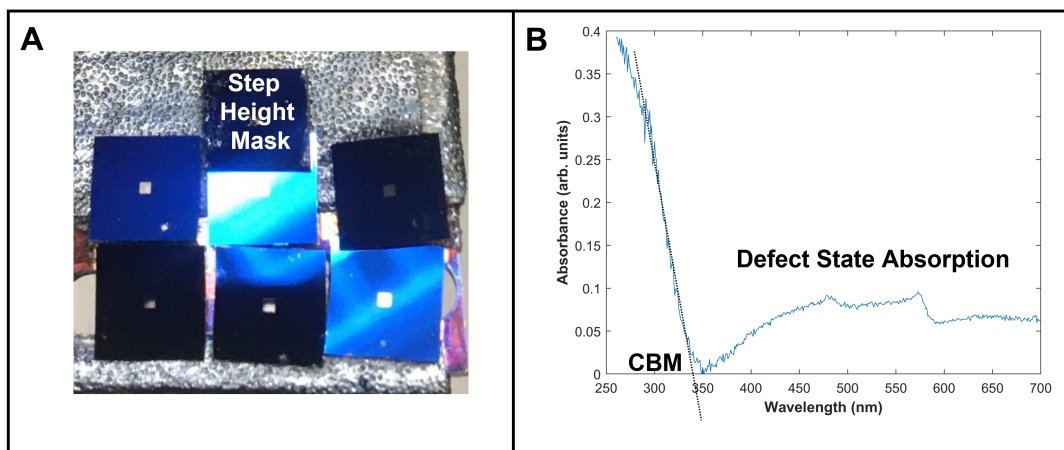
**Fig. 4.8** The x-ray absorbance at the Ti M-edge for a 19 nm  $\text{TiO}_2$  film (purple), was used to determine that a new  $\text{TiO}_2$  sample (blue) was 30 nm thick.

Lastly, if the extinction coefficient of the material is known or the optical density has been previously correlated to material thickness, then an x-ray absorption measurement can be used to calculate an approximate thickness. For example, a 0.3865 change in optical density from 40.13 eV - 45.68 eV at the  $\text{TiO}_2$  absorption edge corresponds to a 19 nm thick

film [27]. Therefore, it can be extrapolated that a  $\text{TiO}_2$  film with a dOD of 0.6132 OD is  $\sim 30$  nm thick (Fig. 4.8).

## 4.6 Metal Oxide Growth

Metal oxides can also be grown with the addition of a partial pressure of oxygen to the growth chamber during metal evaporation. The stoichiometry of metal oxides can be controlled by varying the partial pressure of oxygen present during growth. In this case, resistive heating of the deposition material is preferred as it allows for direct temperature measurement, and the slower evaporation rate provides a greater control over the oxidation state of the final material.

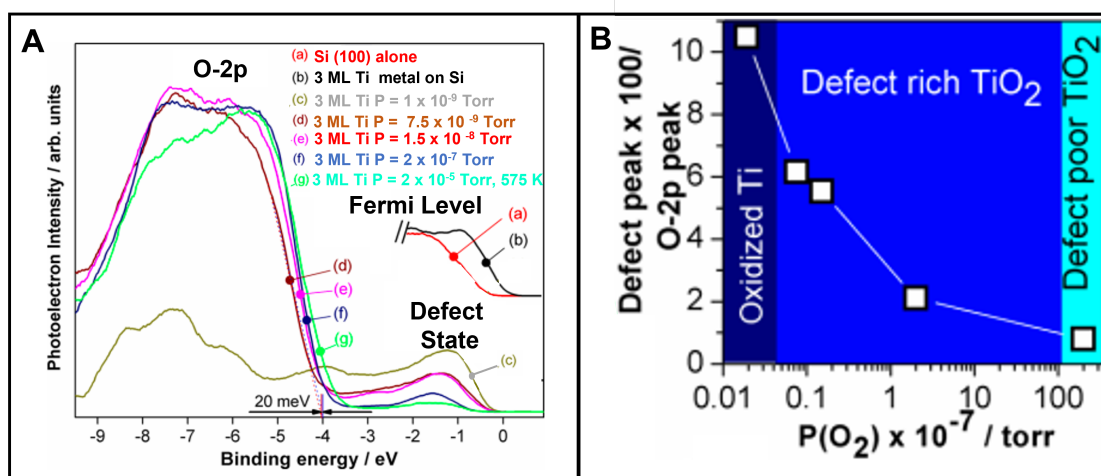


**Fig. 4.9**  $\text{TiO}_2$  samples grown with a 1 nm/hour Ti evaporation rate at an oxygen pressure of  $5 \times 10^{-5}$  Torr are blue in color, which suggests they have a significant amount of oxygen vacancies (A). The ultraviolet-visible light absorption spectrum presented in panel B confirms the presence of oxygen vacancies with the clear broad band absorption below the conduction band minimum (CBM).

In the case of making  $\text{TiO}_2$ , a  $5 \times 10^{-5}$  Torr partial pressure  $>99.999\%$  oxygen was established in the vacuum chamber through a leak valve. Then a Ti wire (99.98% purity) was resistively heated to  $1130^\circ\text{C}$  -  $1155^\circ\text{C}$ . This resulted in a  $\sim 1$  nm per hour growth rate, as determined through cross sectional TEM measurements outlined in section *Nanometer Thick Films for Absorption Studies* [27].

The oxidation state of the film can be qualitatively assessed by observing the color of  $\text{TiO}_2$ . Stoichiometric  $\text{TiO}_2$  is white in color, while blue and black titanium dioxide have been shown to have  $\text{TiO}_{2-0.114}$  and  $\text{TiO}_{2-0.124}$  compositions, respectively, through temperature programmed oxidation measurements [28]. In temperature programmed oxidation measurements the amount of oxygen vacancies is determined by measuring the amount of oxygen required to be absorbed by a sample in order to reach a stoichiometric  $\text{TiO}_2$  composition. This method is preferable to x-ray photoemission measurements as it more accurately measures bulk oxygen vacancies. Additionally, ultraviolet - visible light (UV-VIS) absorption spectroscopy has been shown to measure both the band gap of solids, which is equal to

the y-intercept of the sharp rise in absorption from the conduction band minimum, and mid gap states, which appear as much smaller absorption below the sharp absorption rise of the conduction band minimum [29]. The UV-Vis absorption spectrum of  $\text{TiO}_2$  grown here shows characteristic broad absorption below the conduction band minimum that is consistent with other UV-Vis absorption measurements of blue  $\text{TiO}_2$  (Fig. 4.9B) [28, 30, 31]. The blue color and UV-Vis spectrum most closely matches the  $\text{TiO}_{2-0.114}$  determined using temperature programmed oxidation measurements, making this the most likely stoichiometry of the  $\text{TiO}_2$  made here [28]. However, from these measurements the defect percentage could range from 5.5 % - 6.2%, which means the stoichiometry could range from  $\text{TiO}_{2-0.110}$  to  $\text{TiO}_{2-0.124}$  [28].



**Fig. 4.10** Valence band photoemission of  $\text{TiO}_2$  grown on Si(100) show the presence of a defect state and the growth of the oxygen 2p at various oxygen pressures. Panel B shows the calculated percent oxygen deficiency can be tuned from 6% - 0.07% by varying the oxygen pressure during growth [32].

To observe the effect of the oxygen pressure on the chemical composition, valence band photoemission measurements were taken after 3 monolayers of Ti were deposited under different oxygen pressures [32]. It can be seen that the  $\text{Ti}^{3+}$  defect peak located at 0.6 eV - 0.95 eV below the conduction band minimum (dashed line Fig. 4.10A) decreases as the oxygen pressure present during thermal evaporation increases. The area of the photoemission peaks are proportional to the amount of material contributing to the state from which the photoelectrons were ejected from. Based off of this, the percent oxygen deficiency can be calculated by taking the ratio of the area of the defect state to that of the oxygen 2p state. Figure 4.10B shows that the oxygen deficiency can be tuned from 6% - 0.07% by varying the oxygen pressure in the growth chamber during thermal evaporation of titanium.

## Conclusion

In summary, the theory of thermal evaporation was presented, with particular emphasis on principles that lead to uniform samples for spectroscopic measurements. The tools to assess chemical composition and film growth in the growth vacuum chamber were presented. The different sample growth requirements for photoemission and absorption studies were

discussed and examples of oven styles and successful metal and metal oxide samples grown by thermal evaporation were shown. Lastly, the control over sample oxidation was demonstrated in the case of  $\text{TiO}_2$ . Overall, thermal evaporation provides a versatile and technique that allows for a variety of metal and metal oxide films to be made for spectroscopic study.

# Chapter 5. Dependence of electron thermalization time in metals on the density of states studied by transient attosecond extreme ultraviolet light (XUV) absorption spectroscopy

## 5.1 Introduction

Electrons and holes in non-equilibrium or thermally excited distributions, known as hot carriers, have long been discussed in the context of their role in device operations. In some applications, such as traditional metal oxide semiconductor field effect transistors (MOSFET), lateral double-diffused MOSFET, or fin field effect transistors, hot carrier injection leads to device degradation [33-37]. Other device schemes, like hot carrier solar cells, hot-carrier-assisted photochemical reactions, or hot carrier photodetection, attempt to harness hot carriers to enhance device performance [38-42]. A fundamental understanding of the life time and thermalization mechanisms of hot carriers will benefit both classes of devices as it aids in the ability to select materials that either limit or enhance hot carrier lifetime.

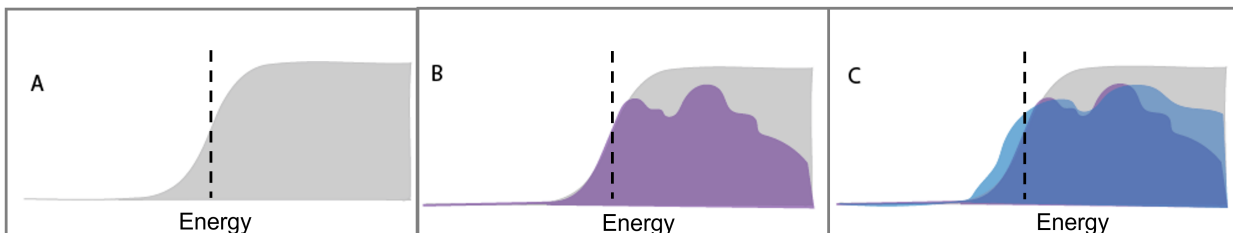
Extreme ultraviolet light attosecond transient absorption spectroscopy (tr-XAS) is a very suitable technique for probing the initial hot carrier thermalization in metals, as it is sensitive to carrier distribution in many cases and has the necessary time resolution to observe these fast dynamics. Previous studies observed a very fast response at the metal adsorption edge of titanium metal upon laser excitation due to a strong local field effect (LFE), which enhances carrier-carrier interactions thereby decreasing carrier thermalization time [43]. However, a much slower response to laser excitation has been observed in other metals, such as nickel [44]. While these previous works provide valuable insight into screening effects in metals and absorption line shape broadening associated with electron temperature, unifying investigations in which the underlying mechanisms that contribute to either a fast or slow initial carrier thermalization have yet to be explored [43,44].

In this chapter the nature of optical excitation in metals and how x-ray absorption spectroscopy (XAS) views the electron and hole distributions after optical excitation will be described. The time scale of hot electron and hot hole thermalization within a metal will be discussed. A comparison of the XAS profile, tr-XAS line shape and carrier lifetime between metals will be made. Finally, a method for predicting whether carriers will thermalize within a few femtoseconds or after ten femtoseconds will be laid out.

## 5.2 Contributing Factors and Examples of XAS Profiles of Metals

As was outlined in section *XUV Absorption Spectroscopy* of chapter 1, the working principle of absorption spectroscopy, as summarized by Fermi's golden rule, is simple. When light impinging on a material has an energy equal to the energy gap of two states a photon is absorbed and an electron is promoted from the initial state to the final state. While this describes the reason for absorption occurring at particular energies it does not capture the shape of an absorption spectrum. For example, if we describe the x-ray absorption spectrum of metals, considering only Fermi's golden rule, the result would be a direct mapping of the

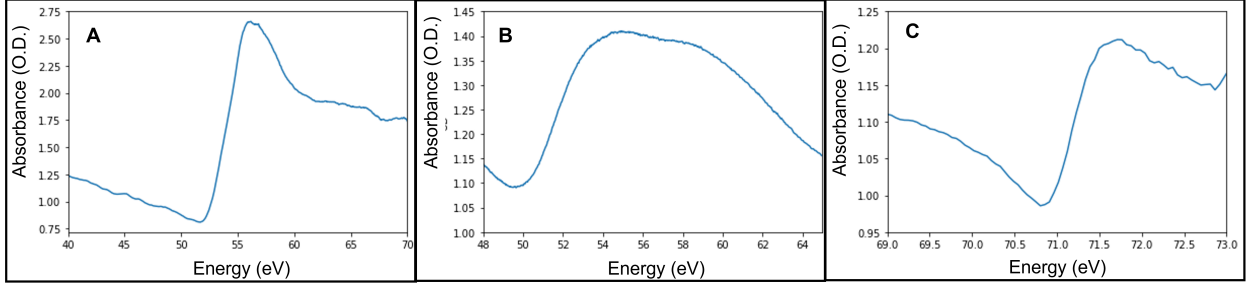
Fermi-Dirac distribution of the electrons to the XAS spectrum (Fig. 5.1A). Often the density of states does not map well onto the XAS spectrum. In reality, there are many factors that give shape to the absorption profile, several of which are common to all metals and are worth exploring.



**Fig. 5.1** Contributions to the absorption profile of metals can be seen by first starting with the line shape that would result from considering only Fermi’s golden rule (A). Then the contribution from the structure of the density of states above the Fermi level is shown in the purple shaded spectrum (B), finally broadening is also added to the final absorption profile in blue (C).

The density of states and absorption selection rules, as discussed in section *XUV Absorption Spectroscopy* of chapter 1, lead to structure above the absorption onset (Fig. 5.1B). Additionally, when the initial core level is split by spin-orbit coupling, two copies of the absorption profile are created, spaced by the value of the spin-orbit splitting. For the upper core levels (M-edge, N-edge, *etc.*) the splitting is usually small and thus the absorption profile created from each spin-orbit split state overlaps, further obscuring the absorption profile. There is also significant lifetime broadening from the core hole for these upper core levels, which ultimately leads to the departure of directly observing the Fermi level with x-ray absorption spectroscopy (Fig. 5.1C) [1]. While the contributions from absorption selection rules, density of states, spin-orbit splitting of core levels, and lifetime broadening are the most basic underlying factors that obscure the x-ray absorption profile of metals, effects like delayed onset, or coupling into available decay channels can also have significant effects on the shape [45, 46].

Figure 2 demonstrates a variety of x-ray absorption profiles exhibited by metals. The Fe  $M_{2,3}$ -edge (Fig. 5.2A) at 52 eV comes from Fe  $3p$  to states above the Fermi level. The Pt  $O_{3-}$  edge at 50 eV, consists of transitions from  $5p_{1/2}$  to states above the Fermi level. Transitions from the Pt  $4f_{7/2}$  into states above the Fermi level create the Pt  $N_7$ -edge, centered at 71 eV. The Fano profile of the Pt  $N_7$ -edge comes from the  $4f5d^{n+1}$  states coupling to a continuum of  $5d$  and  $5p$  photoemission states via Coster Kronig transitions [46]. A summary of the states involved and edge energies is displayed in Table 5.1.



**Fig. 5.2** Panel A shows the static, M<sub>2,3</sub>-edge absorption of Fe, panel B shows the Pt O<sub>3</sub>-edge and panel C shows the Pt N<sub>7</sub>-edge.

| Edge                | Initial State             | Energy (eV) |
|---------------------|---------------------------|-------------|
| Fe M <sub>2,3</sub> | 3 <i>p</i>                | 52          |
| Pt O <sub>3</sub>   | 5 <i>p</i> <sub>1/2</sub> | 50          |
| Pt N <sub>7</sub>   | 4 <i>f</i> <sub>7/2</sub> | 71          |

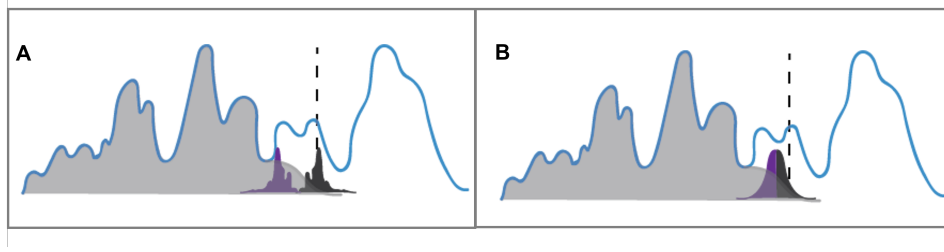
**Table 5.1.** The initial states and absorption edge energy for Fe and Pt are summarized.

A qualitative understanding of the relationship between edge broadening and the core hole lifetime can be gained by comparing the Fe M<sub>2,3</sub>-edge and Pt O<sub>3</sub>-edge. Both of these absorption edges involve transitions from the highest *p*-states into states above the Fermi level, which makes the selection rules similar for these edges, and neither of these edges are spin-orbit split, yet they have very different absorption profiles. The main difference between the Fe M<sub>2,3</sub>-edge and Pt O<sub>3</sub>-edge is the core-hole lifetime, which is 6.8 fs and 2.3 fs, respectively [46]. The energy-time uncertainty principle, which is mathematically expressed as  $\Delta E \Delta t \geq \hbar$ , indicates that a shorter lived core hole leads to more energetic broadening of the absorption edge. This also exemplifies why there is no simple way to observe material characteristics, such as the location of the Fermi-level or electron temperature, from an x-ray absorption spectrum. The complicated absorption profiles, mainly from broadening induced by the core-hole, distort the underlying characteristics of the material. Despite having complex absorption line shapes XAS is still a powerful probe in transient spectroscopy. By carefully considering the changes that take place due to optical excitation, transient XAS can give great insight into carrier dynamics.

