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Ultrafast pump-probe spectroscopy: instrumentation and application to the study of carrier dynamics in graphene

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Universidade do Minho

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Doctoral Degree in Physics
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IFIMUP

Instituto de Física de
Materiais Avançados,
Nanotecnologia e Fotónica
Universidade do Porto

“This process of discovery is science: the continual refinement and testing of our understanding, alongside the digging that reveals even more to be understood.”

Helen Czerski, ‘Storm in a Teacup: The Physics of Everyday Life’

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Resumo

Os processos elementares na física e na química, como o movimento de electrões ou vibrações moleculares, ocorrem em escalas de tempo extremamente curtas, que variam entre poucos picossegundos até attossegundos. Para medir estes eventos e acompanhá-los em tempo real, precisamos de utilizar um evento ainda mais curto. Antes do aparecimento dos impulsos ultracurtos, a medição de eventos no tempo estava limitada pela resolução temporal da electrónica. Os atuais métodos de espectroscopia resolvida no tempo, como a espectroscopia pump-probe, fazem uso de fontes laser ultrarrápidas para estudar fenómenos fundamentais numa escala de tempo sem precedentes. Na primeira parte desta dissertação foi construído um sistema óptico “pump-probe” degenerado. O sistema faz uso de um amplificador laser ultrarápido (Coherent Astrella) com um comprimento de onda central de 800 nm, e impulsos com duração de <35 fs a uma taxa de repetição de 1 kHz. Detalhes da sua construção e da sua implementação são descritos. O sistema tem uma resolução temporal de 60 fs e destina-se principalmente ao estudo da dinâmica de portadores de carga em nanomateriais. Na segunda parte deste trabalho, pretendemos estudar a influência do número de camadas de grafeno na dinâmica dos seus portadores de carga. Para isso usamos o sistema pump-probe para medir os tempos de decaimento dos portadores de carga em amostras de grafeno. Estas amostras foram sintetizadas por deposição química em fase vapor por plasma de microondas em cobre. Foram analisadas amostras de grafeno com aproximadamente 3, 5 e 6 camadas. Nos resultados obtidos as pequenas variações no número de camadas de grafeno não afetaram a dinâmica. Uma possível explicação é que a ordem de empilhamento das camadas esteja a influenciar este resultado. Através desta investigação, esperamos contribuir para uma compreensão mais profunda da dinâmica dos portadores no grafeno, que é essencial não só para a investigação teórica, mas também para aplicações relacionadas com o desenvolvimento de novos dispositivos optoelectrónicos.

Palavras-chave: espectroscopia resolvida no tempo, femtossegundo, grafeno, impulsos ultracurtos, ótica ultrarrápida

Abstract

The dynamics of fundamental physical and chemical processes take place on extremely short time scales, ranging from a few picoseconds to attoseconds. To follow these events in time, we need to use a shorter event. Before the rise of ultrashort laser pulses, the measurement of events in time was limited by the temporal resolution of the fastest electronics. Ultrafast time-resolved spectroscopy methods, such as pump-probe spectroscopy, make use of ultrafast laser sources to study fundamental phenomena on an unprecedented time scale. In the first part of this thesis, a degenerate ultrafast pump-probe optical setup was built. The setup works with an ultrafast laser amplifier (Coherent Astrella) with a central wavelength of 800 nm, delivering <35 fs pulses at a repetition rate of 1 kHz. Details on its design, construction and implementation are given. The system is primarily thought for the study of ultrafast carrier relaxation dynamics in nanomaterials and has a temporal resolution of about 60 fs. In the second part of this work, we aimed to get new insights into the influence of the number of layers on the carrier dynamics of few-layer graphene samples. We use the pump-probe system to measure the ultrafast relaxation times of photogenerated carriers in graphene samples synthesized by microwave plasma chemical vapour deposition. Few-layer graphene with approximately 3, 5, and 6 layers were investigated. Our results demonstrated that small variations in the number of graphene layers did not affect the dynamics. Through this research, we expect to experimentally contribute to a deeper understanding of carrier dynamics in graphene, which is essential not only for fundamental research but also for applications such as the development of novel and faster optoelectronic devices.

Keywords: femtosecond, graphene, pump-probe spectroscopy, time-resolved spectroscopy, ultrafast optics, ultrashort pulses

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List of abbreviations

ANOVA	Analysis of Variance
BS	Beam splitter
CEP	Carrier Envelope Phase
CVD	Chemical Vapour Deposition
DED	Double Exponential Decay
FWHM	Full Width at Half Maximum
GD	Group Delay
GDEDC	Gaussian and Double Exponential Decay Convolution
GDD	Group Delay Dispersion
GUI	Graphical User Interface
MEM	Maximum Entropy Method
MPCVD	Microwave Plasma Chemical Vapour Deposition
NIR	Near Infrared
SEM	Scanning Electron Microscopy
SNR	Signal to Noise Ratio
SHG	Second Harmonic Generation
TOD	Third-Order Dispersion
UV-NIR	Ultraviolet - Near Infrared

1. Introduction

Our perception of the temporal dynamics of nature relies on the temporal resolution of the instruments available to us. If more than a century ago, mechanical shutters increased our temporal perception rate to the millisecond range, today we can follow events fifteen orders of magnitude faster with ultrashort light pulses. Here, we introduce these ultrashort pulses highlighting what makes them so attractive for a wide range of applications. One of these applications includes ultrafast time-resolved spectroscopy, which is the driving topic of this thesis.



1.1. Overview

A human eye, with regular vision and unaided by any other tools, can see objects as small as about $100\text{ }\mu\text{m}$ (we can think about the thickness of a human hair for example) [1, 2]. However, our ability to spatially perceive nature is not limited to this scale. Tools such as magnifying lenses that are part of optical microscopes and telescopes, enhance our spatial resolution, enabling us to observe objects far smaller than the micrometer scale. Other advanced techniques such as high-resolution transmission electron microscopy provides a detailed view of nanostructures and can capture sub-angstrom ($< 10^{-10}\text{ m}$) resolution images, ‘photographing’ the atoms in a crystal lattice [3, 4].

There is a simple experiment called Newton’s disc [5] that can be easily done at home. It consists of a disc (wheel) with coloured sections - typically red, orange, yellow, green, blue, and violet, like coloured pizza slices - that can rotate at different speeds. When the disc is spun slowly, you can see the individual colours and detect their position at

1. Introduction

a given time. However, if you make it spin really fast, you will not be able to ‘resolve’ its motion in time. In other words, you will not be able to distinguish the individual colours (slices), instead you will perceive the colours blending into a whole ‘white/grey’ disc. This experiment is usually used to explain the persistence of vision. The wheel spins so fast that our eyes cannot resolve it in time, doing simply an average of all the frames, summing all and creating a ‘blend’ of the colours. Fortunately, as in the case of spatial resolution, our perception of nature is not limited to this temporal scale. The dynamics of fundamental physical and chemical processes, such as molecular vibrations and electronic transitions, take place within very short time scales – i.e., on the order of picoseconds or less. Nowadays, electronic devices such as high-speed cameras allow us to ‘freeze’ events up to tens of picoseconds. For sure, a high-speed camera would resolve the motion of our Newton’s disc, but not the motion of an electron in a crystal or a molecule. For that, one would need ultrafast lasers (that is to say ultrashort light pulses). We have had gradual access to these pulses since the late 1960s. This became possible initially due to developments in dye laser technology [6] and, later, through solid-state systems like titanium-sapphire oscillators [7]. The drive to achieve ever shorter pulses rapidly accelerated the development of these ultrafast light sources (Figure 1.1 (b)). Due to their extremely short duration, ultrashort pulses can also exhibit other two powerful properties: high peak power (usually megawatts or more) and a broad bandwidth (for example, a Ti:sapphire oscillator delivering sub-10 fs pulses can show a broad spectral bandwidth that goes from 650 to 1000 nm). These three characteristics can be used for a variety of applications, such as materials processing [8, 9], nonlinear optical spectroscopy [10–12], and biomedical imaging [13, 14].

Two-dimensional (2D) nanomaterials such as graphene, have been explored for the development of advanced optoelectronic devices, such as high-speed photodetectors and all-optical modulators. Why graphene? Among other characteristics, the dynamics of the carriers (electron and holes) in graphene is ultrafast. In other words, processes such as carrier-carrier scattering and hot carrier cooling in graphene happen in less than a few picoseconds. We can exploit these phenomena to develop faster electronics and enhance data communication technologies. To study the carrier dynamics in graphene, we can use a time-resolved technique called ultrafast pump-probe spectroscopy. In this technique an ultrashort pulse (the pump) is used to excite the sample and another pulse (the probe), which is delayed relatively to the pump, is used to ‘monitor’ the relaxation response of

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the carriers. The probe can be thought of as a photographer capturing the movement of electrons in graphene, but instead of using a camera, it utilizes ultrashort light pulses on the femtosecond scale.