### 5.3 Optical excitation and XAS probing of metals

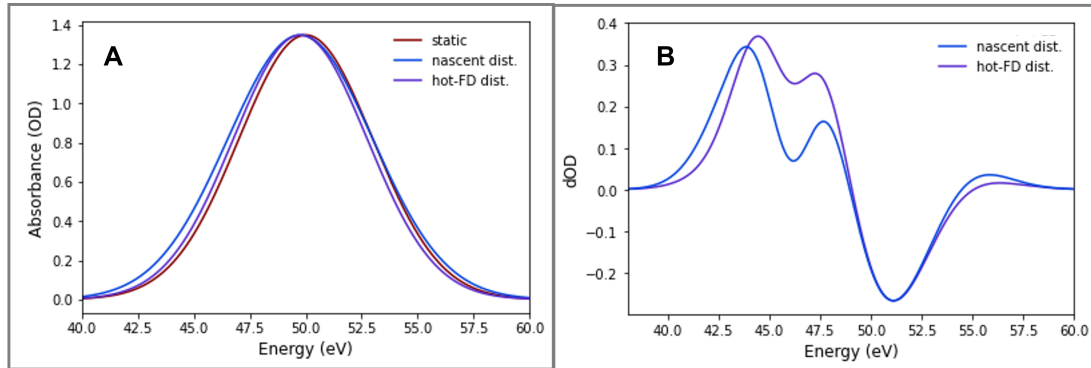
Now that a foundation has been set for understanding how metals are probed with XAS, it is useful to consider the effect of optical excitation on a metal and how this will be interrogated by the XAS probe.

Directly after optical excitation electrons near the Fermi level are promoted to higher states (Fig. 5.3A). As long as the fraction of excited carriers is lower than the density of unoccupied states above the Fermi level the distribution of the electrons and holes matches



**Fig. 5.3** After optical excitation the electrons and holes in a metal have a highly energetic, non-equilibrium distribution (A). After a short period of time, carriers thermalize to a hot Fermi-Dirac distribution. Here the gray shaded area shows the electron occupation before optical excitation, the purple shaded area shows the hole distribution after excitation, the dark grey shaded area shows the electron distribution after excitation, the blue line is the density of states and the Fermi level is marked by a dashed line.

that of the optical pump spectrum. Within the next few-femtoseconds, this nascent electron distribution collapses, through electron-electron scattering or hole-hole scattering, to a hot Fermi-Dirac distribution (Fig. 5.3A). Finally, the hot Fermi-Dirac distribution returns to the original equilibrium distribution by electron-hole recombination and electron-phonon coupling.



**Fig. 5.4** In panel A, the anticipated modification from the nascent carrier distribution (blue) and hot Fermi-Dirac distribution (purple) to a perfectly Gaussian absorption profile (red) is shown. The corresponding transient adsorption profiles are shown in panel B.

Figure 5.4 explores the change in electron and hole population due to optical pumping. For the nascent carrier distribution, the newly created holes near the Fermi level open up XAS absorption that was previously blocked and newly promoted electrons above the Fermi level block absorption transitions that were previously allowed. This results in the onset of absorption moving to lower energies and a decrease in absorption at higher energies, when compared with the static spectrum (Fig. 5.4A). When the nascent carrier distribution collapses to a hot Fermi-Dirac distribution, the hole and electron population shift toward the original Fermi level. This results in the absorption onset moving to slightly higher energy than the nascent distribution, while still being lower in energy than the static absorption.



There is also a more pronounced increase and decrease in absorption around the center of the static absorption profile (Fig. 5.4A). In terms of the change in absorption, which can be viewed as the XAS spectrum after optical excitation being subtracted from the static XAS spectrum, the nascent carrier distribution has a longer tail at high and low energy whereas the intensity of the main increase and decrease in absorption is larger for the hot Fermi-Dirac distribution (Fig. 5.4B).

## 5.4 Attosecond Transient Absorption Measurements of Pt and Fe Films

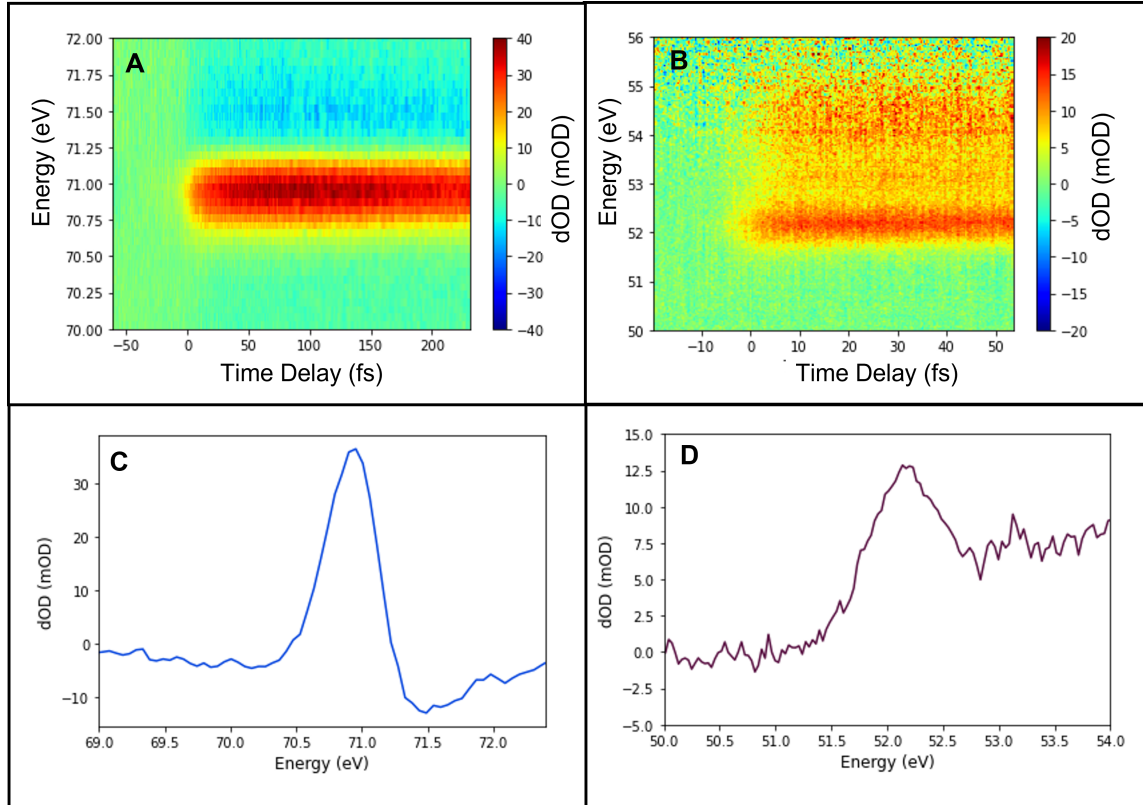
All metal films interrogated by tr-XAS were grown by home-built thermal evaporation ovens as described in chapter 4. A Pt film was grown by thermal evaporation of a Pt wire onto 50 nm silicon nitride SEM membranes. A deposition rate of  $\sim 1$  nm/hr was achieved by keeping the Pt wire between 1330 °C - 1348 °C, which corresponds to a Pt vapor pressure of  $\sim 2 \times 10^{-7}$  Torr. An Fe film was created by flash evaporating an Fe pellet by applying 25 A and 3.5 V for 1.5 hrs onto 30 nm thick silicon nitride membranes. From the XUV absorption the thickness of the Pt and Fe films was determined to be 30 nm and 55 nm, respectively.

Transient absorption measurements were performed with the setup described in chapter 2. For the probe, XUV light extending up to the Al filter cut off energy of 73 eV was generated in Ar gas. The optical pump spectrum energy ranges from 475nm - 925nm and a power of 8.22  $\mu$ J was used to pump the Pt film whereas a power of 10.6  $\mu$ J was used to pump the Fe film. Additionally, the instrument response function, as determined using transient Ne scans discussed in chapter 2, was found to be 5.9 fs for the Pt scan and 5.1 fs for the Fe scan.

The transient absorption spectra of Pt and Fe are shown in figure 5.5. For both metals the main transient absorption features occur just before the energy of the un-pumped, static absorption edge energy. Immediately it is noticeable that the Pt (Fig. 5.5A, C) displays the characteristic increase and decrease in dOD around the absorption edge energy. This is consistent with the state blocking perspective which was laid out in the *Optical excitation and XAS probing of metals* section. It should be noted that the magnitude of the positive and negative features are not equal, indicating there is broadening of the absorption edge in addition to the expected shift due to state blocking. The Fe  $M_{2,3}$ -edge has a major increase in the change of absorption at 52 eV (Fig. 5B, D), but there is not as pronounced a decrease as can be seen in Pt. There are two possible explanations for why Fe deviates from the Pt results.

Firstly, the Fe  $M_{2,3}$ -edge has significant absorption far beyond the onset, so if the edge were simply shifting, the negative feature would be less pronounced than in the Pt  $N_7$ -edge, where the absorption quickly decreases after the onset (Fig. 5.2A ,C). In this scenario the decrease in the change of absorption is expected right after the observed increase and overlaps in energy with another increase feature due to structure above the absorption edge. Overall, this leads to the decrease feature being diminished. In this case, the state-blocking picture still holds, however it is not well resolved due to overlapping features in the energy domain.

Another explanation considers the many-body effects present in many metals. TDDFT simulations of the transient absorption for metallic Ti have shown that local screening near



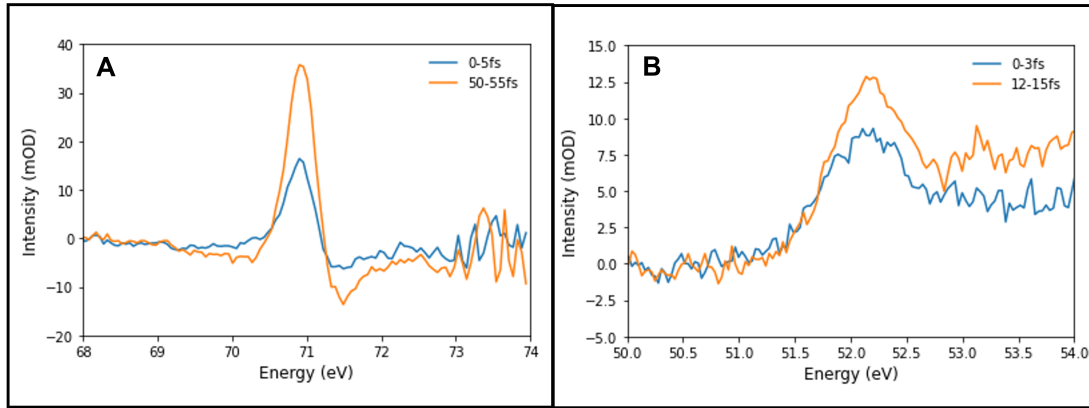
**Fig. 5.5** transient absorption spectra for Pt and Fe are shown in panels A and B, respectively. Panel C shows the spectral profile of Pt 70 fs after excitation and Panel D shows the spectral profile of Fe 7 fs after excitation.

the Fermi level was expressed as a decrease and then an increase in the change of absorption [43, 48]. It should be emphasized that the signature in the change of absorption for the local screening case is the exact opposite of what is expected from state blocking. Therefore, when state-blocking contributions are summed with local screening contributions only an increase in absorption is observed. It is possible that Fe also has strong local screening, which leads to the 'missing' decrease in absorption predicted from a state-blocking only perspective.

## 5.5 Timescale Carrier Thermalization in Pt and Fe Films

As was discussed in section *Optical excitation and XAS probing of metals*, a small difference in line shape of the transient absorption line shape is expected between the nascent carrier distribution and the hot Fermi-Dirac carrier distribution. Specifically, the nascent distribution should have a less intense main increase and decrease features and have tails at high and low energy (Fig. 5.4B). In order to make this comparison the transient absorption spectrum for Pt and Fe were averaged at early and later times (Fig. 5.6).

While there might be a small tail at  $\sim 70.5$  eV at the early times for Pt, the difference is subtle, making it difficult to definitively determine which features come from the nascent distribution and which from the hot Fermi-Dirac distribution. Additionally, the process of



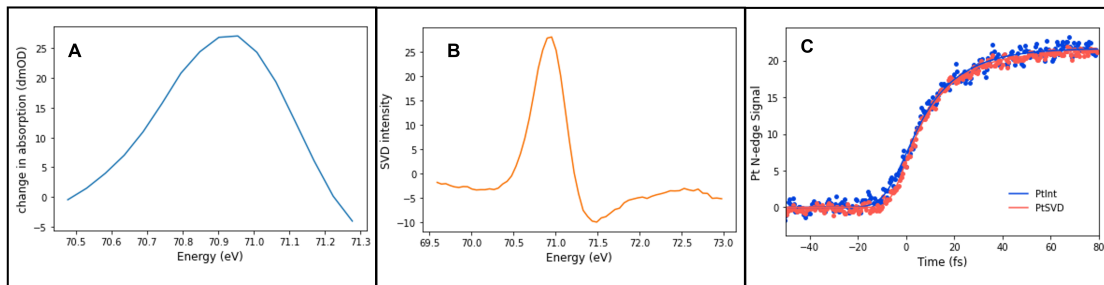
**Fig. 5.6** To observe changes in the transient profile occur over time the transient signal was averaged from 0 - 5 fs and 50 - 55 fs for Pt (A) and from 0 - 3 fs and 12 - 15 fs in Fe (B).

transferring between the two distributions is gradual over time, which adds further difficulty in trying to separate factors from either distribution, as the majority of the time points contain a mix of both distributions. The difference between the nascent distribution and hot Fermi-Dirac distribution was also unclear in transient absorption spectra of Ni and Ti, in which the experiments utilized similar optical pump energies as this study [43, 44]. It is likely that by using a higher pump energy with a narrower spectrum the spectral change between the distributions might be observed more readily as the difference between the carrier distributions would be more pronounced and the thermalization time would likely be increased [49].

Although there is not much change in the shape of the transient absorption features, they do significantly change in intensity, which is also associated with the transition from a nascent carrier distribution to a hot Fermi-Dirac distribution. By tracking the temporal evolution of the main increase (and decrease) features the initial carrier thermalization time (i.e. the time it takes to transition from the nascent to the hot Fermi-Dirac distribution) can be determined. Additionally, it is also possible to discover if the holes and electrons thermalize on the same time scale by comparing the time evolution of different energy regions in the transient signal. Broadening of the absorption edge makes it so that one can no longer assume a one-to-one correspondence between the temporal dependence of the positive or negative spectral features and hole or electron dynamics. However, because the holes still mainly contribute to the positive feature and electrons mainly contribute to the negative feature, if the holes and electrons are thermalizing at different rates then there should be a dependence of the measured thermalization rate on the spectral region. Conversely, if the electrons and holes thermalize at similar rates, then there will be no observed dependence between the thermalization time and the spectral region considered.

To compare the measured thermalization rate for different spectral regions, two filtering methods were used. One method is to track the positive feature by integrating the energy region for which the transient absorption is a positive value. This method captures mostly hole dynamics, as holes are the main contributor to the positive feature, as was shown in the

section entitled *Optical excitation and XAS probing of metals*. The second method is to use singular-value-decomposition (SVD) filtering, which captures both populations by tracking the temporal evolution of specific line shapes. By comparing the carrier thermalization time reported from these two methods we can determine if the time scale of thermalization for electrons and holes is similar or if it is different.



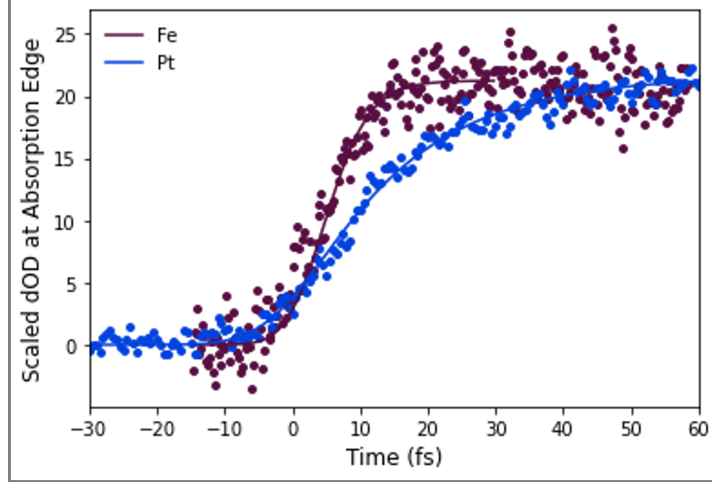
**Fig. 5.7** For Pt, 70.8 eV - 71.3 eV was integrated (A), and SVD filtering was applied to capture the entire transient signature (B). The temporal evolution of these two filtering methods was then compared (C).