In this thesis we designed and built a degenerate optical pump-probe setup to investigate how the number of graphene layers changes its carrier dynamics. Here, we explore the

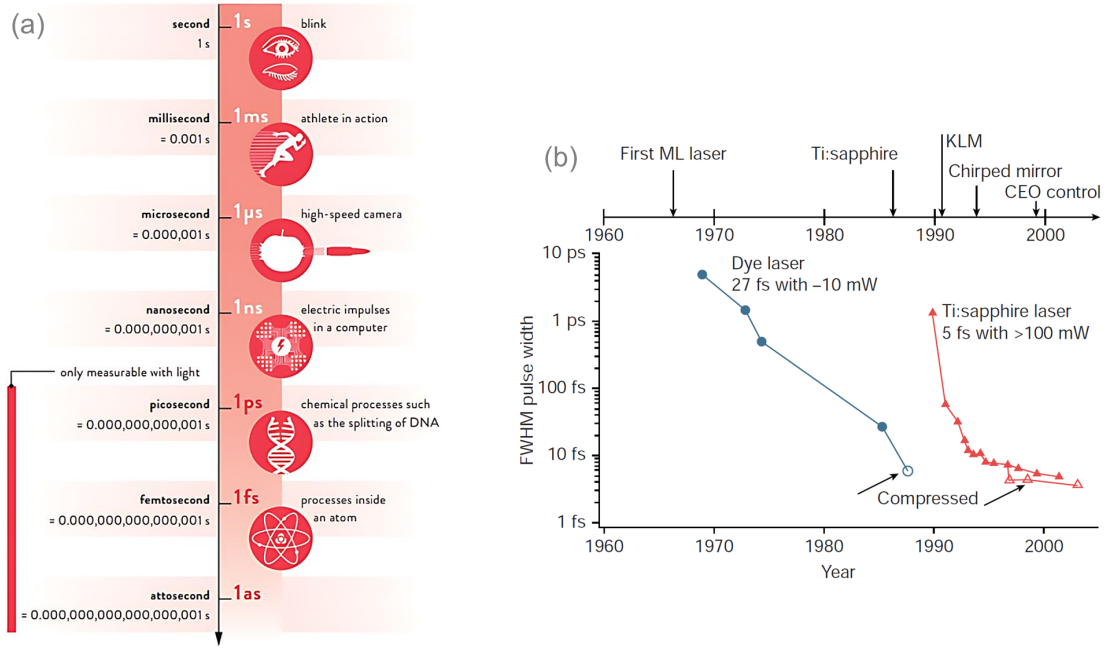


Figure 1.1.: Events in time. (a) Time scale of events ranging from seconds to attoseconds (adapted from [15]). (b) Evolution of ultrashort pulse generation through the years (reproduced from [7]). KLM: Kerr lens modelocking; CEO: Carrier envelope offset.

details regarding the construction of this setup and the application to the study of carrier dynamics in nanomaterials.

1.2. Outline

This thesis is divided as follows. In Chapter 2 an introduction to ultrashort pulses is given. It addresses their mathematical description, their propagation, and some techniques that can be used to measure them. In Chapter 3 theoretical background about pump-probe spectroscopy is given. On Chapter 4 the reader can find a short review regarding graphene synthesis and properties. Chapter 5 covers the experimental details related to the materials, equipment and techniques used during this work. We present the custom-built pump-probe setup in Chapter 6. Finally in Chapter 7, we present the results of the carrier dynamics in graphene, acquired with the pump-probe setup. We draw some

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conclusions in Chapter 8 and present our perspectives for future work.

2. Ultrashort pulses: a primer

Today, laboratories worldwide have easier access to far more stable and compact ultrafast laser sources compared to the early days of ultrafast laser technology. The engineering advancements combined with the increased number of applications of ultrashort pulses in different fields make the area of nonlinear and ultrafast optics much more collaborative and interdisciplinary. Thus, this section was written with particular attention to the newcomers in the field. We hope it covers the most important concepts to have in mind throughout this thesis. The chapter focuses on the description of ultrashort light pulses and their propagation. We will see that to describe an ultrashort pulse, we must look at two different representations: the time and the frequency domains. We will also address some methods used to measure these pulses.



2.1. Introduction

In this thesis, ultrashort laser pulses are used for ultrafast time-resolved spectroscopy measurements. In this type of experiments, characterisation and proper manipulation of the pulses are essential to obtain the highest temporal resolution possible. The present description introduces some important theoretical aspects to understand ultrashort pulses and these manipulations. Since this is a short approach, focused on what we consider the most essential, we refer the reader to the classic Diels' and Rudolph's book [16] or the more recent Keller's book on ultrafast lasers [17] for a more comprehensive understanding. Other references are also given along the text.

2. Ultrashort pulses: a primer

Let us consider a monochromatic electromagnetic wave,¹ oscillating in time t with an electric field $E(t)$ given by

$$E(t) = A \cos(\omega_0 t + \phi_0), \quad (2.1)$$

where ω_0 is the angular frequency, A is the amplitude and ϕ_0 is the temporal phase. It is well known from wave theory that the superposition of two or more waves with the same frequency gives rise to interference which can be completely constructive if the phase difference is $2\pi m$ ($m \in \mathbb{Z}$) or destructive if it is $\pi(2m - 1)$ ($m \in \mathbb{Z}$). However, if the frequencies are different, we will not have completely constructive or destructive interference but we might have the formation of what is known in acoustics as ‘beats’ [18]. Analogously, in the electromagnetic case, we will have the formation of light pulses.

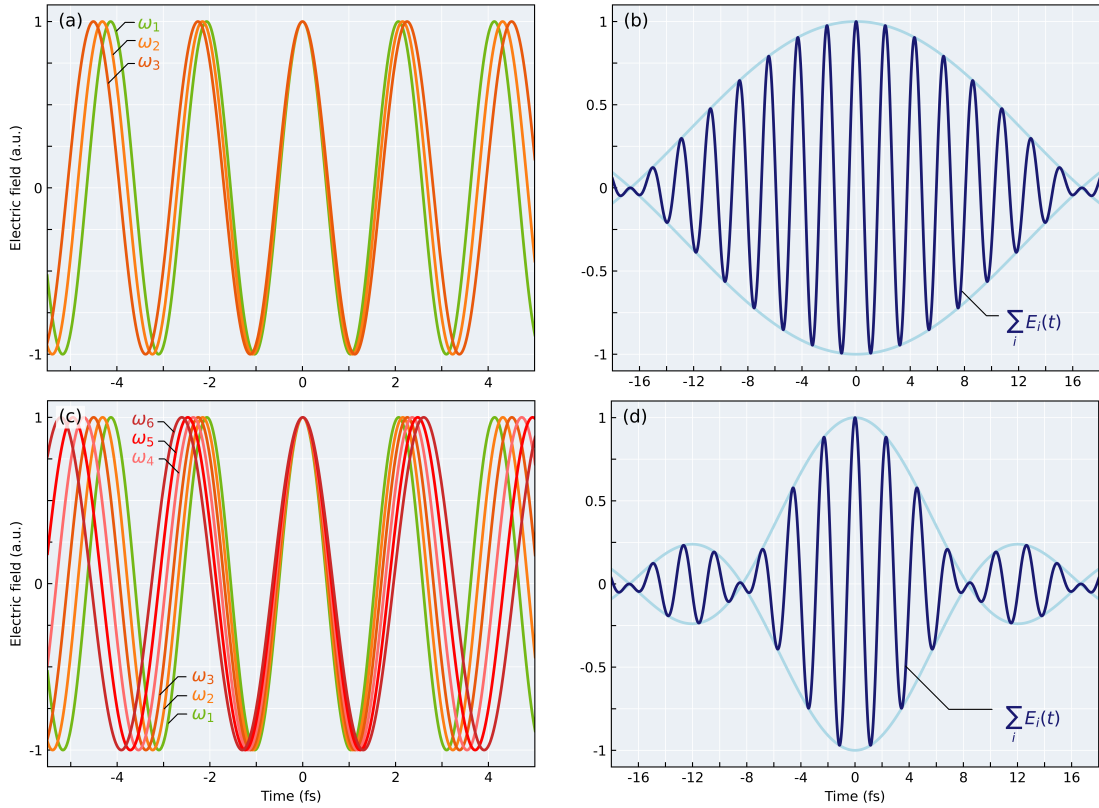


Figure 2.1.: Superposition of electric field waves. Representation of (a) three wave functions with different frequencies ω_0 , spaced by $\Delta\omega$; (b) superposition of waves represented in (a); (c) six wave functions with different frequencies, also spaced by $\Delta\omega$; (d) superposition of the waves in (c). Note that the FWHM of (d) is smaller than in (b).

Let us look to the superposition of three monochromatic waves described by the equation 2.1, all having the same amplitude and phase but different frequencies, ω_i ($i = 1, 2, 3$),

¹We are ignoring for now any spatial dependence of the electric field.

2. Ultrashort pulses: a primer

i.e.

$$E_{\text{superposition}}(t) = \sum_i^N E_i(t) = A \cos(\omega_i t + \phi_0), \quad (i = 1, 2, 3), \quad (2.2)$$

such that the frequencies are equally spaced by a constant amount $\Delta\omega$, as depicted in Figure 2.1(a). As expected, the result of this superposition is a wave packet that is limited in time, i.e the light pulse, which is illustrated in Figure 2.1(b). We can observe that as more frequencies are added, the shorter becomes the wave packet [Figures 2.1(c) and 2.1(d)]. This result is one of the most important and fundamental aspects in the field of ultrashort laser pulses: the relationship between the light pulse duration and its spectral content (and we will discuss it in more detail in Section 2.3). In Figure 2.2 a pulse train

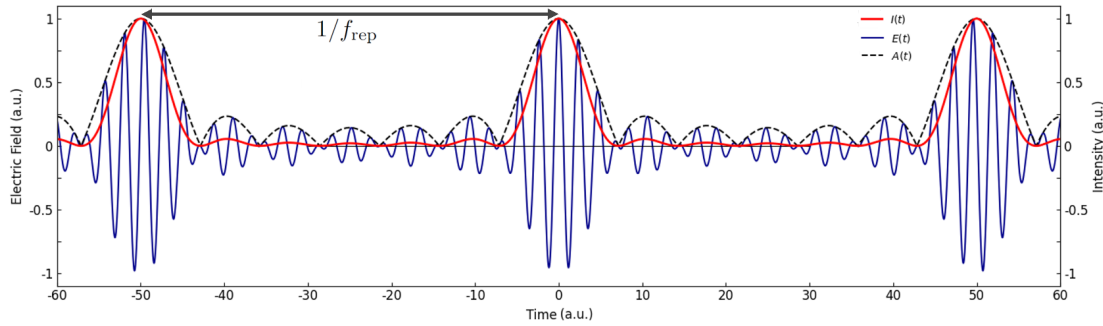


Figure 2.2.: Superposition of electric field waves with repetition rate. $E(t)$ is the electric field, $A(t)$ is the envelope and $I(t)$ is the intensity. The temporal distance between pulses is given by $1/f_{\text{rep}}$, where f_{rep} is the repetition rate.

is represented, that has a corresponding repetition rate, which varies inversely with $\Delta\omega$.

In what follows we will be dealing with the time and spectral components of ultrashort pulses through the Fourier transform. We will see that the product of the pulse duration and frequency bandwidth cannot fall below a certain minimum and we will explore the techniques that enable us to characterise ultrashort pulses. Because it is beyond the scope of this thesis we will not address how ultrashort pulses are generated, which includes topics such as cavity modes, laser cavity designs, mode-locking techniques and theoretical models to predict the shape of the generated pulses. However, we refer the reader to references [16, 19, 20] if interested in these subjects.

2.2. Time representation of ultrashort pulses

To fully describe an ultrashort pulse, we must look at two different representations: the pulse propagation in the temporal domain and the corresponding pulse propagation in the spectral domain. Here we chose to start by the temporal representation. It will

2. Ultrashort pulses: a primer

be convenient to work with the electric field in the form of an exponential instead of a cosine function as done in Section 2.1. Since we know from Euler's formula that $\cos(x) = \frac{1}{2} [e^{ix} + e^{-ix}]$, where i is the imaginary unit, we can simply rewrite equation (2.1) as

$$E(t) = \frac{A}{2} [e^{-i(\omega_0 t + \phi_0)} + e^{i(\omega_0 t + \phi_0)}] . \quad (2.3)$$

In this format, $E(t)$ has positive and negative frequency components. For real signals, the negative frequency component is redundant.² Thus, we can simplify equation (2.3) further by using the analytic signal representation $z(t) = x(t) + iy(t)$, such that

$$V(t) = E(t) + i\mathcal{H}\{E(t)\} , \quad (2.4)$$

where $\mathcal{H}\{\}$ denotes the Hilbert transform. By substituting (2.3) into (2.4) and performing the calculation, we get

$$V(t) = A e^{-i(\omega_0 t + \phi_0)} , \quad (2.5)$$

which is the analytic signal [21, 22] of $E(t)$. If we want to recover the real electric field $E(t)$ we can simply use the relation

$$E(t) = \frac{1}{2} [V(t) + V^*(t)] , \quad (2.6)$$

where the symbol $*$ denotes the complex conjugate. Unless otherwise stated, from now on we always refer to the electric field as being $V(t)$. Nevertheless, the reader should always keep in mind the relation between $E(t)$ and $V(t)$ from in equation (2.6).

We have seen in Section 2.1 that under certain conditions, the superposition of monochromatic waves with different frequencies can give, in the time domain, a pulse. Typically, if the duration of that pulse is on the order of femtoseconds or less, one calls it ‘ultrashort’. In order to model the light pulse propagation in time we add a time-dependent amplitude to the equation (2.1). We can therefore write the electric field $V(t)$ for an ultrashort pulse as

$$V(t) = A(t) e^{i[\omega_0 t + \phi(t)]} , \quad (2.7)$$

where $A(t)$ is the temporal amplitude (also called temporal envelope), ω_0 is now the carrier (or central) angular frequency and $\phi(t)$ is the temporal phase. Here, only the time

²In other words, if you try to compute the spectrum of equation (2.3) the negative frequencies holds the exact same information than that of the positive ones.

2. Ultrashort pulses: a primer

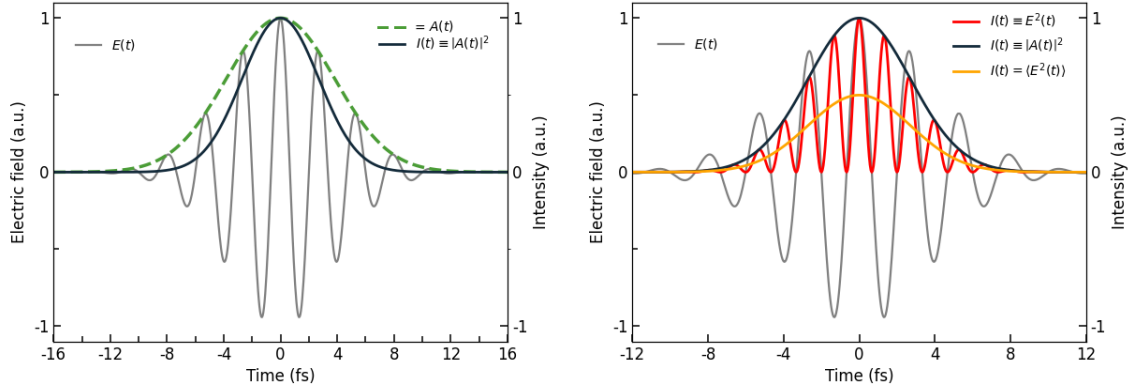


Figure 2.3.: Representation of an ultrashort pulse with a duration (intensity FWHM) of 9 fs with a centre wavelength of 800 nm.

dependence of the electric field is considered, i.e. the discussion is limited to a fixed point in space and we neglected again the vectorial properties of the field for simplicity. It can be easily demonstrated that the envelope $A(t)$ of the field $V(t)$ is simply the magnitude of $V(t)$ [23], i.e.

$$A(t) = \sqrt{V(t)V^*(t)} = |V(t)|. \quad (2.8)$$

The linear term $\omega_0 t$ determines how fast is the oscillation of the field and consequently defines the duration of an optical cycle, i.e., $T = \frac{\pi}{\omega_0}$. The term $\phi(t)$ is a nonlinear term that describes the temporal variation of the pulse frequency. The duration of an ultrashort pulse, Δt , is an important parameter (we will see how to measure it in Section 2.6) and is usually defined from the full width at half maximum (FWHM) of the temporal intensity, which is proportional to the squared envelope, i.e., $A^2(t)$ [24]. Thus, in arbitrary units, we have that

$$I(t) \equiv |V(t)|^2 = A^2(t). \quad (2.9)$$

Some authors refer to this quantity as ‘instantaneous intensity’. Figure 2.3(a) illustrates an example an ultrashort pulse with a central wavelength of 800 nm and a duration of 9 fs with the three main quantities we have discussed so far, namely, $V(t)$, $A(t)$ and $I(t)$.

However, this definition of intensity differs slightly from the ‘classical’ definition, where the intensity is proportional to the magnitude of the Poynting vector³ $\vec{S}$. Using the fact that the amplitude of magnetic field $\vec{B}(t)$ is proportional to that of $\vec{E}(t)$, we can write this definition for the intensity $I'(t)$ as

$$I'(t) \equiv E^2(t). \quad (2.10)$$

³In arbitrary units, the Poynting vector in free space is defined as $\vec{S} = \vec{E} \times \vec{B}$.

2. Ultrashort pulses: a primer

Furthermore, since the detectors integrate the energy flux over a finite time T , we can have yet another definition of intensity [25], which is the time-averaged value of the magnitude of Poynting vector $\vec{S}$ over T , where the latter is considered much larger than the period of oscillation of the electric field [25]. Using this definition, which we distinguish with a subscript T , we can write it as

$$I_T \equiv \langle S \rangle_T . \quad (2.11)$$

where $S = |\vec{S}|$. Using again the fact that the amplitude of magnetic field $\vec{B}(t)$ is proportional to that of $\vec{E}(t)$ and using equations (2.7) and (2.6), we can calculate the time-average intensity $I_T(t)$ over one optical period $T = 2\pi c/\omega_0$ (as a function of time), which in arbitrary units gives [16]

$$I_T(t) = \left\langle E^2(t) \right\rangle_T = \frac{1}{T} \int_{t-\frac{T}{2}}^{t+\frac{T}{2}} E^2(t') dt' , \quad (2.12)$$

This equation can be interpreted as calculating the intensity as a function of time t by ‘moving’ a time window in which the integration is carried out over t' . Assuming that $E(t) = A(t) \cos(\omega t)$, we obtain:

$$I_T(t) = \frac{1}{2} A^2(t) . \quad (2.13)$$

note that, apart from a factor of $\frac{1}{2}$, this definition of intensity yields the same result than that of equation (2.9). However, equation 2.10 yield a different result which in most practical cases is not suitable since the detector (or material response) is much larger than the field oscillations. Figure 2.3(b) illustrates these three different definitions for intensity. Henceforth, when referring to intensity, we will use the definition of equation (2.9) unless stated otherwise.

If the period of integration T is much larger than the ultrashort pulse envelope, then $I_T(t)$ will give the same value for all time t . This is the case for the so-called ‘slow detectors’ which can not resolve a single ultrashort pulse. We can therefore define the total intensity for these slow detectors in arbitrary units as

$$I_D = \int_{-\infty}^{+\infty} V(t) V^*(t) dt . \quad (2.14)$$

This last equation will be useful later in Chapter 3 since we will be working with the analytic signal $V(t)$ and we will need to compute a total intensity for a slow detector.

2. Ultrashort pulses: a primer

Note that, in arbitrary units, the energy density per unit area has the same form [16]:

$$W = \int_{-\infty}^{+\infty} V(t) V^*(t) dt \quad (2.15)$$

The instantaneous power (or peak power) can be obtained by integrating the intensity over the beam's cross area A , i.e.,

$$P(t) = \int_s I(t) dS. \quad (2.16)$$

Likewise, the average power can be calculated through the time-average intensity of equation (2.14):

$$P_{\text{av}} = \int_S I_D dS. \quad (2.17)$$

If we send a beam of ultrashort pulses with repetition rate f_{rep} , it will typically measure the average power P_{av} over a period much longer than $1/f_{\text{rep}}$. Thus, if we wish to find the pulse energy, we simply divide the average power by the repetition rate, i.e.,

$$W = \frac{P_{\text{av}}}{f_{\text{rep}}}. \quad (2.18)$$

In practical cases, it is common for authors to give the energy of the pulse per unit area that reaches a given sample. This quantity, known as fluence, is defined as

$$F = \frac{W}{S}, \quad (2.19)$$

where S is the cross-sectional area over which the energy is distributed.