Both filtering methods will be briefly discussed here using Pt as an example, however the same analysis is shown for Fe in the appendix of this chapter. For the peak integration method in Pt, each time slice was summed from 70.8 eV to 71.3 eV (Fig. 5.7A). For the SVD filtering method, SVD was applied from 69.6 eV to 73.0 eV, where the wider energy window ensures both electron and hole dynamics are being captured (Fig. 5.7B). The temporal evolution of the spectral features captured by these two filtering methods was then fit with an error function convoluted with Gaussian, to account for the temporal duration of the optical pump, which is further described in the appendix of this chapter. In Pt the carrier thermalization time was  $15.9 \pm 2.91$  fs and  $15.1 \pm 2.55$  fs for the integrated peak and the SVD filtering method, respectively. When the same analysis was applied to Fe the thermalization time was found to be  $3.36 \pm 1.75$  fs and  $2.71 \pm 1.96$  fs for the integrated peak method and SVD filtering, respectively. Because there is no statistical difference between the results of the two filtering methods it is likely that the electron and hole thermalization occurs on the same time scale. It is unsurprising that the electrons and holes thermalize on the same timescale in Fe and Pt, as both the velocity and mass of the holes and electrons, which often correlate with the rate of carrier thermalization, tend to be the same in most metals.

## 5.6 Observation of the Local Field Effect in Metals

Throughout the course of this chapter, it has been shown how tr-XAS probes both the electron and hole populations in metals and that the thermalization time of these populations is similar. The discussion now turns to exploring and explaining the differences in carrier thermalization time between metals.

Figure 5.8 shows the temporal evolution of the Pt N<sub>7</sub>-edge and Fe M<sub>2,3</sub>-edge, with the integrated peak method applied. The carrier thermalization time is  $15.9 \pm 2.91$  fs for Pt

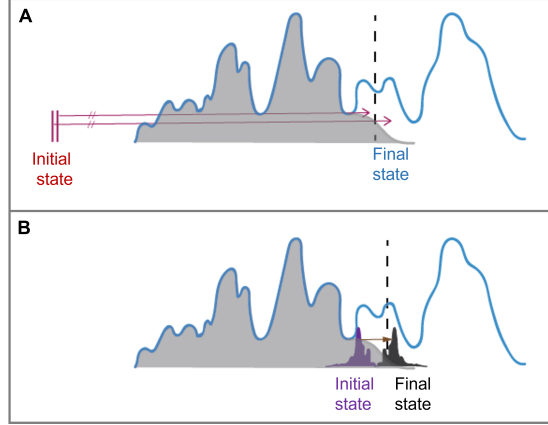


**Fig. 5.8** The carrier thermalization rate was determined by fitting the temporal dependence of the transient absorption signal in Fe and Pt with an error function convoluted with a Gaussian. For Pt, the transient signal from 70.8 eV - 71.3 eV was integrated, and for Fe the region of integration was 51.5 eV - 52.5 eV.

and  $3.36 \pm 1.75$  fs for Fe. Previous results in Ni and Ti found a thermalization time of 13 fs and 1.1 fs, respectively [43, 44]. When the measurements of Pt and Fe are contextualized with these previous results on Ni and Ti a clearer picture of the timescale of and underlying mechanisms behind carrier thermalization in metals can be put together. From these tr-XAS measurements, two classes of metals arise; those in which carrier thermalization is “slow” and occurs at times greater than 10 fs and those in which carrier thermalization is “fast” and occurs within the first few femtoseconds after optical excitation.

Further insight into the mechanism behind a “fast” thermalization time is gained from TDDFT calculations which were performed on Ti [43, 18]. These calculations demonstrated that the static and transient absorption spectral features as well as the very fast electron thermalization time can be attributed to the local field effect (LFE) [43, 18]. The LFE is a many body effect in which carriers are highly influenced by the electric field of nearby carriers [50]. Contributions from the LFE are essential in properly calculating the absorption and reflectance spectra of materials for which either or both the initial and final state in the absorption process is localized [51]. The strength of the LFE can be ordered by observing the initial and final state in an absorption process. The strongest LFE will occur when both the initial and final state in the absorption process are localized, an intermediate strength LFE results from either the initial or final state being localized, and a weak LFE is present when neither the initial nor final state are localized. In tr-XAS spectroscopy there are two absorption processes occurring. For the XAS probe the initial state is in the semi-core energy region and the final state is above the Fermi level (Fig. 5.9A) and for the optical pump the initial state is just below the Fermi level and the final state is just above the Fermi level (Fig. 5.9B). In the context of tr-XAS, the presence of a strong LFE in metals can be seen in both the static absorption and the transient absorption profiles. A strong LFE also leads to a very fast carrier thermalization time.

First, the static x-ray absorption spectrum will be very broad for a metal in which the



**Fig. 5.9** The density of states, in blue, for a metal is shown above. Where the electron occupation is marked by the gray shaded area and the Fermi level is marked by the vertical dashed line. The probe promotes an electrons from an initial core level, marked in red, to a final state above the Fermi level, marked in blue (A). The optical pump takes electrons from below the Fermi level (initial state marked in purple) and puts them in a final state above the Fermi level, where the final state is marked in dark grey (B)).

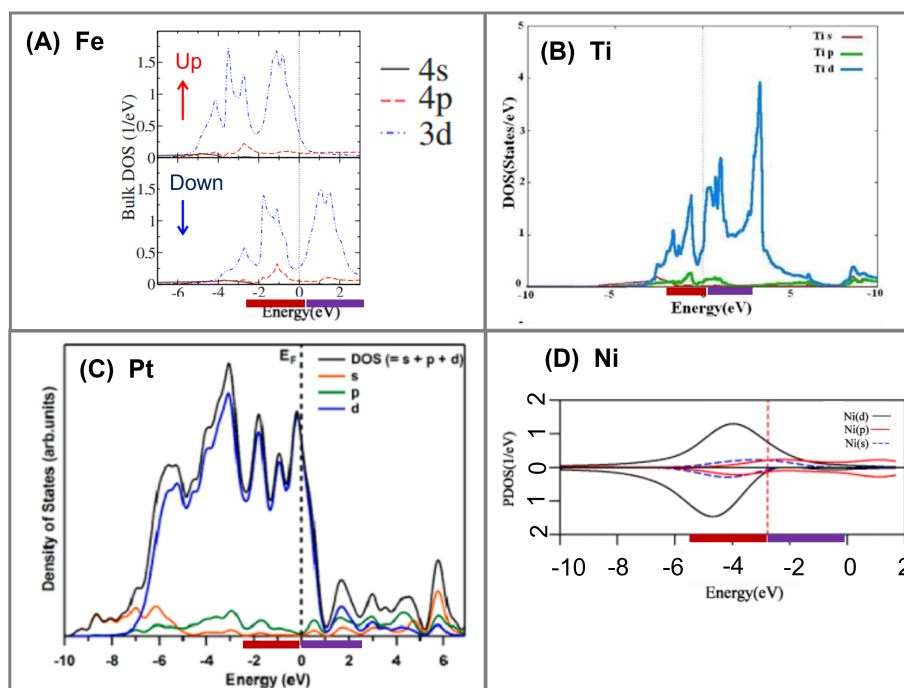
LFE is strong. While all XAS initial states are localized (semi-)core levels, when the final state, above the Fermi level, is also localized the absorption edge experiences significant lifetime broadening from the LFE (Fig. 5.9A) [51]. An example of this can be seen by comparing the static XAS spectrum of the Fe  $M_{2,3}$ -edge, which spans  $\sim 18$  eV, to the Pt  $N_7$ -edge which is much narrower, spanning only  $\sim 3$  eV (Fig. 5.2 A,C). This is also consistent with the Ni  $M_{2,3}$ -edge, which can be well modeled as two Gaussian functions separated by the Ni  $3p$  spin-orbit splitting and spans  $\sim 5$  eV, and Ti  $M_{2,3}$  absorption edge which spans over 20 eV and cannot be modeled without the inclusion of LFE [43, 44, 48].

The LFE also has a significant effect on the shape of the transient absorption spectrum. The strength of the LFE for optically excited electrons can be assessed by considering the states that are accessed by the pump; specifically states directly below (initial state) and above (final state) the Fermi level (Fig. 5.9B). In tr-XAS, the LFE competes with the state-blocking contribution of optical absorption and thereby limits the observation of a decrease in the change of absorption that is expected from a state-blocking perspective [48]. This is directly observed by contrasting the transient absorption spectra of Pt and Fe. In Pt there is a sharp increase followed by a decrease in the change of absorption, whereas in Fe there is no pronounced decrease in the transient absorption measurements (Fig. 5.5C, D).

Lastly, because the LFE enhances carrier-carrier scattering it, thereby, also decreases the carrier thermalization time. This occurs by the very nature of the LFE. It is a many-body effect, which expressly means that the optically excited holes and electrons near the Fermi level are strongly interacting with nearby excited holes or electrons, respectively. It is natural then to see that the carrier thermalization rate, which occurs by carrier-carrier interactions, increases when there is a strong LFE. It then follows that the increase in thermalization rate from a strong LFE is equivalent to a faster thermalization time.

## 5.7 Predicting the Strength of the Local Field Effect in Metals

Finally, because the strength of the LFE arises from the amount of localization in the initial and final state involved in the absorption process, the strength of the LFE in metals can be assessed from the partial density of states (pDOS). One need only look at the distribution of the states for which the optical pump (Fig. 5.9B) and the XAS probe (Fig. 5.9A) interrogate to determine the strength of the LFE. In the measurements performed on Pt and Fe presented here as well as the tr-XAS experiments conducted on Ni and Ti the optical pump spectrum spanned from  $\sim 500$  nm - 900 nm (1.4 eV - 2.5 eV) and the XUV light probed final states near the Fermi level, as was shown in section entitled “*Contributing factors and examples of XAS profiles of metals*”. Therefore, to assess the strength of the LFE in each metal, the states 2.5 eV above and below the Fermi level will be discussed.



**Fig. 5.10** The relative orbital contributions to the density of states near the Fermi level Fe (A), Ti (B), Pt (C) and Ni (D) is shown above. Reprinted with permission from the authors cited.

Figure 5.10 shows the partial density of states for Fe, Ti, Pt, and Ni [52- 55]. Here the added red and purple lines indicate the energies for which the optical pump creates holes and electrons, respectively. For Fe, the optical pump accesses mostly  $d$ -orbitals for both the initial and final states [52]. It should be noted that while the pDOS displays both the orbital and spin dependence of the DOS the experiments performed here were not sensitive to the spin dependence of the orbitals as they were performed with a linearly polarized pump (Fig. 10A). Likewise, in Ti both the initial and the final state in absorption are essentially all  $d$ -orbitals (Fig. 10B) [53]. In contrast to this, the initial states that the pump accesses in Pt are mostly of  $d$ -orbital character, while the final states, particularly above 1 eV, are a



mixture of  $s$ ,  $p$ , and  $d$ -orbitals (Fig. 5.10C) [54]. Similarly to Pt, in Ni the initial states are also mostly comprised of  $d$ -orbitals, however the final state is a mixture of  $p$  and  $d$ -orbitals (Fig. 5.10D) [55]. To summarize, the initial states the pump accesses is mostly localized to the  $d$ -orbitals for all metals, however the final state is localized to the  $d$ -orbitals only for Fe and Ti, whereas final state is more delocalized for Pt and Ni. Therefore it is expected that the LFE is stronger in Fe and Ti and weaker in Pt and Ni.

There are several observations discussed earlier that can be tied to the strength of the LFE. First, metals for which there is a strong LFE, like Fe and Ti, tend to have a broad XAS spectrum. This is because the final state probed by the XAS absorption is localized and therefore the LFE in the final states significantly contributes to life time broadening of the edge [51]. Conversely, the XAS static absorption spectrum for metals in which the LFE is weak, like in Pt and Ni, are comparatively narrow. Second, the shape of the transient absorption spectrum matches the state blocking perspective for metals with a weak LFE, like Pt and Ni, whereas state blocking alone cannot explain the transient absorption spectra of metals where the LFE is strong, like Fe and Ti. Lastly, a strong LFE enhances carrier-carrier scattering and thereby decreases the carrier thermalization time. This adequately describes the result that carrier thermalization time for Fe and Ti, in which there is a strong LFE, was found to be 3.3 fs and 1.1 fs, respectively, whereas the carrier thermalization time in Pt and Ni was found to be 15 fs and 13 fs, respectively.

## 5.8 Conclusion

In conclusion, it was shown that the electron and hole contributions are not easily separated in the tr-XAS measurements, however by comparing the thermalization time reported from processing the tr-XAS data with an integrated peak method and SVD filtering it was shown that the thermalization time is very similar for the hole and electron populations. It was also shown that a strong LFE leads to a broad XAS spectrum, a 'missing' depletion in the transient absorption spectrum line shape, and a few femtosecond carrier thermalization time. Finally, it was demonstrated that the strength of the LFE can be observed in the pDOS, implying that before measurement the broadness of the XAS spectrum, the transient absorption profile, and most importantly, the timescale of carrier thermalization can be anticipated. For example, if the states above and (or) below the Fermi level are localized (i.e. predominantly of one orbital type), then it would be expected that that metal would have a strong LFE and therefore have a broad XAS spectrum, display no significant depletion feature in the transient absorption profile, and have a carrier thermalization time within the first few femtoseconds of optical excitation.

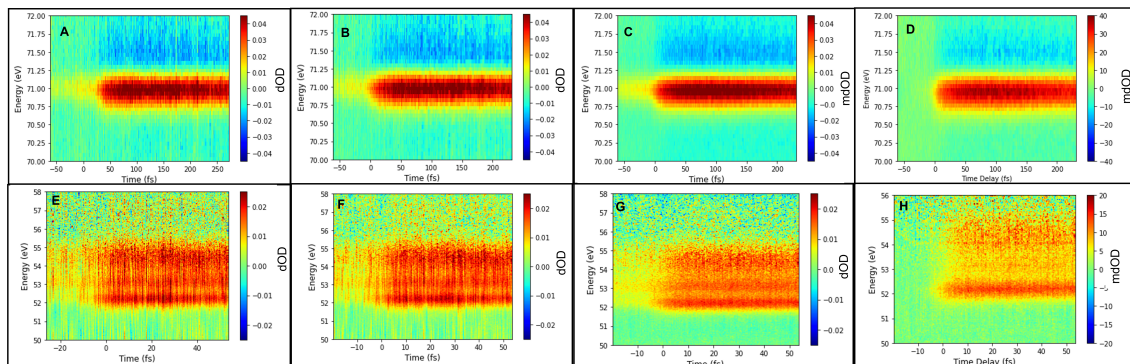
To strengthen these results I intend to measure Mg, which is expected to have a weak LFE, and Co, which is expected to have a strong LFE. Additionally, I am currently working with a theoretician to confirm that the LFE is strong in Fe and weak in Pt. The upcoming TDDFT theory calculations are anticipated to clarify the importance of including LFE contributions for the static XAS spectrum, transient absorption line shape, and carrier thermalization time in Fe. Through these additional measurements and calculations the theory laid out here, namely that the strength of the LFE can be observed in the pDOS of a metal and that a strong LFE leads to a broad static XAS spectrum, the lack of a decrease in



transient absorption line shape, and a fast carrier thermalization time, will be refined and strengthened.

## 5.9 Appendix

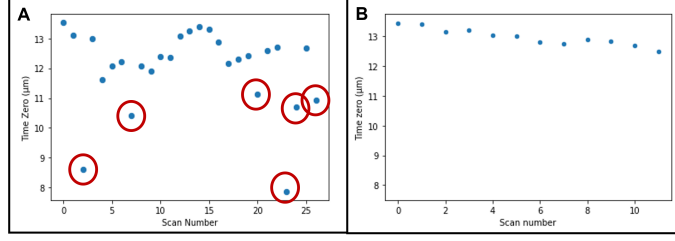
### Transient absorption data filtering and fitting



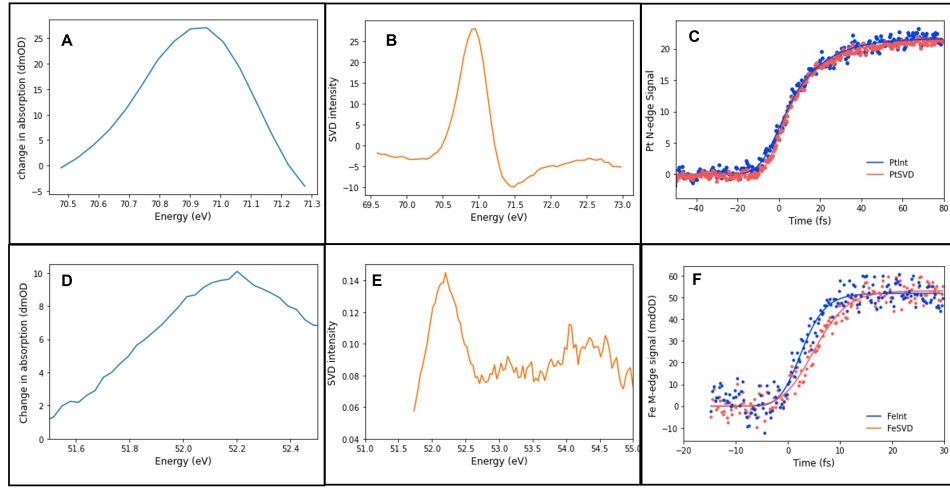
**Fig. 5.11** The transient absorption spectrum after each step of filtering and data correction is shown, where the top row is the Pt N<sub>7</sub>-edge and the bottom row is the Fe M<sub>2,3</sub>-edge. First, the raw data, which is comprised of many averages for each time point is shown (A,E). The data is then corrected for temporal drift (B,F). Next harmonic fluctuations are filtered out using edge referencing (C,G). Finally, the signal before time zero is subtracted (D,H).