2.3. Frequency representation of ultrashort pulses

We will now switch from the temporal domain to the spectral domain. Analogously to the time representation, the electric field of ultrashort pulses can be described in the frequency domain by Fourier transforming $V(t)$, i.e.,

$$U(\omega) = \mathcal{F}_t \{V(t)\}, \quad (2.20)$$

2. Ultrashort pulses: a primer

where $U(\omega)$ is the spectral representation of the electric field $V(t)$ and $\mathcal{F}_t\{\}$ denotes the Fourier Transform with respect to t , i.e.,

$$\mathcal{F}_t\{U(\omega)\} = \int_{-\infty}^{+\infty} V(t) e^{-i\omega t} dt. \quad (2.21)$$

To go back to the time domain, we simply do the inverse Fourier transform

$$V(t) = \mathcal{F}_\omega^{-1}\{V(t)\} = \frac{1}{2\pi} \int U(\omega) e^{i\omega t} d\omega, \quad (2.22)$$

where $\mathcal{F}_\omega^{-1}\{\}$ denotes the inverse Fourier Transform with respect to ω . Thus, the spectral representation of the electric field can be written as:

$$U(\omega) = |U(\omega)| e^{-i\varphi(\omega)}, \quad (2.23)$$

where $|U(\omega)|$ is the spectral amplitude and $\varphi(\omega)$ is the spectral phase. Note that, likewise $V(t)$, $U(\omega)$ is also a complex quantity. Hence, if we want to recover $E(\omega)$ we simply do $E(\omega) = \frac{1}{2} [U(\omega) + U^*(\omega)]$. Similarly to the intensity, the spectral density $S(\omega)$ (or power spectral density) is defined as

$$S(\omega) = |U(\omega)|^2. \quad (2.24)$$

We had defined the pulse duration Δt as the FWHM of the temporal intensity given in equation (2.9). In the same way, the spectral width $\Delta\omega$ (or simply bandwidth) can be defined as the FWHM of $S(\omega)$. The Fourier transform relationship between $V(t)$ and $U(\omega)$ allow us to easily establish relationships between the pulse duration and the spectral width, as we will next discuss.

Since it is difficult to always know the exact shape of an ultrashort pulse, we will use as an example a Gaussian shape pulse. Let $V_G(t)$ be an ultrashort pulse with a Gaussian profile with central frequency ω_0 described as

$$V_G(t) = A_G(t) e^{-i\omega_0 t}, \quad (2.25)$$

where

$$A_G(t) = \exp\left(-\frac{t^2}{\tau_G^2}\right), \quad (2.26)$$

where τ_G is the typical ‘standard deviation’ parameter in Gaussian distributions. In some

2. Ultrashort pulses: a primer

cases (e.g., numerical simulations), it is more useful to work with these parameters rather than the FWHM. The intensity, according to equation (2.9), is simply

$$I_G(t) = \exp\left(-\frac{2t^2}{\tau_G^2}\right). \quad (2.27)$$

Thus, the pulse duration (i.e., FWHM of the intensity profile) for a Gaussian pulse will simply be

$$\Delta t_G = \sqrt{2 \ln 2} \tau_G. \quad (2.28)$$

Since the $V(t)$ and $U(\omega)$ are related through the Fourier transform, the spectral width $\Delta\omega$ and pulse duration Δt are also related and cannot vary independently. The time-bandwidth is thus given by

$$\Delta\omega \Delta t \geq 2\pi \alpha_p, \quad (2.29)$$

where α_p is a numerical constant. For a Gaussian pulse, $\alpha_p \approx 0.441$. So, for instance, to achieve a pulse duration of 7 fs, the spectral width must be $\Delta\omega \geq 3.9584 \times 10^{14}$ rad/s. Thus, the shorter the pulse, the larger the spectral width. However, note that the inequality sign implies that larger spectral widths could also generate the same 7 fs pulse. As we will next see, this is due to dispersion.

2.4. Dispersion

Except in vacuum, the propagation velocity of an electromagnetic wave is frequency dependent⁴. Not all electromagnetic waves travel at the same phase velocity, with longer wavelengths travelling faster than the shorter ones in general. In the previous sections, we have described ultrashort pulses in the time and spectral domains and we have seen that, in general, the larger the spectrum, the shorter the pulse⁵. From that characteristic, we can easily conclude that a shorter pulse will experience a stronger temporal broadening during linear propagation in a dispersive medium. Note however, that its power spectral density, i.e. the spectrum $S(\omega)$, will remain the same (Figure 2.4). Thus a question arises: is a large spectral width a necessary and sufficient condition to obtain an ultrashort pulse in time? If that were the case we could simply use sunlight or an halogen lamp to gener-

⁴This is best observed in nature through the colours of the rainbow

⁵We are, of course, ignoring the effect of the spectral phase for now. Note also that, the reader should look to the spectrum of light in units of frequency, not wavelength - frequency and wavelength are not linearly related.

2. Ultrashort pulses: a primer

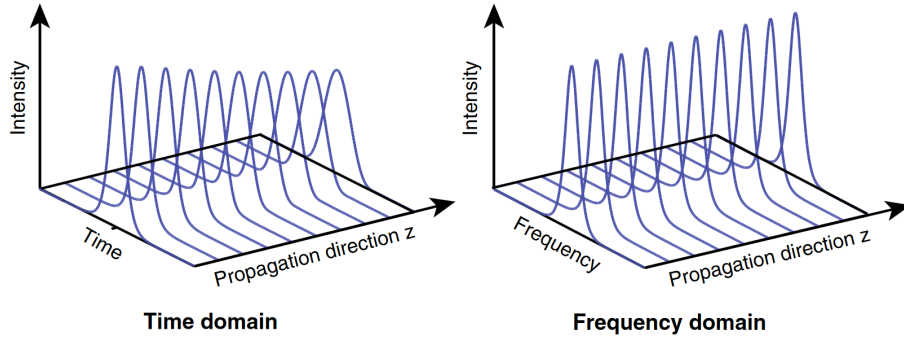


Figure 2.4.: Ultrashort pulse propagation in a dispersive medium for time (left) and frequency (right) domains. During propagation the pulse duration increases while its power spectral density remains the same. Reproduced from [17].

ate ultrashort pulses. Thus, one obviously needs coherent waves and, consequently, well defined spectral phases for each frequency in order to generate ultrashort pulses. Up until now, we have treated the spectral phase $\varphi(\omega)$ of equation (2.23) as constant. In practice, the spectral phase is not a ‘well behaved’ quantity, or in other words, we do not know precisely its shape and, therefore, it is usually described by a Taylor expansion, which is given by

$$\varphi(\omega) = \varphi_0 + \varphi'_0(\omega - \omega_0) + \frac{1}{2!}\varphi''_0(\omega - \omega_0)^2 + \frac{1}{3!}\varphi'''_0(\omega - \omega_0)^3 + \frac{1}{4!}\varphi''''_0(\omega - \omega_0)^4 + \dots, \quad (2.30)$$

where the terms φ_0 , φ'_0 , φ''_0 , φ'''_0 are denoted as the absolute phase, group delay (GD), group delay dispersion (GDD) and third delay dispersion (TOD), respectively, and are defined as

$$\varphi_0 = \varphi(\omega_0), \quad (2.31)$$

$$\varphi'_0 = \left. \frac{\partial \varphi(\omega)}{\partial \omega} \right|_{\omega=\omega_0}, \quad (2.32)$$

$$\varphi''_0 = \left. \frac{\partial^2 \varphi(\omega)}{\partial \omega^2} \right|_{\omega=\omega_0}, \quad (2.33)$$

$$\varphi'''_0 = \left. \frac{\partial^3 \varphi(\omega)}{\partial \omega^3} \right|_{\omega=\omega_0}. \quad (2.34)$$

Other high-order terms can also be included (e.g., forth-order dispersion) if needed, specially in cases where the spectrum is ultrabroadband with a significant amount of dispersion. The first term is the absolute phase and corresponds to an offset between oscillatory carrier and the envelope of the electric field. The absolute phase is best known as carrier envelop phase (CEP). It is only relevant when dealing with few-cycle pulses. The second

2. Ultrashort pulses: a primer

term, the group delay, as the name says is simply a translation of the pulse in time. It is a delay of the pulse (the envelope) with respect to a given origin and does not have any implications for the pulse width. The third term, group delay dispersion, causes an increase in the pulse width, a phenomenon named chirp. In summary, each frequency experiences a delay that linearly increases as we scan through the spectrum. The term third delay dispersion leads in the temporal domain to many pre- or post-pulses. Effect of the spectral phase $\phi(\omega)$ on the pulse shape and duration is depicted in Figure 2.5.

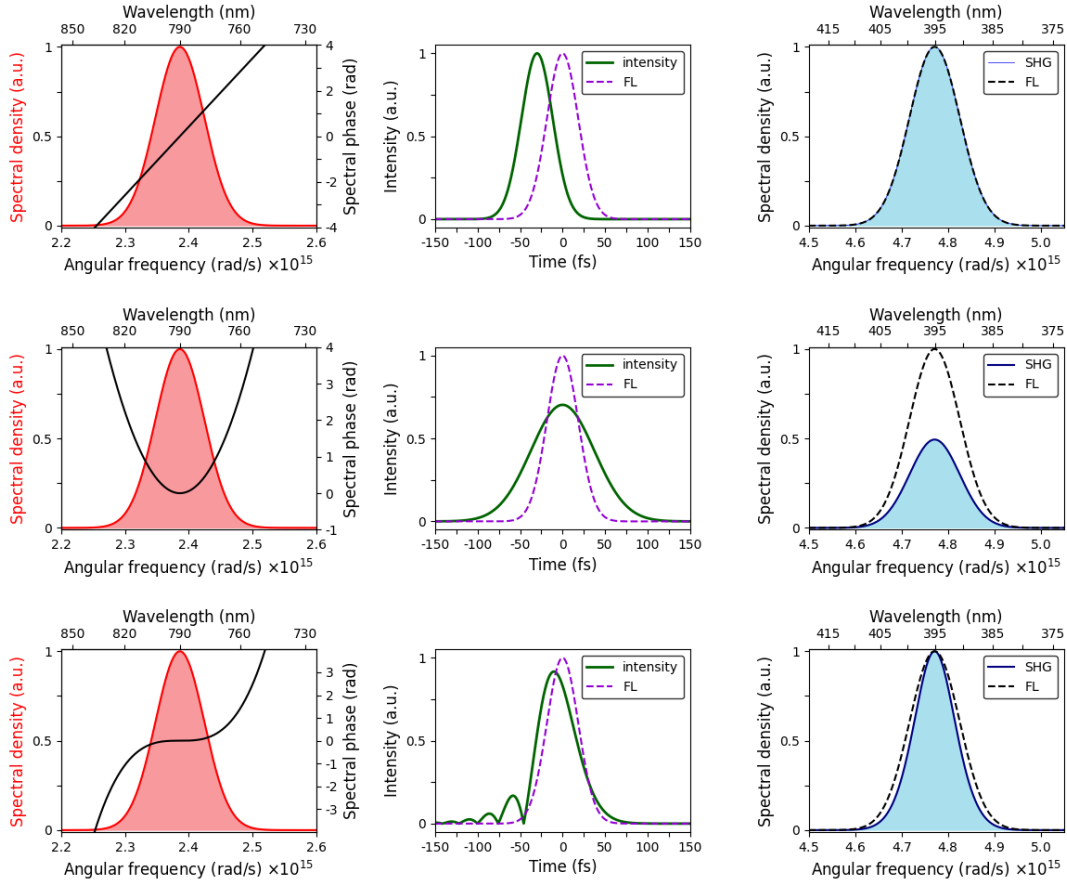


Figure 2.5.: Effect of the spectral phase $\phi(\omega)$ on the pulse shape and duration. In the first row is represented the linear term, in the second row the second-order and in the third row the third-order phase terms.

2.5. Second harmonic generation

The second harmonic generation (SHG) is a nonlinear process where two photons of frequency ω_0 are converted to a single photon with frequency $2\omega_0$ (hence the name second harmonic) [26]. This process is very useful for pulse characterisation because through the resulting spectrum of the second harmonic we can conclude about the main pulse duration.

2. Ultrashort pulses: a primer

Therefore, let's have a look to the conditions needed for the SHG.

When an electromagnetic field propagates through a dielectric medium, the electronic charge of the material is displaced. Electrons respond to the incident oscillating field and are displaced from their equilibrium position, forming an oscillatory dipole with the corresponding positive ion cores, a dipole moment is induced, and thus polarisation takes place. In the presence of a low-intensity electric field, the polarization P is simply modelled by⁶

$$P = \epsilon_0 \chi^{(1)} E, \quad (2.35)$$

where ϵ_0 is the vacuum permittivity and $\chi^{(1)}$ is the linear susceptibility⁷. Here in 2.35, the motion of electrons can be described by a simple harmonic oscillator model. However, for high intensities, which are easily achieved with ultrashort pulses, the response of the medium is driven into a nonlinear regime (anharmonic model). Typically, when the intensities are on the order of 10^{14} W/cm^2 , equation (2.35) fails to describe the response of the system and higher-order terms need to be taken into account. Through the Taylor expansion of equation (2.35) we get a more general description of the electric polarization,

$$P = P_L + P_{NL} = \epsilon_0 \chi^{(1)} E + \epsilon_0 \left(\chi^{(2)} EE + \chi^{(3)} EEE + \dots \right), \quad (2.36)$$

where $\chi^{(n)}$ is n^{th} order ($n = 2, 3, 4, \dots$) nonlinear susceptibility and ‘...’ simply indicates that one can add higher-order contributions. Recalling equation (2.1) for the electric field, the polarisation can be rewritten as

$$\begin{aligned} P = & \epsilon_0 \chi^{(1)} A \cos(\omega_0 t + \phi_0) + \epsilon_0 \chi^{(2)} A^2 \cos^2(\omega_0 t + \phi_0) \\ & + \epsilon_0 \chi^{(3)} A^3 \cos^3(\omega_0 t + \phi_0) + \dots \end{aligned} \quad (2.37)$$

Since $\cos^2(x) = \frac{1}{2} + \frac{1}{2} \cos(2x)$, for the second order non-linear polarisation $P^{(2)}$ we have that

$$P^{(2)} = \frac{\epsilon_0 \chi^{(2)} A^2}{2} [1 + \cos(2\omega_0 t + 2\phi_0)]. \quad (2.38)$$

Thus, if an intense electric field passes through a second-order nonlinear optical material, light with twice of the input frequency will be generated, in other words we observe a SHG. Now, SHG does not occur in centrosymmetric media, therefore one needs a noncentrosym-

⁶Here we are considering linearly polarised light and therefore we treat the field as a scalar

⁷In general, $\chi^{(1)}$ is described as a tensor, meaning that it depends on the orientation of polarisation of the electric field.

2. Ultrashort pulses: a primer

metric medium [27]. The β -BBO (beta-BaB₂O₄) crystal is the most used medium in ultrafast laboratories to generate second harmonic signals with Ti:Sapphire oscillators. The second-harmonic spectral density $S_{\text{SH}}(\omega)$ can be estimated through the fundamental pulse $U(\omega)$ using the following relation [28, 29]

$$S_{\text{SH}}(\omega) = \left| \int \left(\int U(\Omega) e^{izk(\Omega)} e^{i\Omega t} d\Omega \right)^2 e^{-i\omega t} dt \right|^2, \quad (2.39)$$

where Ω also denotes the angular frequency. We can also write it in a more pleasant form for numerical simulation as

$$S_{\text{SH}}(\omega, z) = \left| \mathcal{F}_t \left\{ \left[\underbrace{\mathcal{F}_\omega^{-1} \{ U(\omega) e^{izk(\omega)} \}}_{U(t)} \right]^2 \right\} \right|^2. \quad (2.40)$$

2.6. Characterisation of ultrashort pulses

Until now, we have been mathematically discussing how to model ultrashort pulses. It becomes clear that both magnitude and phase of the electric field, either in the time or frequency domains, must be known in order to fully characterise ultrashort pulses since the Fourier transform of equations (2.22) and (2.23) demand so. Thus, this raises the question. If the response of the current fastest electronic devices is on the order of a few picoseconds, how can we measure shortest events? While some properties can be measured rather straightforwardly (e.g. average power) others are not easily accessible (e.g. pulse duration and energy per pulse). For this reason, characterisation techniques to measure the ultrashort pulses have been developed through the years.

In what follows, we will describe three techniques that were used throughout this thesis to characterise ultrashort pulses, although only one of them can be used to fully characterise it, i.e., in terms of both magnitude and phase of the electric field - the d-scan technique.

2.6.1. Spectral interferometry

Consider an ultrashort pulse $U(\omega)$ which enters a Mach-Zehnder interferometer, where it is split into two beams, $U_1(\omega)$ and $U_2(\omega)$ and later recombined, as depicted in Figure 2.6(a). Assuming that both arms of the interferometer have the same characteristics (e.g., refractive index) with the only difference being the difference in arm length Δl . After the

2. Ultrashort pulses: a primer

second beam splitter, both beams will be collinear and the total field will be the sum of total beams, i.e.,

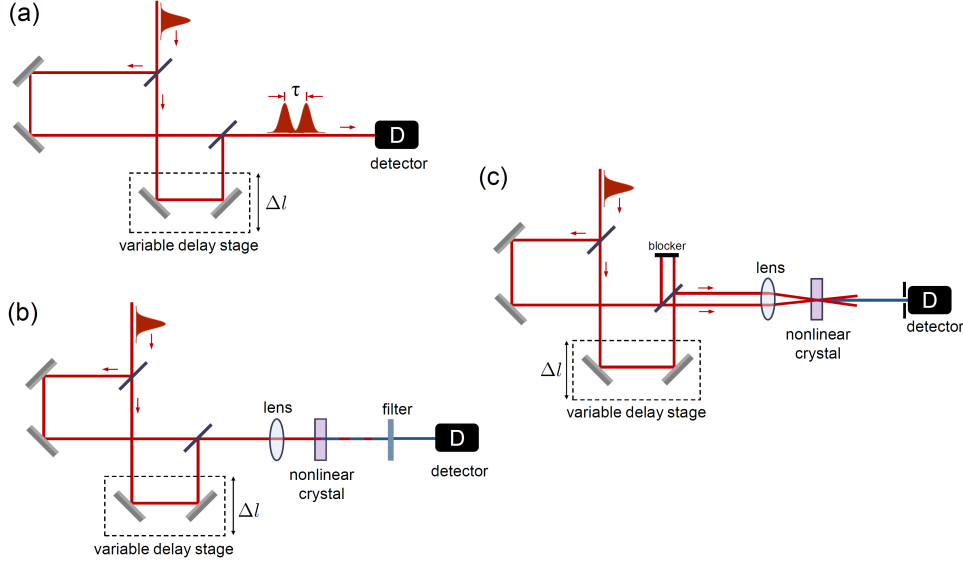


Figure 2.6.: Interferometers for spectral interferometry and intensity autocorrelation. (a) Spectral interferometry configuration. (b) Intensity autocorrelation configuration. (c) Second-harmonic generation configuration.

$$U_T(\omega) = U_1(\omega)e^{i\frac{\omega}{c}n(\omega)\Delta l} + U_2(\omega), \quad (2.41)$$

where $n(\omega)$ is the frequency-dependent refractive index of the medium (e.g., air) and c the speed of light in vacuum. Assuming that the medium is air ($n(\omega) \approx 1$), the time delay between both pulses is

$$\tau = \frac{2\Delta l}{c}, \quad (2.42)$$

where the factor of 2 comes from the fact that the beam $U_1(\omega)$ is retroreflected from the delay stage. Substituting equation (2.42) into equation (2.41) gives

$$U_T(\omega) = U_1(\omega)e^{i\frac{\omega\tau}{2}} + U_2(\omega). \quad (2.43)$$

If we measure the total field with a spectrometer, it will measure spectral density $S(\omega) = |U_T(\omega)|^2$, as discussed before, and therefore, we will have that

$$S_i(\omega) = U_1^2(\omega) + U_2^2(\omega) + 2\sqrt{S_1(\omega)}\sqrt{S_2(\omega)}\cos\left(\frac{\omega\tau}{2}\right). \quad (2.44)$$

where the third term will introduce an interference pattern in the spectrum.