Figure 5.11 shows how the raw transient absorption, panels A and E, is processed. As was described in chapter 2, a tr-XAS measurement of Ne is taken before scanning a full iteration of delay points in Pt or Fe to experimentally account for drifts in the temporal overlap. Figure 5.12 shows the time zero plotted for each successive sample scan. Scans for which the temporal overlap significantly drifted were excluded. The time points for each scan were aligned using the time zero measured before that scan was taken (Fig. 5.11B, F). Edge referencing, which has been shown to accurately account for intensity fluctuations between pump on and pump-off camera images which lead to noise in tr-XAS experiments, was also applied (Fig. 5.11C, G) [56]. The energy range used for the edge pixels was 58 eV - 68 eV for Pt and 45 eV - 50 eV for Fe. Lastly, the signal before time zero was subtracted (Fig. 5.11D, H). This originates from laser heating of the metal films, which persists for milliseconds. Both in these experiments and the Ti work done by *Volkov et. al.* the transient signal after subtraction was the same as transient absorption measurements where the background heating was experimentally eliminated by chopping and/or spinning the sample [43].

Two methods were used to evaluate the time dependence of features. First, the main increase in the transient absorption spectrum was integrated. Second, singular-value-decomposition filtering was used to fit the full line shape. In Pt, values between 70.8 eV and 71.3 eV were integrated for the integration method (Fig. 5.13A) and SVD filtering was applied from 69.6 eV to 73.0 eV (Fig. 5.13B). In Fe, values between 51.5 eV and 52.5 eV were integrated in



**Fig. 5.12** The position of temporal overlap on the delay stage is calculated for each time iteration to account for temporal drift in the experiment. Panel A shows the calculated position of temporal overlap for the Pt results and panel B shows the same values for the Fe results.



**Fig. 5.13** A narrow energy region was integrated for Pt (A) and Fe (D) and then compared with the SVD filtering of the entire transient absorption profile for Pt (B) and Fe (E). The temporal dependence of these features in Pt and Fe, panel C and F respectively, were fit to obtain the thermalization time.

the integration method (Fig. 5.13D) and SVD filtering was applied from 51.0 eV to 55.0 eV (Fig. 5.13E).

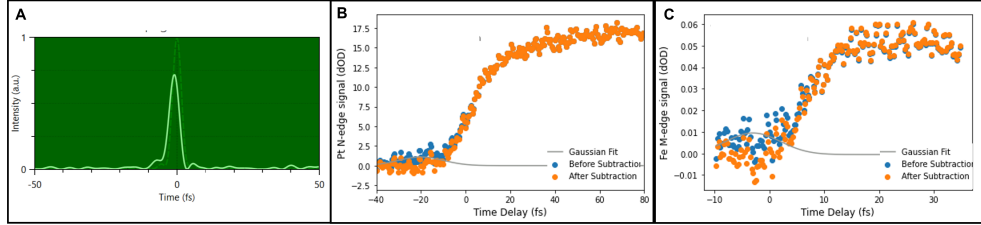
The results of the two filtering methods were fit with a Gaussian convoluted with an error function (Fig. 5.13C, F).

$$f(x, \mu, \sigma, \lambda) = \frac{\lambda}{2} \exp\left[\frac{\lambda}{2}(2\mu + \lambda\sigma^2 - 2x)\right] \otimes \operatorname{erfc}\left(\frac{\mu + \lambda\sigma^2 - x}{\sqrt{2}\sigma}\right) \quad (5.1)$$

where  $\mu$  is the mean of the Gaussian component,  $\lambda$  is the rate of the rise,  $\sigma$  is the variance of the Gaussian component. In the context of tr-XAS,  $\mu$  is equal to the value of time zero,  $\sigma$  is equal to the temporal instrument response function, and  $\lambda$  is the rate of the rise in the signal being fitted. Moreover, the time scale of the signal being fit is found by taking the inverse of  $\lambda$ . Additionally, as was described in chapter 2, the instrument response function is measured in Ne before any scan, which makes the value of  $\sigma$  known for each experiment

run. In the measurements presented above, the instrument response function was found to be 5.1 fs and 5.9 fs for Fe and Pt, respectively. These values are then used for  $s$ .

Lastly, a small Gaussian function (less than 3 % of the total signal) was fit 5 fs before time zero to account for a minor pre-pulse that has been well characterized through dispersion scanning (Fig. 5.14) .



**Fig. 5.14** A small pre-pulse can be seen on the dispersion scan spectrum (A). This is then accounted for in the experimental results of Pt and Fe, panel B and C respectively, by subtracting a small Gaussian (B, C).

# Chapter 6. Insights into charge transfer in a Pt/TiO<sub>2</sub> junction studied by attosecond transient extreme ultraviolet light (XUV) absorption spectroscopy

## 6.1 Introduction

Layering a metal on top of a semiconductor has been a common strategy used to decrease surface degradation, enhance photoactivity, and increase charge separation for devices that use light-generated electrons or holes to perform work (i.e. solar cells, photocatalyst, and photoelectrochemical cells) [57-59]. Defect engineering of the semiconductor and nanostructuring of either or both the metal and semiconductor layers has been successfully shown to further improve device efficiency [60-62]. While device optimization has been possible, the underlying mechanisms responsible for the measured increase in device function remain obscure, primarily because initial charge injection from the metal to the semiconductor occurs quickly, within tens of femtoseconds, and it is often difficult to disentangle dynamics between layers.

Attosecond, extreme ultraviolet light (XUV) transient absorption spectroscopy provides both the necessary time resolution and elemental selectivity to give insight into the earliest dynamics that occur within a heterostructure. The XUV light used in transient XUV absorption can clearly distinguish between dynamics within different layers of a heterostructure, given that the materials used for each individual junction layers are comprised of different elements. This technique has also been shown to be sensitive to oxidation state, which allows for the possibility of resolving contributions from defect states.

In this chapter, titanium dioxide coated with platinum is studied as a model metal decorated semiconductor junction system. The effect of optical excitation and the following electron dynamics are discussed. Then, attosecond transient XUV absorption is used to detect the timescale of electron injection from the Pt into the TiO<sub>2</sub> layer and the role of Ti<sup>3+</sup> defect states in charge transport is considered. The electron diffusivity in Pt and injection efficiency for the junction are also calculated.

## 6.2 Band Alignment After Junction Formation

The electronic character of a heterostructure is not equal to the summation of the electronic properties for each individual layer. Combining materials into layered structures allows for tuning of desirable characteristics, suppression of unwanted properties and stabilization of previously less favorable states. Although the electronic character of a junction is more complex than the individual layers, it can still be predicted with simple equations that describe charge carrier minimization (i.e. that electrons will be more stable at lower energies and holes will be more stable at higher energies in the system). In this section I focus on describing Pt/TiO<sub>2</sub>, however the basic principles can be easily extended to other junction systems.

When two materials come into contact with one another, holes and electrons are exchanged across the interface until their Fermi levels equilibrate. This ultimately results in a new position of the Fermi level for the junction, which leads to the build up of an electric

field and band bending at the interface. Poisson's equation can be used to describe how charges distribute in space to minimize their energy.

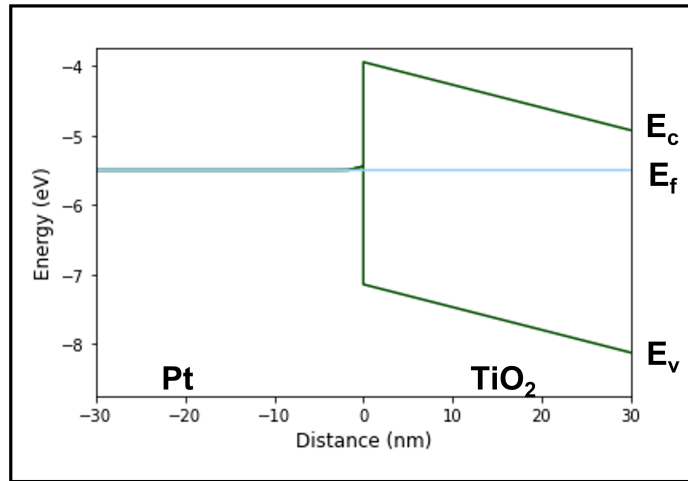
$$\frac{\partial^2 \phi}{\partial x^2} = -\frac{\rho}{\epsilon} = -\frac{q}{\epsilon_s}(p - n + N_d^+ - N_a^-) \quad (6.1)$$

Here,  $\phi$  is the electric field resulting from the charge distribution  $\rho$ , and  $\epsilon$  is the permittivity of the environment around the charges. In the context of heterostructures  $\epsilon$  is the dielectric constant of the material ( $\epsilon_s$ ) and the charge distribution is equal to the elementary charge unit ( $q$ ), multiplied by the summation of the density of holes ( $p$ ), electrons ( $n$ ), charge donors ( $N_d^+$ ), and charge acceptors ( $N_a^-$ ). By making the depletion approximation, which assumes that the electric field is confined to the interfacial, depletion region, Poisson's equation now has a closed form solution and results in the following useful equations describing the depletion region length ( $x_d$ ), built-in potential ( $\phi_i$ ), and amount of band bending ( $E_b$ ) relative to the conduction band minimum ( $E_c$ ).

$$x_d = \sqrt{\frac{2\epsilon_s \phi_i}{qN_d^+}} \quad (6.2)$$

$$E_b = q\phi_i + E_c \quad (6.3)$$

Here, AFOSR-HET, which is a free software that solves Poisson's equations (eq. 6.1) to model heterostructures, was used to model the band alignment of a Pt/TiO<sub>2</sub> junction, where both layers are 30 nm thick and the TiO<sub>2</sub> has excess electrons (i.e. n-doping) from oxygen vacancies, as was described in the *thermal evaporation of metals and metal oxides* section of chapter 4 (Fig. 6.1) [63]. The Fermi level position is 5.5 eV, the depletion region length is  $1 \times 10^{-4}$ cm, and the amount of band bending for the TiO<sub>2</sub> is 1.5 eV.

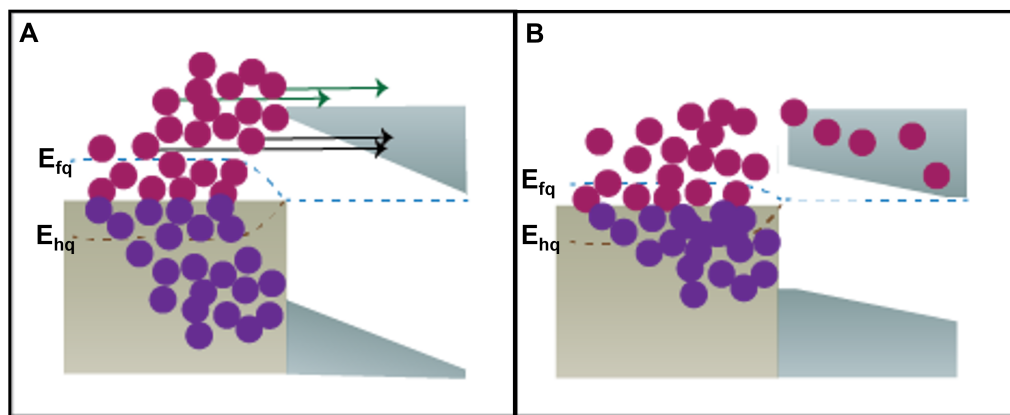


**Fig. 6.1** The band alignment diagram Pt/TiO<sub>2</sub>, as modeled with AFORS-HET, shows the Fermi level ( $E_f$ ) is at 5.5 eV, the depletion region is  $1 \times 10^{-4}$ cm in length, and the TiO<sub>2</sub> valence ( $E_v$ ) and conduction ( $E_c$ ) bands bend by 1.5 eV.

### 6.3 Interlayer Charge Transfer After Optical Excitation

Now that the band alignment at equilibrium has been discussed the effect of optical excitation of Pt/TiO<sub>2</sub> can be understood. The energy of the optical pump, which spans from 1.3 - 2.5 eV, is less than the 3.2 eV band gap of TiO<sub>2</sub>. Therefore, the optical pump will be able to excite electrons in only the Pt layer. The excited electrons in Pt will then have several pathways available for relaxation within the first hundred femtoseconds.

Upon laser excitation, highly excited electrons in the Pt layer can either thermalize within the Pt layer or transfer into the TiO<sub>2</sub> layer. The analysis presented in this chapter will focus on electron transport from the Pt layer into the TiO<sub>2</sub> layer as the early time dynamics of Pt alone were discussed in detail in chapter 5. There are two conditions that restrict which electrons can transfer from the Pt electron source layer to the TiO<sub>2</sub> electron drain layer. First, an electron must spatially move from the source to the drain layer. This spatial requirement dictates the temporal response of carrier injection, as it will take longer for electrons generated farther from the interface to transfer into the drain layer in comparison with those generated near the interface. Second, an electron must have enough energy to transfer into the conduction band of the drain layer. This means that the energy of an electron at the interface must be large enough to either directly transfer (Fig. 6.2A green arrow) or tunnel (Fig. 6.2A black arrow) into the conduction band of the drain layer.



**Fig. 6.2** The optical pump excites electrons (red circles) in Pt, leaving holes (purple circles) around the Fermi level (A). Some of the excited electrons in Pt arrive in the TiO<sub>2</sub> layer by either direct transfer (green arrow) or by tunneling (black arrow). After electrons transfer over the electric field in the depletion region decreases and subsequently the band bending of the TiO<sub>2</sub> also decreases (B). Additionally, the quasi electron (blue dashed line) and hole (brown dashed line) move closer to the original Fermi level position as electrons transfer into the TiO<sub>2</sub> and holes thermalize to form a hot Fermi-Dirac distribution in the Pt.

From this it is natural to see that the temporal component of the transient absorption signal can be broken down into two regimes, ballistic transport, where no scattering events take place before an electron reaches the drain layer, and diffusive transport, where the electron experiences at least one scattering event before reaching the drain layer. Battiatto *et. al* successfully modeled inter-layer electron transport as a function of time and space

[64]. Briefly, they broke down electron transport into two steps. First, the velocity of excited electrons is distributed evenly over all solid angles and their trajectories are assumed to follow a straight line. In other words, no directional preference is assumed for the electrons and the electrons will infinitely travel in the same direction. In this first step, electrons that travel from their originating point into the drain layer are considered to have ballistically transferred into the drain layer. In the second step, electrons scatter either elastically, which results in no energy loss and a randomized momentum, or inelastically, which results in energy loss and the momentum after the collision is correlated to the momentum of both particles before collision. Scattered electrons that have a high enough energy to transfer into the conduction band of the drain layer after spatially making it to the interface account for electrons that transfer by diffusion. Importantly, the ballistic transport described in the first step is limited to times before the scattering time of an electron which eliminates the unrealistic outcome of electrons traveling at the original excitation energy for infinite time.

The final result of this model shows that the population of electrons in the drain material should follow a bi-exponential trend, where the faster, first rise is due to ballistic transport and the slower second rise comes diffusion based transport. While the approximations made in this model, namely neglecting the correlation or particle momentum before and after inelastic collisions and internal electric fields from the electron distribution serve to underestimate the total number of electrons that can transfer into the drain layer, the temporal form adequately describes a number of transient experiments exploring electron transport [64-67]. From this, it is expected that the transient absorption signal in the  $\text{TiO}_2$  layer will follow a bi-exponentially increase, where the first component arises from ballistic transport and the second component corresponds to electron diffusion.

## 6.4 Attosecond Transient Absorption Measurements in $\text{Pt}/\text{TiO}_2$

To understand which dynamics are related to the junction and which are from the single layers, Pt on 30 nm silicon nitride,  $\text{TiO}_2$  on 30 nm silicon nitride, and  $\text{Pt}/\text{TiO}_2$  on 30 nm silicon nitride were deposited by home built thermal evaporation ovens. A brief summary of the growth conditions will be given here, but more detail can be found in chapter 4. To grow the  $\text{TiO}_2$ , oxygen was leaked into a vacuum chamber to establish an oxygen pressure of  $5 \times 10^{-5}$  Torr. Once the oxygen pressure was established, a titanium wire was heated to 1135 - 1180 °C, which results in a Ti vapor pressure of  $\sim 5 \times 10^{-7}$  Torr. Then silicon nitride membranes were placed in front of the oven. After the desired thickness of  $\text{TiO}_2$  was achieved, some  $\text{TiO}_2$  samples were reserved for transient absorption experiments ( $\text{TiO}_2$  alone). Pt was then deposited on blank silicon nitride, to make the Pt alone samples, and on the remaining  $\text{TiO}_2$  samples, to create the  $\text{Pt}/\text{TiO}_2$  heterostructure samples. The Pt deposition was accomplished by keeping a Pt wire between 1330 - 1348 °C, which corresponds to a Pt vapor pressure of  $2 \times 10^{-7}$  Torr. Growing the Pt alone and  $\text{TiO}_2$  alone alongside the  $\text{Pt}/\text{TiO}_2$  samples ensures that the growth conditions and thicknesses were the same between the single materials and the junction samples. From the static absorption the thickness of the Pt and  $\text{TiO}_2$  layers was found to be 28.5 nm and 30.5 nm, respectively.