2.6.2. Intensity autocorrelation

If we do not have any information about the pulse, then intensity autocorrelation is probably one of the simplest technique to use in order to have some information about the pulse, namely, its duration and shape [22]. This technique consists basically on a Mach-Zehnder interferometer.

$$G(\tau) = \int_{-\infty}^{+\infty} I(t)I(t - \tau) dt. \quad (2.45)$$

For instance, if the input ultrashort pulse $U(t)$ has a Gaussian envelope, then the autocorrelation signal $G(\tau)$ will also be a Gaussian and the relation between the FWHM of $G(\tau)$ and $V(t)$ is straightforward. This technique forms the basis of FROG - Frequency-Resolved Optical Gating. We refer the reader to reference [21] for more information on this technique.

2.6.3. d-scan technique

The d-scan technique was proposed and demonstrated by Miranda et al. [28, 29] in 2012. The idea is simple [30]. Let $V(t)$ and $U(\omega)$ be the electric field of an ultrashort pulse in the time and frequency domain, respectively, which we want to quantify in terms of its amplitude and phase. As we saw in Section (2.3), we can either write it in the time or frequency domain and then use the Fourier transform to jump between both representations. Let also $U_{SH}(\omega)$ be the second harmonic generated with $U(\omega)$ using, for instance, a BBO crystal⁸. According to equation (2.39), if the spectral phase $\varphi(\omega)$ changes, the spectral density $S_{SH}(\omega)$ of the second harmonic will also change. Thus, the principle behind the d-scan technique is to applied different spectral phases $\varphi(\omega)$ to an ultrashort pulse, record their respective second harmonic spectra $S_{SH}(\omega)$ to build a trace (or spectrogram) and then use the trace information to recover the spectral phase using iterative algorithms, similar to what is done with FROG [21]. Figure 2.7 illustrates the concept of the d-scan technique.

2.7. Key conclusions

To summarise, some key aspects from this chapter are listed below.

- (i) The description of ultrashort pulses in time and frequency domains was presented.

⁸We will consider that, ideally, all wavelengths are in perfect phase matching.

2. Ultrashort pulses: a primer

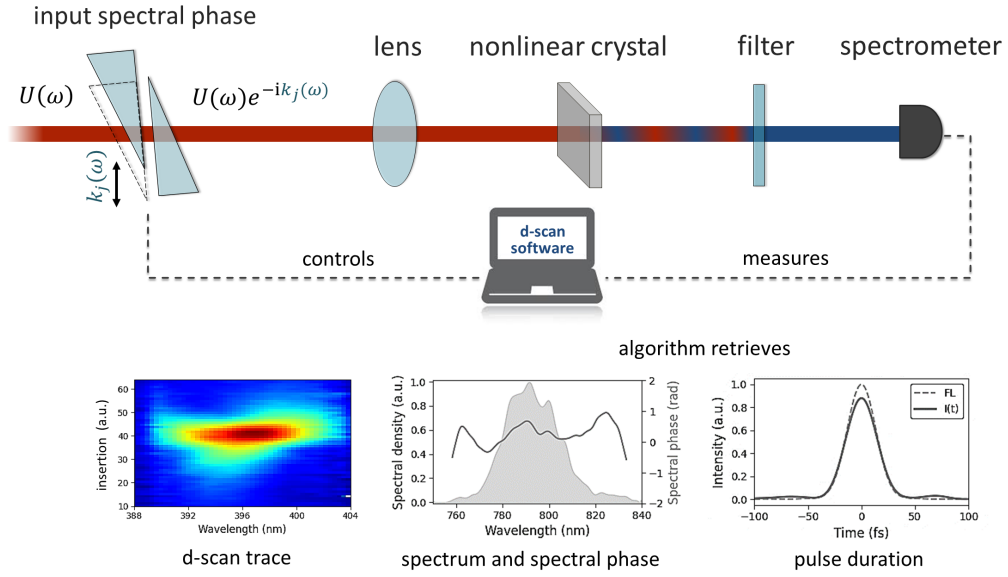


Figure 2.7.: Illustration of for the concept of the d-scan technique. Several second harmonic spectra $S_{SH}(\omega)$ of the ultrashort pulse $U(\omega)$ are measured as a function of the input spectral phase $k(\omega)$ (e.g., moving glass wedges of variable thickness). Then, using the acquired trace, one uses a phase retrieve algorithm which will then guess the spectral phase. By knowing the magnitude and phase of the fundamental beam we can then Fourier transform to know the pulse duration and shape.

- (ii) The duration of a Gaussian ultrashort pulse is typically defined as the FWHM of its temporal intensity profile.
- (iii) An ultrashort pulse achieves its shortest possible duration for a given spectral bandwidth when it is Fourier-limited, in other words, it is characterised by having a constant spectral phase. In this regime, as shorter the pulse broader the spectrum.
- (iv) The intensity autocorrelation measures the temporal overlap between two ultrashort pulses, providing an estimation of the achievable temporal resolution for resolving nonlinear processes.
- (v) The intensity autocorrelation method can provide a reasonable estimation of the temporal width of the fundamental ultrashort pulse but does not provide information about the spectral phase. This means it cannot distinguish between a Fourier-limited pulse and a chirped pulse if they have the same intensity profile.
- (vi) The d-scan technique, is a pulse characterisation technique that retrieves the temporal intensity and the spectral phase of the ultrashort pulses. It uses SHG spectra as a function of inserted optical dispersion to retrieve the spectral phase of the fundamental ultrashort pulse.

3. Ultrafast time-resolved spectroscopy

Femtosecond pump-probe spectroscopy is a powerful and versatile time-resolved technique. In a conceptually simple configuration it uses ultrashort optical pulses to investigate dynamical processes in several systems, including molecular and solid-state materials. In this chapter we introduce the basics of pump-probe spectroscopy, and we address general considerations related to the interpretation of the pump-probe signal. Instrumental aspects will however, be discussed in Chapter 6, where the construction of the custom-built pump-probe system is presented.



3.1. Introduction

The principle of pump-probe spectroscopy is illustrated in Figure 3.1 (a). In this technique a first optical pulse, that we call pump, is resonant with a vibrational or an electronic transition of the sample under study, promoting it to a non-equilibrium state. The response of the sample to the pump excitation is then monitored by another (weaker) pulse, called probe. The later is temporally delayed relatively to the pump by means of a translation stage that controls the probe optical path length. Therefore, the temporal delay τ between the two pulses is simply given by the path length difference Δx divided by the speed of light. The variation of the transmitted probe intensity, in the presence and absence of the pump¹ ΔT , is detected as function of the temporal delay. Note that the probe pulse energy should be much weaker than the pump, usually at least one order of

¹See Section 6.1.2 for more details.

3. Ultrafast time-resolved spectroscopy

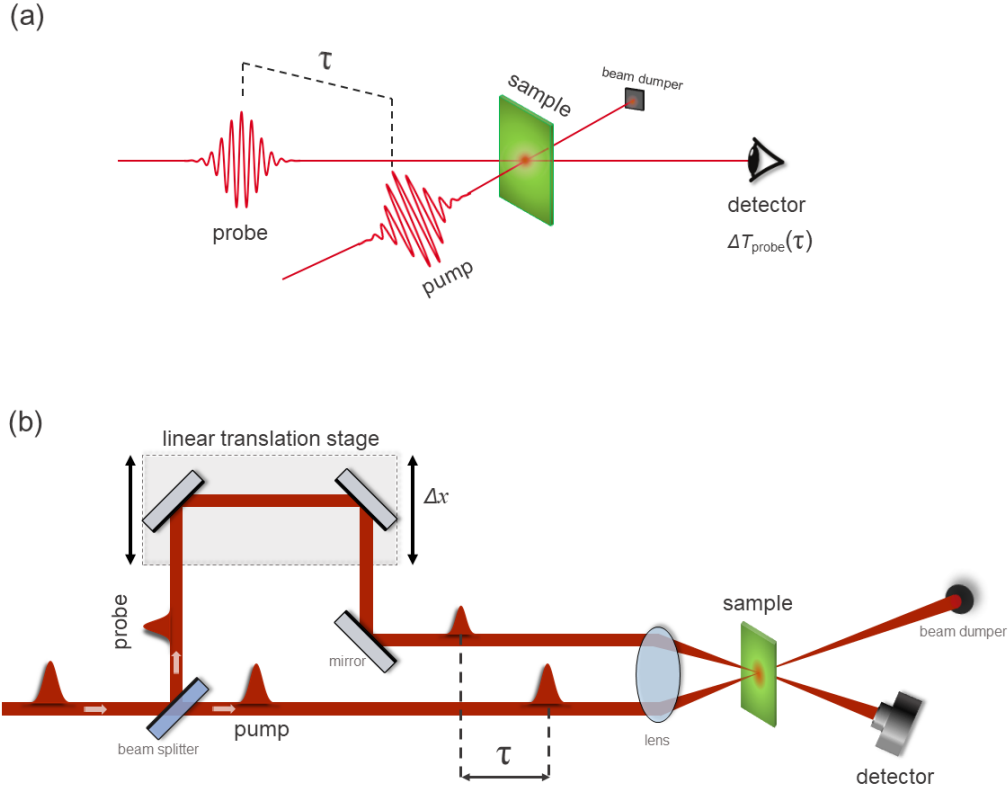


Figure 3.1.: Principle of pump-probe spectroscopy. A pump pulse hits the sample and is then picked up by a blocker. A probe pulse, temporally delayed relative to the pump, hits the sample in the transient state and monitors its behaviour. (a) Conceptual scheme. (b) Representation of a non-collinear degenerate pump-probe configuration. The probe beam is typically modulated using a chopper (not shown). Δx - variation of probe optical path; τ - temporal delay; ΔT - probe differential transmission.

magnitude [31,32]. This is because the only purpose of the probe is to track changes in the sample transmission. Thus, it should not induce any additional changes that could lead to misleading results [33]. A possible representation for a non-collinear degenerate (same colour) pump-probe configuration is shown in Figure 3.1 (b). A non-collinear configuration is typically used to spatially separate the pump from the probe beam after sample interaction. One refers to a non-degenerate² system when the pump and probe beams have different wavelengths.