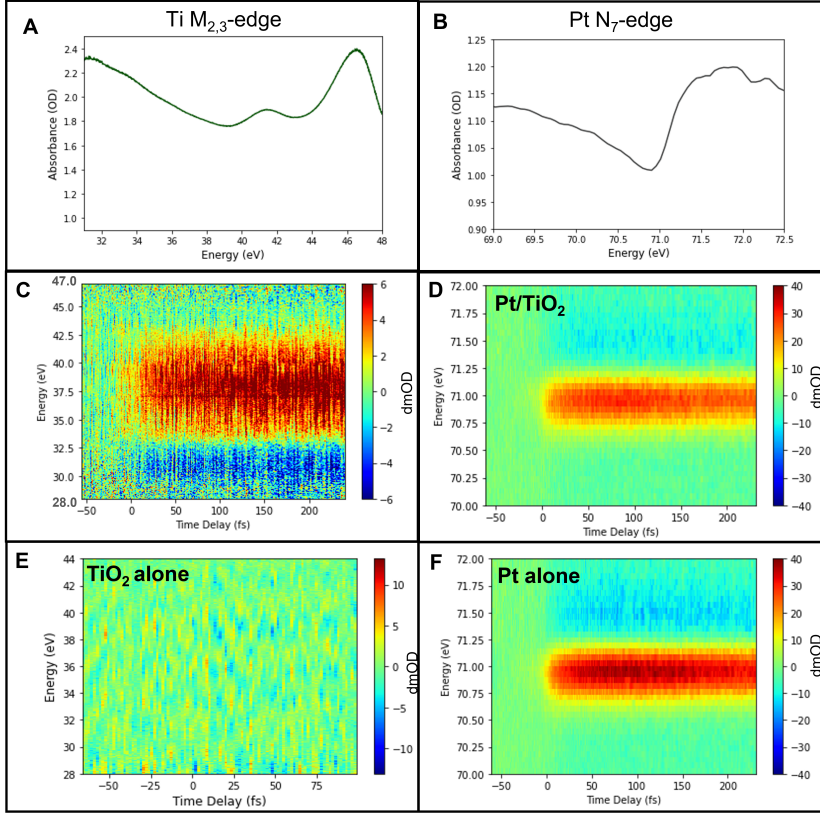
The transient absorption measurements were obtained using the experimental apparatus outlined in the chapter 2. Extreme ultraviolet (XUV) light generated in Ar gas, which

extends past the Al filter energy (73 eV) was used in measurements taken at the Pt N<sub>7</sub>-edge. For the Ti M<sub>2,3</sub>-edge measurements, XUV light generated in Kr gas, which does not extend to the Pt N<sub>7</sub>-edge, was used in order to eliminate the second order diffraction of XUV radiation at the Pt-edge from obscuring the dynamics at the Ti M<sub>2,3</sub>-edge. To ensure fluctuations in pump intensity and temporal overlap were the same between the transient absorption spectrum at the Pt N<sub>7</sub>-edge for the Pt alone and Pt/TiO<sub>2</sub> samples a dual sample scanning procedure was used. In this scanning method, first time zero is determined by scanning Ne, then XUV spectra with the optical pump present and absent are collected for the Pt alone sample for all specified time delay positions. Immediately after the Pt alone is measured, XUV spectra with the optical pump absent and present for all specified time delay positions are collected for the Pt/TiO<sub>2</sub> sample. This process is repeated and the measured transient absorption for each sample and is averaged at each time delay point to reduce noise. The optical pump spectrum energy ranges from 475 nm - 925 nm and a power of  $22.6 \frac{mJ}{cm^2}$  was used to pump the Pt alone and Pt/TiO<sub>2</sub> films whereas a higher power,  $30.3 \frac{mJ}{cm^2}$  was used to pump the TiO<sub>2</sub> alone film, to ensure it was transparent to the optical pump. Additionally, the instrument response function, as determined using transient Ne scans discussed in chapter 2, was found to be 5.9 fs for the Pt N<sub>7</sub>-edge measurements and 8.8 fs for the Ti M<sub>2,3</sub>-edge measurements. Static absorption at the Ti M<sub>2,3</sub>-edge shows a main peak at 46.5 eV, which corresponds to absorption from the Ti 3*p*-orbitals to the Ti<sup>4+</sup> conduction band states (Fig. 6.3A) [27,68]. The smaller peak located at 41.4 eV corresponds to transitions between the Ti 3*p*-orbitals and the T<sup>3+</sup> defect states, which are positioned  $\sim 1$  eV below the conduction band minimum [69-72]. The static absorption at the Pt N<sub>7</sub>-edge arises from transitions between the Pt 4*f*<sub>7/2</sub> to empty states just above the Fermi level (figure 6.3B). The Pt N<sub>7</sub>-edge is centered at 71 eV and the Fano profile comes from coupling between the 4*f*5*d*<sup>*n*+1</sup> states and a continuum of 5*d* and 5*p* photoemission states via Coster Kronig transitions [16]. The full static and transient absorption for the Pt/TiO<sub>2</sub> film as well as a description of all filtering that was applied to the transient absorption spectra can be found in the appendix section of this chapter.

The transient absorption spectra at the Ti M<sub>2,3</sub>-edge of the Pt/TiO<sub>2</sub> film and the TiO<sub>2</sub> alone are shown, respectively, in panels C and E of figure 6.3, while the transient absorption spectra at the Pt N<sub>7</sub>-edge for the Pt/TiO<sub>2</sub> and the Pt alone are shown, respectively, in panels D and F of figure 6.3. All the same filtering and data processing was applied for all scans. A more detailed description of the methods used here can be found in the appendix of this chapter. It is immediately noticeable that there is no transient signal observed in the TiO<sub>2</sub> sample alone (Fig. 6.3E). This confirms that all signal observed at the Ti M<sub>2,3</sub>-edge in the Pt/TiO<sub>2</sub> samples arises from carriers transferring from the Pt into the TiO<sub>2</sub>. Additionally, it can be seen that the total amount of signal at the Pt N<sub>7</sub>-edge is lower for the junction sample in comparison with the Pt film alone, which is also indicative of charge transfer from the Pt layer to the TiO<sub>2</sub> layer in the junction sample.

The direction that the Ti M<sub>2,3</sub>-edge moves after optical excitation can be used to determine if electrons or holes are arriving in the TiO<sub>2</sub>. It has been observed in previous transient absorption measurements that a shift toward lower (higher) energy of the Ti M<sub>2,3</sub>-edge is consistent with the presence of electrons (holes) [27]. Putting these observations together it is clear that electrons are transferring from the Pt into the TiO<sub>2</sub> after optical excitation. This is also consistent with what is expected from the band energy diagram of the Pt/TiO<sub>2</sub>



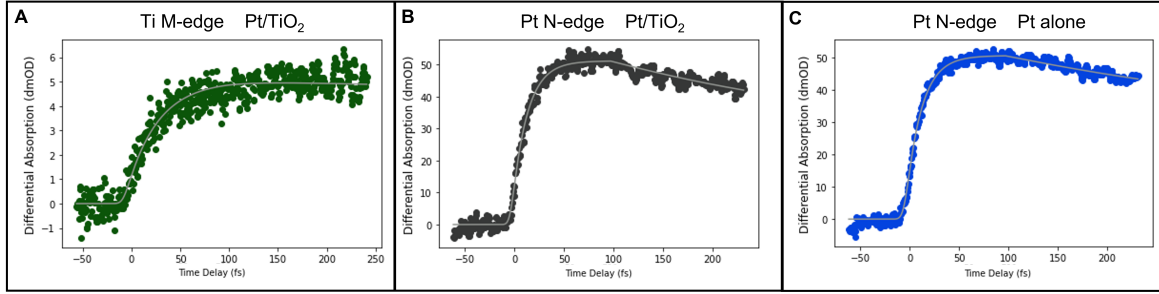


**Fig. 6.3** Static absorption for the Pt/TiO<sub>2</sub> sample at the Ti M<sub>2,3</sub>-edge (A) and Pt N<sub>7</sub>-edge (B) was taken with Ar and Kr harmonics, respectively. The transient absorption spectrum shows a clear signal at the Ti M<sub>2,3</sub>-edge (C) and the Pt N<sub>7</sub>-edge (D). Whereas there is no signal observed at the Ti M<sub>2,3</sub>-edge for TiO<sub>2</sub> alone (E) and there is more signal observed at the Pt N<sub>7</sub>-edge in the Pt alone (F).

system, as discussed in section *Interlayer charge transfer after optical excitation* (Fig. 6.2). Lastly, transient absorption signal at the Ti M<sub>2,3</sub>-edge occurs from 28 eV - 42 eV, which corresponds to a shifting of the smaller, Ti<sup>3+</sup> absorption peak to lower energies. There is no transient absorption signal observed from 43 eV - 47 eV at the main Ti<sup>4+</sup> absorption peak, which suggests that electrons are transferring into the Ti<sup>3+</sup> defect states rather than into the conduction band minimum of the TiO<sub>2</sub>.

## 6.5 Inter-layer Electron Transfer Time

In order to determine the timescale of the dynamics observed in the transient absorption spectra, the signal was integrated from 34 eV - 43 eV to capture the positive feature near the Ti M<sub>2,3</sub>-edge (Fig. 6.4A) and from 70.8 eV - 71.3 eV to capture the positive feature near the Pt N<sub>7</sub>-edge (Fig. 6.4B). The temporal evolution follows the bi-exponential increase at the Ti M<sub>2,3</sub>-edge anticipated from the theoretical modeling of interlayer transport from Battiatto *et. al*, which was summarized in section *Interlayer charge transfer after optical*



**Fig. 6.4** The positive transient absorption features near the Ti  $M_{2,3}$ -edge for the Pt/TiO<sub>2</sub> sample (A), the Pt  $N_7$ -edge for the Pt/TiO<sub>2</sub> sample (B) the Pt  $N_7$ -edge for the Pt alone sample were fit, as outlined in the text, to obtain the timescale for ballistic transfer and electron diffusion into TiO<sub>2</sub> as well as the electron thermalization and cooling time in Pt.

*excitation* [64]. The Ti  $M_{2,3}$ -edge signal was fit with a bi-exponential increase, convoluted with a Gaussian of width 8.8 fs to account for the optical pump. From this, the timescales for ballistic electrons and diffusing electrons was found to be  $24.0 \pm 17.1$  fs and  $1680 \pm 708$  fs, respectively. To determine the timescale of electron thermalization and electron cooling in the Pt and Pt/TiO<sub>2</sub> samples, the signal at the Pt  $N_7$ -edge was fit with an exponential increase followed by an exponential decrease and was also convoluted with a Gaussian pulse (width 5.6 fs) to account for the optical pump. The electron thermalization time was found to be  $14.9 \pm 2.4$  fs and  $15.6 \pm 4.8$  fs for the Pt alone and Pt/TiO<sub>2</sub> films, respectively and the electron cooling time was found to be  $796 \pm 26.3$  fs and  $741 \pm 26.5$  fs for the Pt alone and Pt/TiO<sub>2</sub> samples, respectively. These timescales are summarized in table 6.1.

| initial to final state          | Pt-edge Pt (fs) | Pt-edge Pt/TiO <sub>2</sub> (fs) | Ti-edge Pt/TiO <sub>2</sub> (fs) |
|---------------------------------|-----------------|----------------------------------|----------------------------------|
| Pt elec. Therm.                 | 14.9 (2.4)      | 15.6 (4.8)                       |                                  |
| Ballistic transfer              |                 |                                  | 24.0 (17.1)                      |
| Pt electron cooling             | 796 (26.3)      | 741 (26.5)                       |                                  |
| Diffusion into TiO <sub>2</sub> |                 |                                  | 1680 (708)                       |

**Table 6.1.** Timescales from exponential fits to the Pt  $N_7$ -edge for the Pt alone (first column) and the Pt/TiO<sub>2</sub> film (second column). The timescale for the bi-exponential fit at the Ti  $M_{2,3}$ -edge for the Pt/TiO<sub>2</sub> sample is listed in the third column.

Comparing the electron thermalization and electron cooling timescales between the Pt alone and Pt/TiO<sub>2</sub> films gives insight into the effect that electron transfer between the junction layers has on the Pt layer in the junction. The electron thermalization time, while very similar between the two samples, appears to be slightly longer in the Pt/TiO<sub>2</sub> film than in the Pt alone. As was detailed in chapter 5, electron thermalization takes place through electron-electron interactions. For the junction sample, a portion of the optically excited electrons is immediately transferred into the TiO<sub>2</sub> layer. Therefore, for the same optical excitation power density, there are fewer electrons left in the Pt/TiO<sub>2</sub> sample to be involved in thermalization, which thereby slows the electron thermalization time in the Pt/TiO<sub>2</sub> sample in comparison with the Pt film alone.

The electron cooling time measured in Pt is consistent with electron cooling times for various metals, which are typically from 600 - 1000 fs [13, 73-75]. Here, the electron cooling time might be slightly lower for the Pt layer of the junction than the Pt layer alone. This result can be understood through the mechanism of electron cooling, which is dependent on the equilibration of the temperatures between the electrons and the lattice, and is accomplished through electron-phonon interactions. The electron-phonon coupling is intrinsic to the material, making it the same for the Pt alone and the Pt layer in the Pt/TiO<sub>2</sub> heterostructure. Therefore, the electron cooling time should be the same or slightly lower in the Pt/TiO<sub>2</sub> junction, as there are fewer electrons to thermalize in the Pt layer of the junction sample in comparison with the Pt alone film.

Looking at the ballistic and diffusion timescale for electron transfer into the TiO<sub>2</sub> layer gives insight into the aspects of the junction that contribute to the injection time and efficiency of the charge transfer. The diffusion timescale depends on the diffusivity of the electrons in the Pt layer, as this marks the time it takes electrons to diffuse through the Pt layer to make it into the TiO<sub>2</sub> layer. Here, a timescale of 1680 fs corresponds to an electron diffusivity in Pt of  $5.35 \frac{\text{cm}^2}{\text{s}}$ , which is consistent with drift diffusion values of 8-10  $\frac{\text{cm}^2}{\text{s}}$  reported for similar metals [76]. The ballistic electron injection time is much longer than the electron thermalization timescale of Pt. This suggests that the timescale of the initial electron transfer is not dependent on the properties of the metal, but rather on properties of the junction itself, such as the strength of the electric field in the depletion region or the energetic alignment of the available states in the TiO<sub>2</sub> electron accepting layer with the optically excited electrons in the Pt electron source layer. Additionally, most of the electrons are transferred ballistically. The significance of the majority of electrons being ballistically transferred, which depends on junction properties, into Ti<sup>3+</sup> defect states, is that overall efficiency of electron transfer primarily depends on properties of the junction, rather than properties of the individual materials.

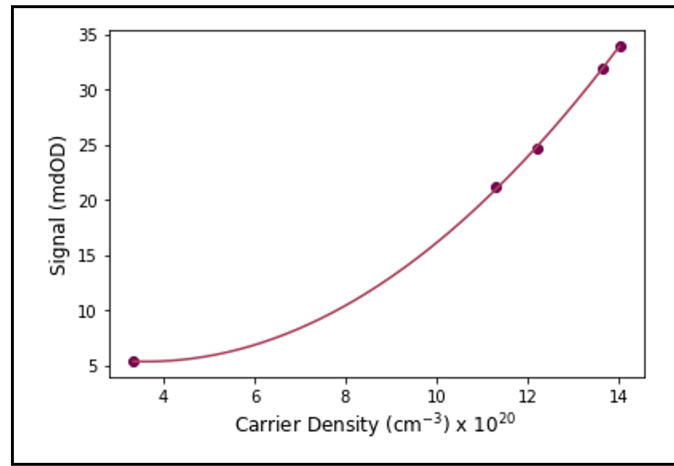
This conclusion leads to two possible strategies for improving efficiency of the charge transfer. The first route is to create more Ti<sup>3+</sup> defect states, which would open more available states for excited electrons in Pt to transfer into. Another route to increasing electron injection efficiency would be pairing the TiO<sub>2</sub> layer with a metal that has a higher Fermi level than Pt. This would increase the overlap between excited electrons and the defect states.

## 6.6 Efficiency of Electron Injection from Pt into TiO<sub>2</sub>

In order to calculate the electron injection efficiency the number of electrons generated in the Pt layer and the number of electrons transferred into the TiO<sub>2</sub> layer must be known. The initial number of electrons generated in the Pt layer by the laser can be calculated by multiplying the fraction of light absorbed in the Pt layer by the number of photons per unit volume. Specifically, for the energy density of the optical pump used here ( $22.6 \frac{\text{mJ}}{\text{cm}^3}$ ),  $14.0 \times 10^{20}$  electrons per cm<sup>3</sup> are excited in Pt.

Determining the number of electrons injected into the TiO<sub>2</sub> layer is less straight forward, but can be found through correlating the magnitude of the transient absorption signal observed at the Pt N<sub>7</sub>-edge to the number of electrons present in the Pt layer. For the same

pump fluence (i.e. same number of electrons excited in Pt alone film), there is a larger transient absorption signal observed in the Pt alone film compared to the Pt layer of the Pt/TiO<sub>2</sub> sample. The difference in observed signal between the two samples can be accounted for by the electron transfer from Pt layer to TiO<sub>2</sub> layer in the junction. This shows that the number of electrons injected into the TiO<sub>2</sub> layer is equal to the difference between the number of electrons generated in the Pt alone film and the number of electrons present in the Pt layer of the Pt/TiO<sub>2</sub> heterostructure. The number of electrons present in the Pt layer of the Pt/TiO<sub>2</sub> heterostructure after charge transfer has occurred can be determined by correlating the signal observed at the Pt N<sub>7</sub>-edge and the number of electrons present in Pt. This relationship between the number of electrons generated in the Pt layer and the observed transient absorption signal at the Pt N<sub>7</sub>-edge was found by measuring the transient absorption of the Pt alone film at various pump fluences (i.e. various number of electrons generated in Pt) (Fig. 6.5). Using this relationship, the number of carriers present in the Pt layer of the Pt/TiO<sub>2</sub> junction was calculated to be  $12.3 \times 10^{20}$  electrons per cm<sup>3</sup>.



**Fig. 6.5** The number of electrons excited in Pt was correlated to the amount signal observed at the Pt N<sub>7</sub>-edge through power dependent measurements performed on the Pt alone film.

The number of electrons injected into the TiO<sub>2</sub> layer is equal to the difference between the number of electrons generated in Pt and the number of electrons present in Pt after charge transfer has occurred. Namely, the number of electrons injected into the TiO<sub>2</sub> is equal to the  $12.3 \times 10^{20}$  electrons per cm<sup>3</sup> present in the Pt layer after charge transfer subtracted from the  $14.0 \times 10^{20}$  electrons per cm<sup>3</sup> initially generated in the Pt layer. Therefore,  $1.75 \times 10^{20}$  electrons per cm<sup>3</sup> were injected into TiO<sub>2</sub>. This corresponds to an electron injection efficiency of  $14 \pm 7.4\%$ . The error was found by propagating the estimated one standard deviation confidence interval from the covariance in the optimization of the polynomial fit to the carrier density and the observed transient absorption signal. To put this in to context for the electron injection efficiency of other materials, metal nanoparticles on TiO<sub>2</sub> have shown an efficiency of 15 -20%, silicon based solar cells typically range from 20-30%, and dye sensitized solar cells show a maximum efficiency around 12% [60, 72, 77].

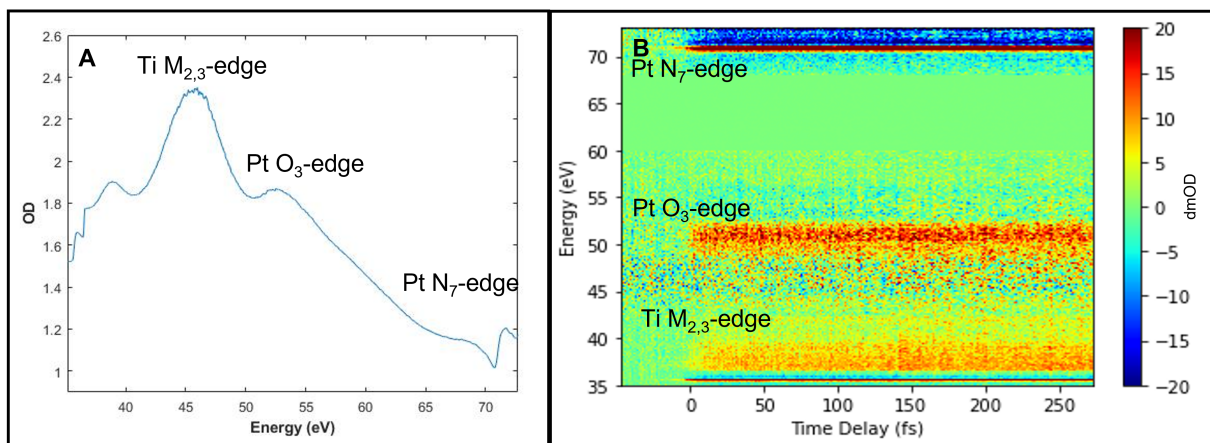
## 6.7 Conclusion

In conclusion, the unique elemental sensitivity and attosecond timescale of transient XUV absorption spectroscopy was leveraged to gain several key insights into the nature of charge transfer in a Pt/TiO<sub>2</sub> junction. First, the elemental sensitivity provided by transient XUV absorption spectroscopy allowed for direct observation that the Ti<sup>3+</sup> defect state is primarily participate in the electron transfer within the junction. Second, the short time resolution was crucial in disentangling whether the fastest dynamics are a property of the single materials or the junction as a whole. Lastly, it was directly observed that the majority of electrons are injected ballistically, which suggests that optimizing factors that enhance ballistic electron transfer will have the largest effect on improving overall electron device efficiency.

The insight that electrons are predominantly ballistically transferred into Ti<sup>3+</sup> states suggests several strategies for improving the electron injection efficiency of the charge transfer. The first route is to create more Ti<sup>3+</sup> defect states, which would result in more available states for electrons to transfer into. Another route to increasing electron injection efficiency would be pairing the TiO<sub>2</sub> layer with a metal that has a higher Fermi level than Pt. This would increase the overlap between excited electrons and the defect states.

## 6.8 Appendix

### Full static and transient of Pt/TiO<sub>2</sub>



**Fig. 6.6** The static absorption of Pt/TiO<sub>2</sub> sample taken with Ar harmonics shows the Ti M<sub>2,3</sub>-edge, Pt O<sub>3</sub>-edge, and Pt N<sub>7</sub>-edge(A). The transient absorption spectrum for the full junction shows the optical response for both layers simultaneously, but the Pt N<sub>7</sub>-edge overlaps with the transient response at the Ti M<sub>2,3</sub>-edge (B).

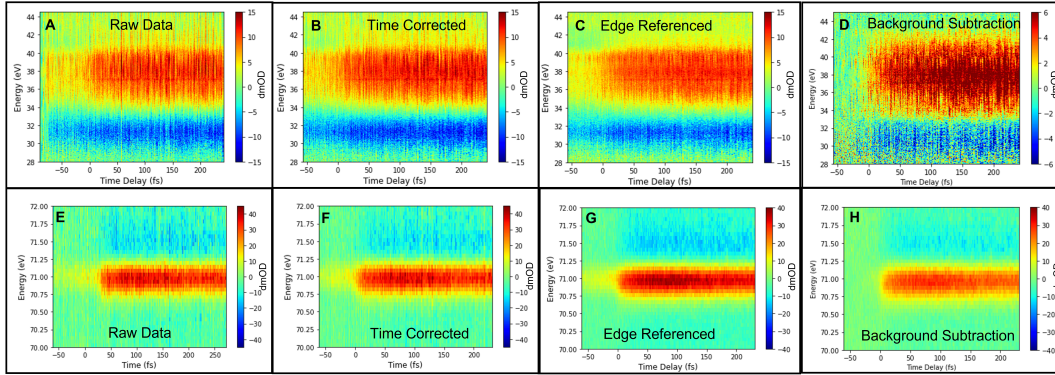
The full static and transient absorption taken with XUV light generated in argon gas, shows the Ti M<sub>2,3</sub>-edge, Pt O<sub>3</sub>-edge, and the Pt N<sub>7</sub>-edge (Fig. 6.6A). It can be seen here that the second order diffraction of the Pt N<sub>7</sub>-edge overlaps with the Ti M<sub>2,3</sub>-edge (Fig. 6.6B). For this reason, XUV light generated in Kr gas was used to measured the response to optical excitation at the Ti M<sub>2,3</sub>-edge in the text above. Edge referencing, where the edge



reference region was taken to be 60 eV - 68 eV, was used to reduce the noise from harmonic fluctuations between the collection of pump on and pump off camera spectra. Additionally, the temporal evolution at the Pt O<sub>3</sub>-edge was not discussed here as it overlaps with the high energy tail of the Ti M<sub>2,3</sub>-edge and the Pt response is readily more clearly resolved Pt N<sub>7</sub>-edge.

### Filtering applied to transient absorption spectra

Figure 6.7 shows how the raw transient absorption, panels A and E, is processed. As was

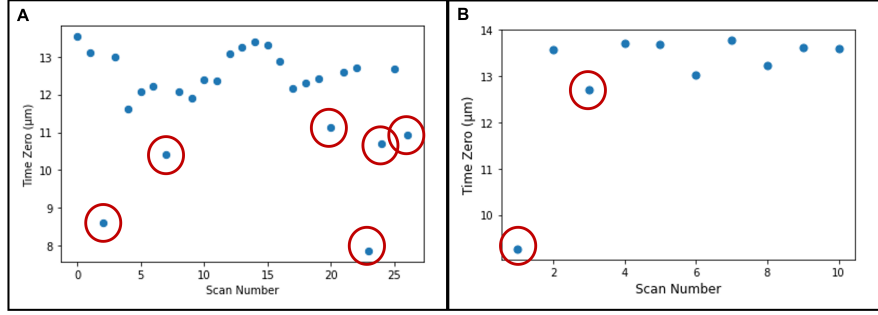


**Fig. 6.7** The transient absorption spectrum after each step of filtering and data processing is shown, where the top row is the Ti M<sub>2,3</sub>-edge and the bottom row is the Pt N<sub>7</sub>-edge. First, the raw data, which is comprised of many averages for each time point is shown (A,E). The data is then corrected for temporal drift (B,F) as explained in the text. Next harmonic fluctuations are filtered out using edge referencing (C,G). Finally, the signal before time zero is subtracted (D,H).

described in chapter 2, a tr-XAS measurement of Ne is taken before scanning a full iteration of delay points to experimentally account for drifts in the temporal overlap. Figure 6.8 shows the time zero plotted for each successive sample scan for the Ti M<sub>2,3</sub>-edge measurement in panel A and for the Pt N<sub>7</sub>-edge measurement taken by dual scanning the Pt alone and Pt/TiO<sub>2</sub> sample in panel B. Scans for which the temporal overlap significantly drifted, which are circled in red in figure 6.8, were excluded. The time points for each scan were aligned using the time zero measured before that scan was taken (Fig. 6.7 B, F). Edge referencing, which has been shown to accurately account for intensity fluctuations between pump on and pump-off camera images which lead to noise in tr-XAS experiments, was also applied [26]. The energy range used for the edge pixels was 47.5 eV – 45 eV for the Ti M<sub>2,3</sub>-edge (Fig. 6.7C) and 60 eV - 68 eV for Pt N<sub>7</sub>-edge (Fig. 6.7H). Finally, the constant heat background, which arises from laser heating of the films and persists on the millisecond timescale, is subtracted. Both in these experiments and the Ti work done by *Volkov et. al.* the transient signal after subtraction was the same as transient absorption measurements where the background heating was experimentally eliminated by chopping and/or spinning the sample [12].

### Transient temporal fitting functions

In *Interlayer charge transfer after optical excitation* it was shown that a bi-exponential increase corresponding to ballistic and diffusion electron transfer was the anticipated response



**Fig. 6.8** The position of temporal overlap on the delay stage is calculated for each iteration through the time delay points to account for temporal drift in the experiment. This is further detailed in the chapter 2. Panel A shows the calculated position of temporal overlap for the Ti M<sub>2,3</sub>-edge results and panel B shows the same values for the Pt N<sub>7</sub>-edge results.

of the Ti M<sub>2,3</sub>-edge. In chapter 5 it was shown that the Pt N<sub>7</sub>-edge displays an exponential increase corresponding to electron thermalization via electron-electron scattering followed by a decrease corresponding to electron cooling. For the TiO<sub>2</sub> layer, it was shown that the electron transfer into this layer is well described as a bi-exponential increase, where the first rate corresponds to ballistic electron injection and the second rate corresponds to transfer of electrons that have diffused through the Pt layer. To make these exponential fit equations compatible with the transient absorption measurements, the fit functions were convoluted with a Gaussian function to account for the pump pulse, where the width of the Gaussian was set by the instrument response measured before each scan (5.9 fs for Pt N<sub>7</sub>-edge measurements and 8.8 fs for the Ti M<sub>2,3</sub>-edge measurements). The fit functions were also multiplied by a Heaviside function to satisfy the initial condition that the electron population of the excited states is zero before optical excitation. The final form of the fit functions shown in figure 6.4 and described here is.

$$TiM_{2,3} - edge = A \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}(\frac{t-t_0}{\sigma})^2} \otimes \left[ 1 - e^{-(t-t_0)k_{ball}} - e^{-(t-t_{start})k_{diff}} \right] \mathcal{H}(t - t_0) \quad (6.4)$$

$$PtN_7 - edge = A \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}(\frac{t-t_0}{\sigma})^2} \otimes \left[ e^{(t-t_0)k_{th}} + (1 - e^{-(t-t_{start})k_{cool}}) \right] \mathcal{H}(t - t_0) \quad (6.5)$$

In both equation 6.4 and 6.5,  $A$  controls the amplitude of the function,  $\sigma$  is the width of the Gaussian,  $t_0$  is when the pump and probe beams are overlapped in time and controls the central position of the Gaussian, the location the Heaviside function  $\mathcal{H}(t - t_0)$  switches from a value of zero to one, and the offset of the first dynamic component. The start of the second dynamic component is controlled by  $t_{start}$  and the rate of decay for each exponential component is set by  $k_{ball}$ ,  $k_{diff}$ ,  $k_{th}$ , and  $k_{cool}$  for the rate of ballistic transfer, diffusion transfer, electron thermalization, and electron cooling, respectively. A non-linear least squares minimization algorithm was used to find the values of  $A$ ,  $t_{start}$ , and the rates present at each edge  $k_{ball}$  and  $k_{diff}$  for the Ti M<sub>2,3</sub>-edge and  $k_{cool}$  and  $k_{th}$  for the Pt N<sub>7</sub>-edge.

### Calculating the number of electrons excited in Pt by the optical pump

Assuming that each photon absorbed by Pt excites only one electron, the number of electrons

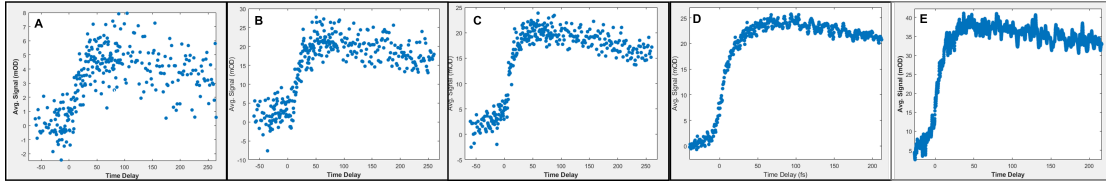
( $N_e$ ) generated in Pt is equal to the number of photons in the pump scaled by how many photons are absorbed by the Pt film [78, 79].

$$N_e = \frac{F}{Ed}(1 - R)(1 - e^{-\alpha d})(1 + Re^{-\alpha d}) \quad (6.6)$$

Here,  $F$  is the pump fluence,  $E$  is the energy of the photons,  $d$  is the thickness of the Pt layer,  $R$  is the reflectivity, and  $\alpha$  is the absorption coefficient. For the scans presented in figure 6.3,  $F = 2.6 \frac{mJ}{cm^2}$ ,  $E = \frac{hc}{760nm}$ ,  $R = 0.947$ , and  $\alpha = 8.31 \times 10^5 \text{ cm}^{-1}$ , which gives  $N_e = 14.0 \times 10^{20}$  electrons per  $cm^3$ .

### Power dependent measurements in Pt

Power dependent measurements in Pt were used to correlate the amount of signal measured at the Pt  $N_7$ -edge with the number of electrons in Pt. This relationship was ultimately used to calculate the number of electrons 'missing' in the Pt layer of the Pt/TiO<sub>2</sub> sample and therefore the number of electrons injected into the TiO<sub>2</sub> layer of the junction. Figure 6.9 shows the integrated signal from 70.8 eV to 71.3 eV for Pt alone pumped with  $5.34 \frac{mJ}{cm^2}$  (Fig. 6.9A),  $18.3 \frac{mJ}{cm^2}$  (Fig. 6.9B),  $19.7 \frac{mJ}{cm^2}$  (Fig. 6.9C),  $22.1 \frac{mJ}{cm^2}$  (Fig. 6.9D), and  $22.6 \frac{mJ}{cm^2}$  (Fig. 6.9E). The amount of signal at the edge was taken to be the average of the maximum of the rise. The electron cooling portion (i.e. the exponential decrease) of the spectra was avoided in order to get an accurate correlation between the amount of signal observed and the number of excited electrons.



**Fig. 6.9** The Pt  $N_7$ -edge shows more signal for increasing pump power.  $5.34 \frac{mJ}{cm^2}$ ,  $18.3 \frac{mJ}{cm^2}$ ,  $19.7 \frac{mJ}{cm^2}$ ,  $22.1 \frac{mJ}{cm^2}$ , and  $22.6 \frac{mJ}{cm^2}$  are shown in panels A-E, respectively.



| Flunce (mJ cm <sup>-3</sup> ) | Number of electrons x<br>10 <sup>20</sup> cm <sup>-3</sup> | N <sub>7</sub> -edge signal<br>(mOD) |
|-------------------------------|------------------------------------------------------------|--------------------------------------|
| 5.3                           | 3.34                                                       | 5.34                                 |
| 18.3                          | 11.3                                                       | 21.2                                 |
| 19.7                          | 12.2                                                       | 24.7                                 |
| 22.1                          | 13.7                                                       | 31.9                                 |
| 22.6                          | 14.0                                                       | 34.0                                 |

**Table 6.2.** The carrier density of excited electrons in Pt is calculated and the signal at the Pt N<sub>7</sub>-edge is displayed for the different fluences measured.

### Electron Injection Efficiency

The electron injection efficiency (*Eff*) is equal to the number of electrons transferred into the TiO<sub>2</sub> ( $N_{e,TiO_2}$ ) divided by the number of electrons excited by the laser in the Pt layer ( $N_{e,ex}$ ). The number of electrons excited by the laser was calculated in the appendix section of this chapter. This makes the only unknown quantity the number of electrons transferred into TiO<sub>2</sub>. The number of electrons that have transferred can be seen as the increase of signal at the Ti-M<sub>2,3</sub>edge or the reduction of signal at the Pt N<sub>7</sub>-edge in comparison with the signal observed in the Pt alone film.

$$Eff = \frac{N_{e,TiO_2}}{N_{e,ex}} * 100 \quad (6.7)$$

The amount of signal at the Pt N<sub>7</sub>-edge was related to the number of electrons at the Pt N<sub>7</sub>-edge by fitting the signal observed in Pt at different number of excited electrons (i.e. powers). This relationship was fit with a second degree polynomial. In the above section it was shown that the 22.6  $\frac{mJ}{cm^2}$  pump initially excited 14.0 x 10<sup>20</sup> electrons per cm<sup>3</sup>. The signal observed after initial electron injection on the Pt N<sub>7</sub>-edge in the Pt layer of the Pt/TiO<sub>2</sub> junction sample was 25.2 mOD. From the polynomial fit relating signal at the Pt N<sub>7</sub>-edge to the number of electrons in Pt (Fig. 6.5), the measured 25.2 mOD signal corresponds to 12.3 x 10<sup>20</sup> electrons per cm<sup>3</sup> in the Pt layer. The number of electrons injected into the TiO<sub>2</sub> layer is equal to the difference between the number of electrons before and after carrier injection. Namely, the number of electrons injected into the TiO<sub>2</sub> layer is 14.0 x 10<sup>20</sup> electrons per cm<sup>3</sup> - 12.3 x 10<sup>20</sup> electrons per cm<sup>3</sup>, which is 1.75 x 10<sup>20</sup> electrons per cm<sup>3</sup>. This gives an electron injection efficiency of 14 ± 7.4%. The error was found by propagating the estimated one standard deviation confidence interval from the covariance in the optimization of the polynomial fit to the carrier density and the observed transient absorption signal.