The relaxation dynamics for a given sample will depend on its energy levels (or band structure) and on the frequency of both pump and probe beams. There are three typical pump-probe traces associated to the differential transmission of the probe signal, as illustrated in Figure 3.2. One is related to the process of ground-state bleaching (GSB). In GSB, the pump is absorbed by the sample, significantly decreasing or depleting its

²Also named ‘two-color pump-probe’ system.

3. Ultrafast time-resolved spectroscopy

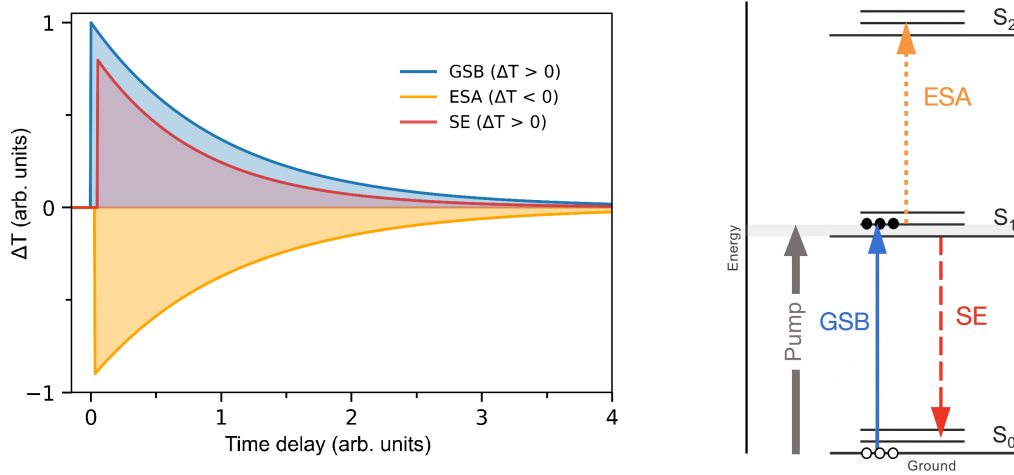


Figure 3.2.: Representation of the three major processes monitored in a pump-probe experiment, namely, ground-state bleaching (GSB), excited state absorption (ESA) and stimulated emission (SE). On the left: plot displaying kinetic curves for GSB, ESA and SE. On the right: schematic diagram depicting the corresponding processes, where the grey arrow corresponds to the pump excitation, that depletes ground-state. The blue, yellow and red arrows corresponds to the probe interactions.

ground-state population. The probe should also get absorbed, but due to the pump, at $\tau \approx 0$, the ground-state population is absent. Therefore, the absorption of the probe will be negligible, i.e., the probe transmission increases and ΔT is positive. As the sample recovers from pump excitation ($\tau \rightarrow +\infty$) the transmission of the probe decreases until the sample returns to the fundamental state.

In the case of stimulated emission (SE), ΔT is also positive, but it is caused by the light emission of the sample. Again, the pump triggers the transition to an higher energy level. The probe, slightly redshifted relative to the pump, has a frequency tuned to the emission of the excited carriers and induces a transition to a lower energy state ($\hbar\omega_{\text{pump}} - \hbar\omega_{\text{probe}}$) with the emission of a photon. This emission has the same frequency and direction of the probe, resulting in increased probe transmission due to optical gain.

Another possible response is the excited state absorption (ESA). In this process the probe frequency is higher than the pump. Consider the three level system in Figure 3.2 (b), we can see that the pump is resonant with the transition from the ground-state to S_1 while the probe is resonant with the $S_1 \rightarrow S_2$ transition. If the pump is off, the probe cannot promote $S_0 \rightarrow S_1$ transition because it is not resonant with it, neither the transition $S_1 \rightarrow S_2$ because at equilibrium that level is depopulated. Consequently, there is no absorption of the probe. When the sample is pumped and S_1 level populated, the probe is allowed to trigger the $S_1 \rightarrow S_2$ transition being absorbed by the sample. We

3. Ultrafast time-resolved spectroscopy

observe a prompt decrease in probe transmission close to $\tau = 0$ and the ΔT signal is negative.

Each one of the phenomena described above has a time constant associated, that we want to measure. To resolve it in time, we need a precise control over the pump and probe delay. However, what ultimately determines the temporal resolution of the experiment is the instrument response function, which is related to the duration of both the pump and probe pulses. We will demonstrate that in the next section. It is worth noting that, to resolve the faster dynamics, we need the shortest pulses. However, recall from Chapter 2, that due to the Fourier theorem, a shorter pulse has a broader bandwidth. Ideally in a pump-probe experiment one wants a narrow pump and a broad probe. A narrow pump for a selective excitation and to reduce spectral overlap with the probe. A broadband probe to be able to monitor spectral resolution.

In the next section we address in more detail the model of a degenerate pump-probe experiment and the system response. We refer the reader to the following references for complementary details on pump-probe principles and applications [34–38].

3.2. Pump-probe scalar model

We will now take a look at the theoretical description of degenerate pump-probe spectroscopy [34, 39–42] and demonstrate that the instrument response function depends on the pump and the probe durations. Let us consider an electric field $V(t, z)$ passing through a sample with thickness L and an absorption coefficient α [39, 43]. Let us also consider that the electric field varies along the propagation direction according to the following differential equation:

$$\frac{\partial V(t, z)}{\partial z} = -\frac{\alpha}{2} V(t, z). \quad (3.1)$$

Assuming that the electric field propagates through the sample from $z = 0$ to $z = L$, the solution of equation (3.1) gives

$$V(t) = V_0(t) e^{-\alpha L/2}, \quad (3.2)$$

or, writing in a different notation,

$$V_{\text{out}}(t) = V_{\text{in}}(t) e^{-\alpha L/2}, \quad (3.3)$$

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where $V_{\text{out}}(t)$ and $V_{\text{in}}(t) = V_0(t)$ are the output ($z = L$) and input ($z = 0$) fields, respectively. The complex modulus of equation (3.3) is the well known Lambert's law [44].

Let us now assume that the absorption coefficient is time-dependent such that,

$$\alpha(t) \equiv \alpha_0 + \Delta\alpha(t), \quad (3.4)$$

where α_0 is a constant absorption coefficient and $\Delta\alpha(t)$ is a time-dependent absorption variation. This change in the optical absorption we consider small ($\Delta\alpha(t) \ll \alpha_0$) but not negligible, and is caused by an external perturbation in the sample. We can write $\Delta\alpha(t)$ as [34, 41]

$$\Delta\alpha(t) = - \int_{-\infty}^t B(t') h(t - t') dt', \quad (3.5)$$

where $h(t)$ is the impulse response function of the sample to the external perturbation $B(t)$. The minus sign before the integral is interpreted as a positive response of the sample as a decrease in the absorption.

In the context of pump-probe spectroscopy, $V_{\text{in}}(t)$ and $V_{\text{out}}(t)$ of equation (3.3) are the electric fields of the probe pulse at $z = 0$ and $z = L$, respectively. In turn, $\Delta\alpha(t)$ is assumed to be caused by the pump pulse. This means we are assuming that the pump pulse is significantly more intense than the probe pulse i.e., $I_{\text{pump}}(t) \gg I_{\text{probe}}(t)$. Thus, we can rewrite equation (3.5) as

$$\Delta\alpha(t) = - \int_{-\infty}^{+\infty} I_{\text{pump}}(t') h(t - t') dt', \quad (3.6)$$

where $I_{\text{pump}}(t')$ is defined as

$$I_{\text{pump}}(t') = |V_{\text{pump}}(t')|^2 \quad (3.7)$$

and equation (3.4) becomes

$$\alpha(t) \equiv \alpha_0 - \int_{-\infty}^{+\infty} I_{\text{pump}}(t') h(t - t') dt'. \quad (3.8)$$

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Substituting equation (3.4) into equation (3.3) for probe, we have

$$V_{\text{probe,out}}(t) = V_{\text{probe,in}}(t) \exp \left[-\frac{L}{2} \alpha(t) \right]. \quad (3.9)$$

At this point, it is important to remember that in pump-probe spectroscopy we measure the transmitted probe with a slow detector. In other words, we measure the total intensity of the probe signal, and from equation (2.14) of Chapter 2 we can write the transmitted probe intensity as

$$I_{\text{probe,out}} = \int_{-\infty}^{+\infty} V_{\text{probe,out}}(t) V_{\text{probe,out}}^*(t) dt. \quad (3.10)$$

Substituting equation (3.9) into equation (3.10), we have

$$I_{\text{probe,out}}(\tau) = \int_{-\infty}^{+\infty} |V_{\text{probe,in}}(t + \tau)|^2 \exp[-L\alpha(t)] dt. \quad (3.11)$$

Notice that, now the intensity of the transmitted probe depends on the time variable τ , which here represents a time delay between the incident pump and probe beams. If we expand the exponential term to the first order, we obtain

$$I_{\text{probe,out}}(\tau) = \int_{-\infty}^{+\infty} |V_{\text{probe,in}}(t + \tau)|^2 [1 - L\alpha(t)] dt. \quad (3.12)$$

Substituting equation (3.8) into equation (3.12) gives

$$I_{\text{probe,out}}(\tau) = \int_{-\infty}^{+\infty} |V_{\text{probe,in}}(t + \tau)|^2 \left[1 - L\alpha_0 + L \int_{-\infty}^{+\infty} I_{\text{pump}}(t') h(t - t') dt' \right] dt. \quad (3.13)$$