## Chapter 7. Ultrafast time-resolved extreme ultraviolet (XUV) photoelectron spectroscopy of hole transfer in a Zn/n-GaP Schottky junction<sup>79</sup>

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### 7.1 Introduction

Gallium phosphide has received significant attention for applications in photocatalysis, optics, and electronics [81]. For photocatalytic applications the efficiency of charge separation and corrosion resistance can be increased through the addition of a metal overlayer [82]. In these metal-GaP heterostructures, the metal layer serves to form a Schottky barrier, which discourages charge recombination, and adds additional protection from surface contaminants. The efficiency of charge separation in metal-GaP systems has been further improved with nanostructuring either layer, or alloying and defect engineering of the GaP semiconductor [83-85]. Although this has yet to be applied to a metal-GaP system, bi-layer excitation is another route of improving device efficiency that is commonly pursued [84, 87].

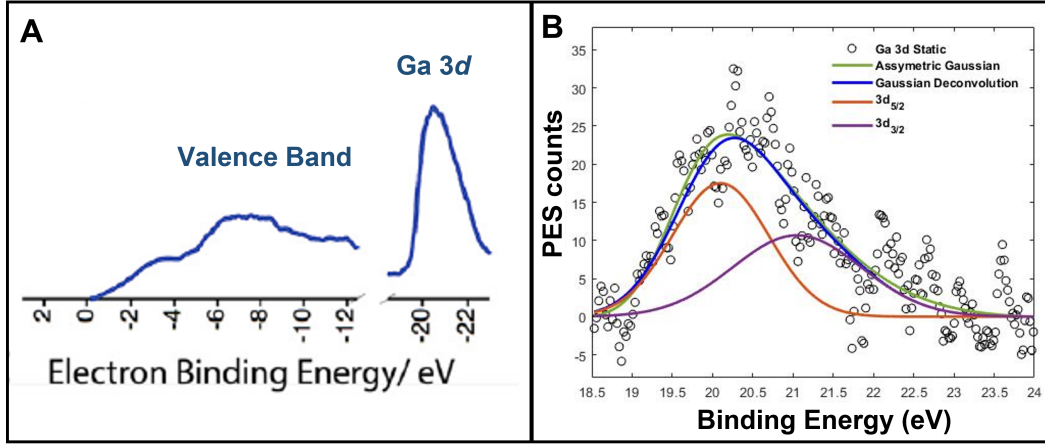
In the following chapter, the band alignment and Schottky barrier height of Zn/n-GaP will be determined using photoemission measurements. Then transient XUV photoemission spectroscopy will be used to gain insight into the picosecond dynamics following bi-layer excitation of the heterostructure.

### 7.2 Photoemission and Energy Band Alignment of n-GaP

A Schottky barrier serves to separate electrons and holes between layers and discourage back transfer of charges across a metal-semiconductor heterostructure. Photoemission spectroscopy can be used to directly measure the valence band maximum (VBM) position, relative to the Fermi level, of a material. These values, along with known constants, such as the band gap, can be used to calculate the conduction band minimum (CBM) of any sample and the Schottky barrier height (SBH) in heterostructure samples. In the end this provides a full energetic profile of the material being studied.

The photoemission spectrum of n-GaP shows broad features in the valence band (VB) region (0-12 eV Binding Energy) and a sharp feature at a binding energy (BE) of 20.6 eV (Fig. 7.1A). DFT calculations of the partial density of states for the VB indicate the feature at  $\sim 3$  eV comes from P  $3p$  and Ga  $4p$  orbitals, and the feature at  $\sim 8$  eV comes from a contribution of all the outer shell orbitals of Ga and P, namely the P  $3s$ ,  $3p$ , and  $3d$  and the Ga  $4s$  and  $4p$ , and  $4d$  orbitals [88].

The feature at 20.6 eV BE (Fig. 7.1B) comes from the summation of the spin-orbit-split Ga  $3d_{\frac{3}{2}}$  and Ga  $3d_{\frac{5}{2}}$  states [89]. The observed asymmetric Gaussian profile of the Ga  $3d$  state shown here is directly related to the energy splitting and degeneracy of the respective spin-orbit-split states. The alignment of the spin and angular momentum vectors for the  $3d$  orbitals gives the relative positioning of these states. The  $3d_{\frac{5}{2}}$  has an anti-parallel



**Fig. 7.1** The static photoemission of the clean n-GaP wafer shows characteristic valence band features and the Ga 3d core level peak (A). The Ga 3d core level can be decomposed into the spin-orbit split  $3d_{5/2}$  and  $3d_{3/2}$  states (B).

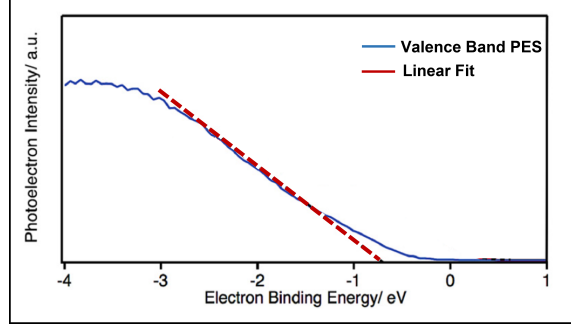
alignment of the angular momentum and spin quantum vector of the orbital. This anti-parallel alignment is more energetically favorable than the parallel alignment of the  $3d_{3/2}$ , which results in the  $3d_{5/2}$  appearing at a lower BE than the  $3d_{3/2}$  (Fig. 7.1B).

The degeneracy of the splitting gives the number of states contributing to that energy level, which in the context of PES shows the area intensity ratio of the two peaks. The degeneracy of the states is equal to  $2J + 1$ , where  $J$  is the total angular momentum quantum number. For the  $3d_{5/2}$  the angular quantum number is 2 and the spin quantum number is  $+\frac{1}{2}$ . This gives  $J = 2.5$  and a degeneracy of 6 for the  $3d_{5/2}$ . For the  $3d_{3/2}$  the angular quantum number is 2 and the spin quantum number is  $-\frac{1}{2}$ . This means the  $3d_{3/2}$  has  $J = 1.5$  and a degeneracy of 4. From this the expected weighting of the  $3d_{3/2}$  to  $3d_{5/2}$  states is 4:6 (reduced to 2:3). Putting this all together, the Ga 3d PES peak is composed of two Gaussian where the lower energy Gaussian corresponds to the  $3d_{5/2}$  and has a larger area than the higher energy  $3d_{3/2}$  Gaussian, which explains the asymmetric Gaussian profile of the Ga 3d state presented in figure 7.1B.

It should be noted that although the energy resolution of the PES time-of-flight photoelectron detector is not sufficient to resolve these two states, this will not effect the interpretation as both the Ga  $3d_{3/2}$  and Ga  $3d_{5/2}$  report on the local environment of the Gallium atom in the GaP and should provide the same response to Zn deposition explored here and charge transfer explored in the transient photoemission section.

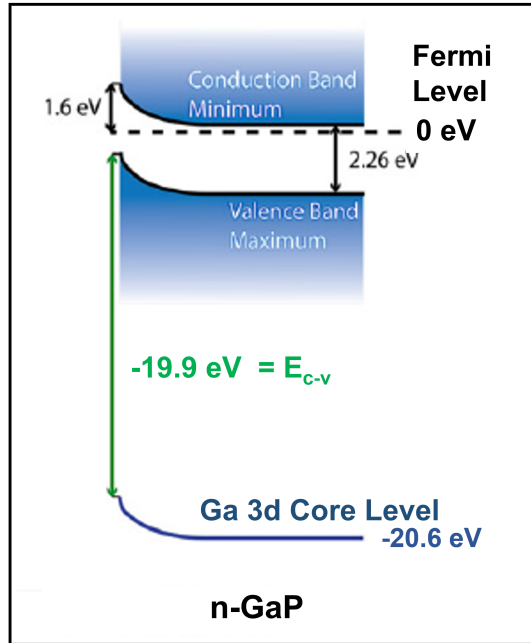
The position of the VBM can be determined from these measurements. The VBM is equal to the x-intercept from a linear fitting of the VB onset. The linear fitting shown in figure 7.2 gives a VBM of -0.70 eV, where the Fermi level is at 0 eV BE. The position of the CBM relative to the Fermi level is equal to the difference between the absolute value of VBM and the band gap ( $E_{BGd}$ ) of the material, which is a constant parameter of the material.

$$CBM = E_{BG} - |VBM| \quad (7.1)$$



**Fig. 7.2** By fitting a linear function to the valence band photoemission of GaP the valence band maximum was found to be at 0.70 eV below the Fermi level.

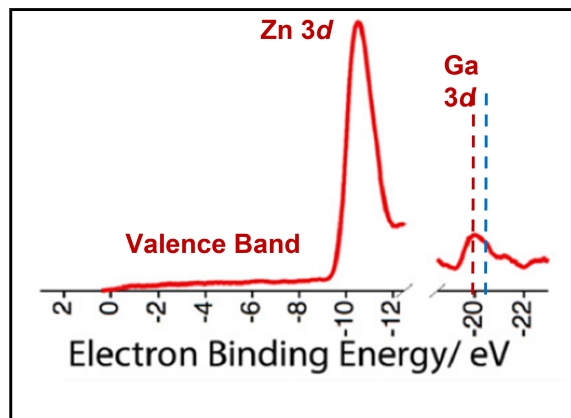
For GaP the band gap is known to be 2.26 eV, this puts the CBM 1.56 eV above the Fermi level. The difference between the Ga 3d core level position and the VBM is a constant value throughout the material and will be used in the next section to calculate the SBH. The difference between the Ga 3d core level and VBM is  $-20.6 \text{ eV} - (-0.70 \text{ eV})$ , making  $(E_{C-V})$  -19.9 eV. These values can be used to construct the Energy diagram shown in figure 7.3.



**Fig. 7.3** A diagram of the relative positioning of the conduction band maximum, valence band minimum, Fermi level, and Ga 3d core level is constructed from the PES measurements of a cleaned, n-GaP(100) wafer.

### 7.3 Schottky Barrier Characterization of Zn/n-GaP

When a metal is deposited on a semiconductor electrons flow between the materials to establish a new equilibrium position of the Fermi level. This creates a depletion region between the two materials. As a result of the electric field in the depletion region, the bands of the semiconductor bend at the interface. This process was further detailed in chapter 6 where the band alignment of the Pt/TiO<sub>2</sub> system was calculated. One of the strengths of PES in comparison with the absorption measurements presented in earlier chapters is the ability to directly characterize the energy alignment of the material under investigation.



**Fig. 7.4** The photoelectron spectrum of 10 monolayers of Zn deposited onto a clean, n-GaP(100) wafer shows the characteristic Zn 3d peak and a shift in the position of Ga 3d peak in comparison to the clean GaP is observed.

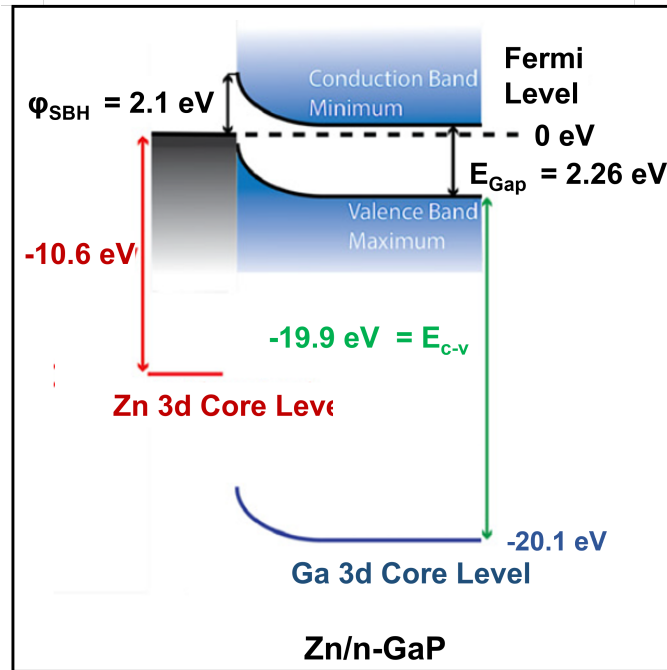
The PES spectrum for 10 ML of Zn deposited onto n-GaP is shown in figure 7.4. The deposition process was detailed in chapter 4, and a brief summary will be presented again here. Surface contaminants were removed from a 100 n-GaP single crystal (MTI Corporation) with an Ar ion sputtering gun. Once the wafer was clean, Zn was deposited using a home-built thermal evaporation oven. The rate of evaporation was found to be 0.714 monolayers (ML) per minute using Auger electron spectroscopy. The photoemission spectrum shown in figure 7.4 was taken after 14.25 min. of deposition, meaning there are 10 ML of Zn on top of the n-GaP wafer.

There are several clear changes to the photoemission spectrum after the addition of Zn. First, the Zn 3d appears at -10.6 eV BE. There is also a reduction in the intensity of the Ga 3d feature. This is directly related to the surface sensitivity of PES. As the GaP wafer is now covered with 10 ML of Zn only interfacial region of GaP is being measured. In addition to the Ga 3d peak intensity being reduced, the feature also shifts from its original -20.6 eV BE position (Fig. 7.4 blue line) in the wafer alone to -20.1 eV BE in the junction system (Fig. 7.4 red line). After Zn deposition the signal to noise ratio of the Ga 3d is too low to deconvolute the feature with Gaussian functions for the Ga 3d<sub>5/2</sub> and 3d<sub>3/2</sub>. For the remainder of the analysis an asymmetric Gaussian, which was shown in the previous section to capture the overall profile of the feature (Fig. 7.1B), will be used.

The shift in the Ga 3d core level can be used to calculate the band bending and SBH of the system. For a metal deposited on an n-type semiconductor the SBH ( $\phi_{SBH}$ ) is found by subtracting the band gap ( $E_{gap}$ ) from the core level shift in the presence of the metal (i.e. the amount of band bending induced by metal deposition) [90]. The shift in binding energy from the core level is equal to the  $E_{C-V}$  value determined in the previous section subtracted from the measured core level BE after Zn deposition ( $E_{CL}$ ).

$$\phi_{SBH} = E_{gap} - |(E_{CL} - E_{C-V})| \quad (7.2)$$

Gallium phosphide has a band gap of 2.26 eV,  $E_{CL}$  was measured to be -20.1 eV and  $E_{C-V}$  was measured to be -19.9 eV. Using these values the SBH is determined to be 2.1 eV. The calculated values are used to make the energy band diagram presented in figure 7.5.



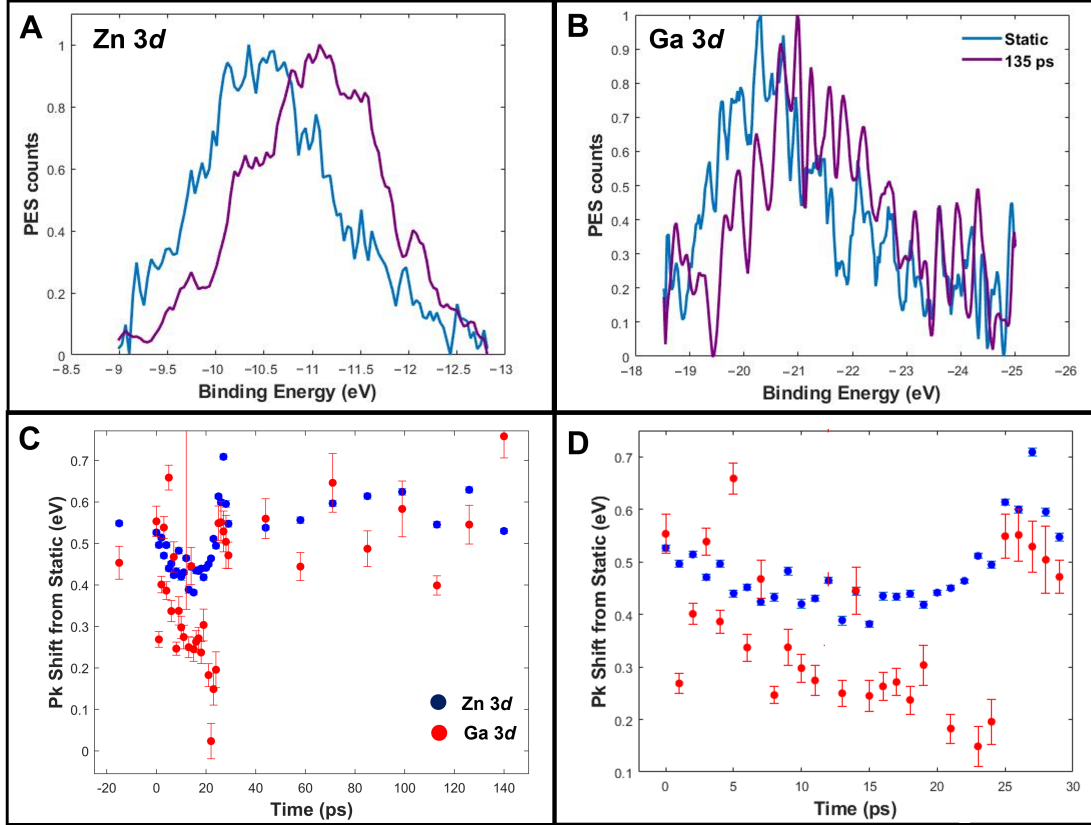
**Fig. 7.5** The photoemission measurements of clean n-GaP and Zn/n-GaP were used to construct an energy level diagram.

## 7.4 Transient Photoemission Measurements of Zn/n-GaP

Now that the energy alignment of the junction has been fully characterized the effect of pump excitation on the system can be understood. In this study  $2.5 \frac{mJ}{cm^2}$ , 400 nm (3.1 eV) pump was used in order to study the relaxation dynamics from bi-layer excitation in the Zn/n-GaP heterostructure.

The transient photoemission measurements were taken with the experimental apparatus outlined in chapter 3. Briefly, odd harmonics are generated in Ar gas with an 800 nm driving laser. The 27<sup>th</sup> harmonic was selected with an XUV monochromator, and then used

as the incident light for the PES probe, where an electron time-of-flight detector collects the ejected photoelectrons. The pump is converted from 800 nm to 400 nm with a BBO and  $2.5 \frac{mJ}{cm^2}$  illuminates the sample. The relative timing between the pump and probe is varied by adjusting the path length of the pump arm. Lastly, the temporal duration of the instrument is limited to 0.67 ps by a tilted pulse front that occurs from the grating used in the XUV monochromator.



**Fig. 7.6** Photoemission spectra without the pump and 135 ps after pump excitation are shown for the Zn 3d, in panel A, and the Ga 3d, in panel B. These features were fit as described in the text and the peak center, relative to the static, is plotted as a function of time. In panel C the full time delay points are shown and in panel D, the same transient is shown focusing on the trend from -5 - 30 ps.

To get an overall picture of the observed PES response to photo excitation, the photoemission spectrum of the Zn 3d and Ga 3d core levels is shown in figure 7.6A, B for the static (i.e. no optical pump present) and 135 ps after optical excitation. Both the Zn and Ga 3d shift to higher binding energy after optical excitation. By fitting the Zn peak with a Gaussian and the Ga peak with an asymmetric Gaussian, the changes in the photoemission peak positions as a function of pump probe time delay can be monitored. In panels C and D of figure 7.6 the peak shift, that is the difference between the peak position at a specific time delay versus the un-pumped PES spectrum, over time for Ga and Zn is shown.

Immediately from observing the temporal dependence it is clear that the peak shift is

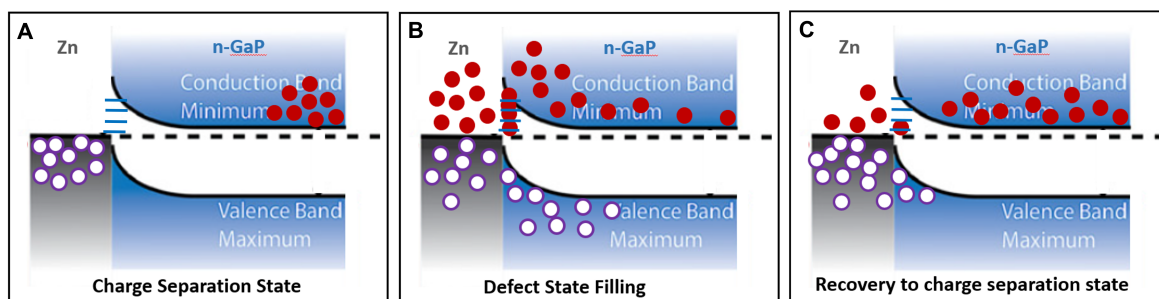
the same for both elements at negative time delays, which corresponds to the XUV probe arriving before the optical pump, and for time delays after  $\sim 30$  ps. The direction of the peak shift, to higher BE, indicates the presence of holes within the probing depth of both layers. The magnitude of the peak shift being the same before temporal overlap suggests that the junction does not return to equilibrium before consecutive laser pulses. This reveals that the electron-hole separation across the junction is established  $\sim 30$  ps after optical excitation and persists for longer than the 1 ms time between laser pulses. Similar, long-lived charge separation states have been shown to persist from the millisecond to second time frame in other junction materials [91-93].

The temporal trend for the peak position of the Zn and Ga  $3d$  is very similar. Although all of the transient PES spectra taken have a positive peak shift relative to the static XUV spectrum, from 0 - 12 ps the PES peaks shift to lower binding energy relative to the long-lived charge separation state present after  $\sim 30$  ps and at negative time delays. The shift to lower BE can be thought of in two ways; either there is less positive charge at the surface of the heterostructure or there is an accumulation of negative charge at the surface. Considering the first case, less positive charge implies that optical excitation causes holes to migrate away from the surface of the heterostructure. This is unlikely, as the band alignment shows that holes are more energetically stable in the Zn over-layer than the n-GaP (Fig. 7.5), and the long lived charge separation state corresponding to hole migration toward the surface of the junction. The second, more likely case, that there is an accumulation of negative charge would suggest that there are more electrons than holes aggregating in the surface layers during this time. Additionally, the Ga  $3d$  appears to shift to lower BE than the Zn  $3d$  from 0 - 12 ps. Considering the difference in magnitude along with the peaks shifting to lower BE, it is possible during this time that electrons are accumulating in defect states, which are known to form at the surface of the n-GaP, usually located just below the Fermi level [94-96]. As the Zn film is very thin, the Zn layer is still influenced by the defect states being filled with electrons, however because these states are in the GaP layer it would influence the Ga  $3d$  more. Additionally, electron trapping in defect states has been observed to occur within the same timescale in perovskites, which are also prone to similar deep level defect states [97]. In summary, it is most likely that the shift to lower BE during the period of 0 - 12 ps comes from optically excited electrons filling defect surface states in the n-GaP.

In the next portion of the transient, from 12 - 30 ps, the photoemission spectra shifts to higher BE, until it fully recovers back to the long lived charge separation state. There are three possible explanations for this. In the first scenario, the same number of electrons are occupying the defect states, while more holes continue to accumulate on the surface causing the observed shift to higher BE in the transient. This is unlikely, as it would require that electrons fill the defect states for longer than a millisecond to align with the long-lived charge separation state. In the second case, electrons could be leaving the trap states, while there is not change in the hole occupation at the surface. This would also result in the observed shift to higher BE. Again, this is unlikely, as there is no direct reason that can be ascribed for why the hole occupation at the junction surface would remain static. The third option combines the first two suggested scenarios. In this case, electrons are leaving defect states and holes continue to accumulate at the surface. This case seems the most likely, as it includes hole migration, which is consistent with the observed long-lived charge separation, and does not required electrons to remain in defect states on the millisecond timescale.



The last feature to highlight is the peak in the positive shift of the Zn peak around 27 ps. Although the data is noisy here, it could strengthen the description of the dynamics from 12 - 30 ps involving hole migration to the surface. It is possible that this peak in BE shift for the Zn 3*d* arises from more holes being injected into the Zn layer than can exist in the long-lived charge separation state. Consequently, a small portion of holes back transfers into the GaP to combine with available electrons until the quasi-stable long-lived charge separation state is fully established.



**Fig. 7.7** A schematic of the suggested dynamics is presented here. The long-lived charge separation state occurs when electrons accumulate on at the back of the n-GaP wafer and holes collect at the surface Zn layer (A). Right after pump excitation it is suggested that defect states at the surface of n-GaP are slowly filled with electrons, while holes begin to accumulate in the Zn layer (B). Finally, the electrons leave the defect states and holes continue to arrive at the surface of the junction, while electrons continue moving to the back (C).

Although the noise of this data and the lack of data taken on a Zn alone and n-GaP alone sample severely limits the confidence of the interpretation presented here, never the less some key insights can be suggested from this study. First, it is clear the junction starts in a long-lived charge separated state, where holes have accumulated at the front and electrons at the back, outside of the PES probing window, of the heterostructure (Fig. 7.7A). After optical excitation, it is likely that the dynamics are dominated by electrons being trapped in the defect states at the n-GaP surface. Lastly, there is a recover back to the long-lived charge separation state (Fig. 7.7B). This final recovery most probably corresponds to electrons leaving the defect states and continued hole accumulation at the surface until the quasi-equilibrium, long-lived charge separation state is established again (Fig. 7.7C).

## 7.5 Conclusion

During the first portion of this study, photoemission measurements of clean n-GaP and Zn/n-GaP were used to determine the band alignment of the junction. Through these measurements it was found that Zn/n-GaP has a 2.1 eV Schottky barrier. In the second portion of this study, the temporal response of the PES heterostructure profile to 400 nm (3.1 eV) illumination was observed. Although the signal to noise ratio, particularly at the weaker Ga 3*d* PES feature, greatly limits the strength of the conclusions made, some insight into

the junction response to bi-layer excitation can still be suggested. There is a general shift to higher BE of both the Zn and Ga  $3d$  after  $\sim 30$  ps and at negative time delays (where the XUV arrives before the optical pump). This is interpreted as a long-lived charge separation state, where holes accumulate at the surface and electrons at the back of the n-GaP wafer. The following shift to binding energies lower than the charge separation state is most likely from electron accumulation in defect states at the n-GaP surface. Finally, it is likely that electrons migrate out of the defect states while holes continue to accumulate at the front of the sample until the long-lived charge separation state is re-established.

This work could be greatly strengthened by several adjustments. First, by depositing less Zn on the surface of the n-GaP, a clearer difference between the layers might be observed and the signal of the Ga  $3d$  would be increased. Measuring the photoemission response of Zn alone, and n-GaP would give clearer insight into which aspects of the transient photoemission measurements presented here can be attributed to single layer dynamics and which can be attributed to junction dynamics. Finally, measuring the same sample with a complimentary technique that probe the electronic structure deeper within the sample, like transient XUV absorption or reflectivity spectroscopy, could give more insight into the long-lived charge separation state that is suggested by this study. Overall, some interesting insights are gained by this study, but it could be greatly strengthened by additional results from the same or complementary techniques.

## 7.6 Appendix

**Gaussian Fitting Zn  $3d$  peak** The secondary electron background was fit with a linear function around the core level peak (Fig. 7.8A). Then, a Gaussian function, as defined in equation 7.3, was used to fit the Zn  $3d$  (Fig. 7.8B).

$$G = Ae^{-\frac{(x-C)^2}{2w^2}} \quad (7.3)$$

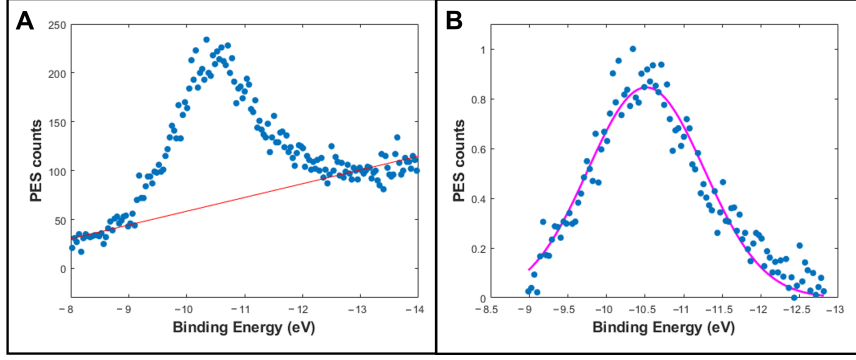
The Gaussian profile ( $G$ ) is has an amplitude  $A$ , a center position  $C$  and a width  $W$ . For the photoemission peaks, the width change of the peak often indicates space charging, which was not evidenced in this study. The peak shift  $C$  is associated with the change in local chemical environment from charge transport and the amplitude is set by the amount of material.

**Gaussian Fitting Ga  $3d$  peak** After a linear subtraction was applied to remove the secondary electron background, the Ga  $3d$  was fit with an asymmetric Gaussian profile. This was done to account for the  $3d_{5/2}$  and  $3d_{3/2}$  states that contribute to the overall shape of the Ga  $3d$  feature. After the deposition of Zn the Ga feature was too weak to be deconvoluted into the contributing components, so an asymmetric Gaussian profile was used to track the peak center shift.

The asymmetric Gaussian function is shown in equation 7.4.

$$G_{skew} = AG(x)\Phi(\alpha x) \quad (7.4)$$

where  $A$  scales the amplitude of the function,  $G(x)$  is a Gaussian function with the form



**Fig. 7.8** A linear fit background subtraction (red line) was performed to remove the secondary electron signal from the Zn 3*d* region (A). Then a Gaussian profile (red line) was fit to determine the position of the peak (B).

above, and  $\Phi(\alpha x)$  accounts for the skew and is defined in equation 7.5.

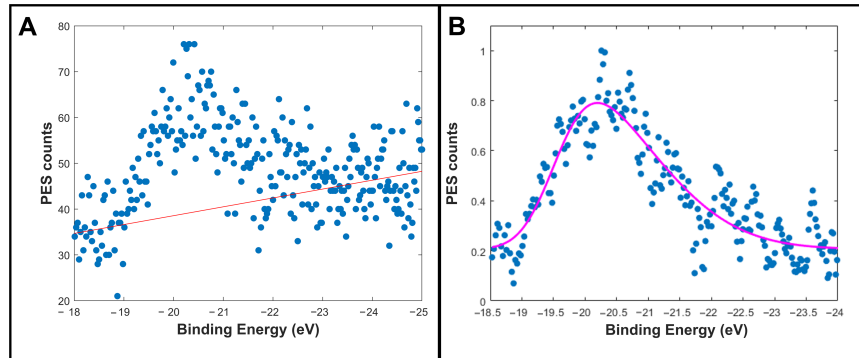
$$\Phi(\alpha x) = \frac{1}{2} \left[ 1 + \operatorname{erfc} \left( \alpha \frac{(x - C)}{W \sqrt{(2)}} \right) \right] \quad (7.5)$$

Here,  $C$  is still the center of the Gaussian component,  $W$  is the width of the Gaussian component and  $\alpha$  is the skew factor. The center of the skewed Gaussian ( $C_{skew}$ ) is defined in equation 7.6.

$$C_{skew} = C + W \delta \sqrt{\frac{2}{\pi}} \quad (7.6)$$

$$\delta = \frac{\alpha}{1 + \alpha^2} \quad (7.7)$$

An application of this fitting can be seen in figure 7.9B.



**Fig. 7.9** A linear fit background subtraction (red line) was performed to remove the secondary electron signal from the Ga 3*d* region (A). Then an asymmetric Gaussian profile (red line) was fit to determine the position of the peak (B).

## Chapter 8. Conclusion

Throughout the course of this thesis, transient XUV absorption and transient XUV photoemission spectroscopy were used to study solid state materials. The capabilities and strengths of these techniques are apparent by contrasting the information gained from each set of experiments.

In the study of metals, the attosecond time resolution of the XUV transient absorption apparatus gives the unique ability to observe the very fastest dynamics that occur within a metal. While it is often assumed that metals respond instantaneously to laser excitation, the excellent time resolution of the apparatus used here, allowed for the observation of a correlation between the structure in the density of states above the Fermi level and the initial electron thermalization time after optical excitation. Namely, that a greater variety of available orbitals above the Fermi level leads to a slower thermalization time.

In the transient absorption study of Pt/TiO<sub>2</sub> the ballistic and diffusion based charge transfer from Pt to TiO<sub>2</sub> was monitored and the charge injection efficiency of the junction was calculated. It was also found that electrons transfer predominantly into Ti<sup>3+</sup> defect states. The insight that electrons are predominantly ballistically transferred into Ti<sup>3+</sup> states suggests several strategies for improving the electron injection efficiency of the charge transfer. The first route is to create more Ti<sup>3+</sup> defect states, which would result in more available states for electrons to transfer into. Another route to increasing electron injection efficiency would be pairing the TiO<sub>2</sub> layer with a metal that has a higher Fermi level than Pt. This would increase the overlap between excited electrons and the defect states.

Finally, Zn/n-GaP was studied using transient XUV photoemission spectroscopy on the picosecond timescale. Through this study it was shown that a long-lived charge separation state persists for longer than a millisecond. Electron filling of n-GaP surface defect states at the Zn/GaP interface and hole accumulation at the surface are the most likely dynamics occurring within the first 12 ps after optical excitation. After this, electrons leave the defect states, while holes continue to accumulate at the surface from 12 - 30 ps, until the long-lived charge transfer state is re-established.

From these studies it is clear that the attosecond time resolution lends itself to the unique capability of studying the fastest, electron dynamics in materials. However, there are several limitations of this method. First, in transmission measurements, the sample thicknesses required are from 5 - 200 nm. Many materials cannot be fabricated for these thicknesses. Additionally, the thin samples are prone to heating, which can obscure dynamics, lead to sample ablation, or, in the more extreme cases, destroying the sample. Ambiguity in the absorption probe response, from many body effects in solids or core-hole screening, often requires theoretical collaboration to interpret.

On the other hand, the photoemission gives a very clear transient response, as it the photoemission probe is less subject to many body effects since the final state (i.e. the free photoelectron) is no longer in the material. It also allows the use of very thick samples, which are much easier to work with than the delicate thin sample. However, the surface sensitivity requires cleaving or cleaning the surface of the material being studied or the deposition of a fresh sample for every experiment. Additionally, the surface sensitivity of this technique allows for the unique insight into the first few nanometers of a material, an ability that few other techniques possess. However, this also means that a full picture of the material cannot

be gained from this technique.

Overall, both techniques have their strengths and weaknesses. In the end, to gain a complete understanding of material dynamics it would be desirable that both techniques be employed.

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