We can write equation (3.13) in a more convenient form

$$I_{\text{probe,out}}(\tau) = (1 - L\alpha_0) \int_{-\infty}^{+\infty} I_{\text{probe,in}}(t + \tau) dt + L\gamma(\tau), \quad (3.14)$$

where

$$I_{\text{probe,in}}(t + \tau) = |V_{\text{probe,in}}(t + \tau)|^2, \quad (3.15)$$

and applying the associative and comutative properties of convolution, we define $\gamma(\tau)$ as

3. Ultrafast time-resolved spectroscopy

$$\gamma(\tau) = \int_{-\infty}^{+\infty} h(\tau - t) \left[\int_{-\infty}^{+\infty} I_{\text{probe,in}}(t') I_{\text{pump}}(t - t') dt' \right] dt, \quad (3.16)$$

which represents the convolution between the pump and probe pulses convoluted with the sample's response function. Note that, in degenerate pump-probe, the second integral of $\gamma(\tau)$ in equation (3.16) is simply the intensity autocorrelation (see Section 2.6.2) and using equation (2.45), we can write

$$\gamma(\tau) = \int_{-\infty}^{+\infty} h(\tau - \tau') G(\tau') d\tau'. \quad (3.17)$$

The $\gamma(\tau)$ is now a convolution between the material's response function $h(\tau)$ and the instrument response function $G(\tau)$ - as represented in Figure 3.3. This means that the intensity autocorrelation of the pump and probe pulses ultimately defines the temporal resolution of the measurement of $h(\tau)$. If, however, the temporal characteristics of $G(\tau)$ are much shorter than that of $h(\tau)$, then we may say that $\gamma(\tau)$ is approximately the material response function, i.e.,

$$\gamma(\tau) \approx h(\tau). \quad (3.18)$$

This model is useful in understanding the acquired signal in a pump-probe experiment. However, it does not contain another feature that, in practice, can also be present - the so-called 'coherent artefact' [40, 45]. Using a more general model [40], equation (3.14) will turn out to be

$$I_{\text{probe,out}}(\tau) = (1 - L\alpha_0) \int_{-\infty}^{+\infty} I_{\text{probe,in}}(t + \tau) dt + L [\gamma(\tau) + \beta(\tau)], \quad (3.19)$$

where $\beta(\tau)$ is the coherent artefact given by

$$\beta(\tau) = \int_{-\infty}^{+\infty} V_{\text{pump}}^*(t - t') V_{\text{probe,in}}(t') dt \int_{-\infty}^{+\infty} h(t - t') V_{\text{probe,in}}^*(t') V_{\text{pump}}(t - t') dt'. \quad (3.20)$$

If we measure only the difference in intensity, $\Delta I_{\text{probe,out}}(\tau)$, we are left with two terms, $\gamma(\tau)$ and $\beta(\tau)$, i.e.,

$$\Delta I_{\text{probe,out}}(\tau) = L [\gamma(\tau) + \beta(\tau)]. \quad (3.21)$$

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The coherent artefact can be ‘non negligible’ when the pump pulse falls into the probe direction after passing the sample, due to scattering for example. Thus, $\beta(\tau)$ is only non-zero when both the pump and probe pulses are temporally overlapped. Therefore, it only lasts for small delays of the order of the pump (or probe) pulse width. In a non-degenerate configuration, where the pump and probe beams do not spectrally overlap, this term vanishes.

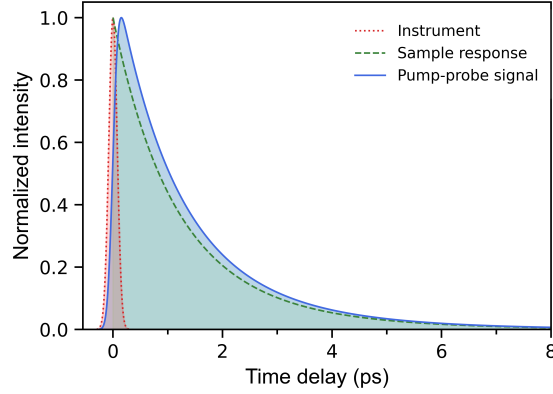


Figure 3.3.: Representation of the autocorrelation function, the sample response function, and the pump-probe signal.

3.2.1. Pump modulation

Let us now consider that the pump beam is modulated by a chopper that is connected to lock-in amplifier, we can replace $V_{\text{pump}}(t)$ in equation (3.19) by $V_{\text{pump}}(t) M(t)$, where $M(t)$ is the modulation function of the pump beam with values 0 or 1 such that $M^2(t) = M(t)$. With this change, equation (3.14) becomes

$$\begin{aligned}
 I_{\text{probe,out}}(\tau) = & (1 - L\alpha_0) \int_{-\infty}^{+\infty} |V_{\text{probe,in}}(t + \tau)|^2 dt, \\
 & + L \int_{-\infty}^{+\infty} h(\tau - t) \left[\int_{-\infty}^{+\infty} |V_{\text{probe,in}}(t)|^2 M(t - t') |V_{\text{pump}}(t - t')|^2 dt' \right] dt, \\
 & + L \int_{-\infty}^{+\infty} M(t - t') V_{\text{pump}}^*(t - t') V_{\text{probe,in}}(t') dt \\
 & \times \int_{-\infty}^{+\infty} h(t - t') V_{\text{probe,in}}^*(t') V_{\text{pump}}(t - t') M(t - t') dt'. \tag{3.22}
 \end{aligned}$$

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The lock-in amplifier will only retrieve the ‘modulated terms’, which in this case is the second and third terms. We will denote the lock-in amplifier retrieved intensity³ as $I_L(\tau)$, which gives

$$I_L(\tau) = L[\gamma(\tau) + \beta(\tau)], \quad (3.23)$$

where we made the substitution $M(t) = 1$. Thus, the lock-in amplifier will only retrieve equation (3.21). This is extremely useful since usually $\gamma(\tau)$ is very small when compared to the input intensity of the probe. Nevertheless, one has to be careful since the coherent artefact $\beta(\tau)$ can also be present in the signal. In what follows, we will ignore the presence of this artefact, unless stated otherwise.

3.2.2. Differential transmission

Ultimately, from a pump-probe experiment, we want to measure the differential transmission ΔT ,

$$\Delta T(\tau) = I_{\text{probe}}^{\text{pump,on}}(\tau) - I_{\text{probe}}^{\text{pump,off}}(\tau), \quad (3.24)$$

where I_{probe} is the total intensity (see equation 2.14) of the probe pulse transmitted through the sample, which we can write in arbitrary units as

$$I_{\text{probe}} = \int_{-\infty}^{+\infty} |V_{\text{probe}}(t)|^2 dt. \quad (3.25)$$

Although, we typically express the signal as a normalised differential transmission,

$$\frac{\Delta T}{T_0}(\tau) = \frac{[I_{\text{probe}}^{\text{pump,on}}(\tau) - I_{\text{probe}}^{\text{pump,off}}(\tau)]}{I_{\text{probe}}^{\text{pump,off}}(\tau)}, \quad (3.26)$$

to reduce baseline contribution and to take into account probe intensity alterations, making results more comparable between experiments.

Consider the intensity measured by the probe detector in equation (3.14). To calculate ΔT , we first need to calculate the intensity without the contribution of the pump. This

³Note that the lock-in amplifier returns a voltage and so we are assuming that we are already converting to units of intensity the retrieved signal.

3. Ultrafast time-resolved spectroscopy

is easily done by setting $\gamma(\tau) = 0$ in equation (3.16), which gives

$$I_{\text{probe}}^{\text{pump,off}}(\tau) = (1 - L\alpha_0) \int_{-\infty}^{+\infty} I_{\text{probe}}(t) dt, \quad (3.27)$$

Substituting equations (3.27) and (3.14) into (3.24), we have that

$$\Delta T(\tau) = L \int_{-\infty}^{+\infty} h(\tau - t) dt \int_{-\infty}^{+\infty} I_{\text{pump}}(t') I_{\text{probe}}(t - t') dt', \quad (3.28)$$

and, therefore, we have that

$$\Delta T \propto I_L(\tau). \quad (3.29)$$

Therefore, we can say that the lock-in amplifier measures the differential transmission ΔT when the pump beam is being modulated.

3.3. Data analysis model

As we saw in Section 3.2.1, the pump-induced changes in the transmitted probe corresponds to the convolution of the response function of the sample, $h(\tau)$, and the cross-correlation function $G(\tau)$. Assuming that the lock-in amplifier measures the portion of the probe beam that is being modulated by the pump, the signal $\Delta T(\tau)$ measured by the lock-in amplifier is given by equation (3.28), i.e.,

$$\Delta T(\tau) = L \int h(\tau - \tau') G(\tau') d\tau', \quad (3.30)$$

where τ is the time delay between the pump and probe pulses and $G(\tau)$ is the intensity cross correlation between the pump and the probe pulses. By measuring both $G(\tau)$ and $\Delta T(\tau)$, we can retrieve the material response function $h(\tau)$. However, in some cases, we already know in advance the behaviour of $h(\tau)$ (i.e., the sample's response), but lack information on its parameters. In what follows, we will introduce a model for $h(\tau)$ which is commonly employed when performing pump-probe in semiconductor samples [46].

The most common model for the response function $h(\tau)$ of solid state samples is described by a double decay exponential model [47],

$$h(\tau) = A_1 \exp\left(-\frac{\tau}{\tau_1}\right) + A_2 \exp\left(-\frac{\tau}{\tau_2}\right), \quad (\tau \geq 0), \quad (3.31)$$

3. Ultrafast time-resolved spectroscopy

where A_1 and A_2 are constants and τ_1 and τ_2 are lifetimes. Usually, τ_1 is defined as the shorter lifetime, while τ_2 is longer. If $G(\tau)$ was much shorter than the material response $h(\tau)$, then equation reduces to

$$\Delta T(\tau) = A'_1 \exp\left(-\frac{\tau}{\tau_1}\right) + A'_2 \exp\left(-\frac{\tau}{\tau_2}\right), \quad (3.32)$$

where the constants are now $A'_1 = LA_1$ and $A'_2 = LA_2$. If that is not the case, then we need to take into consideration the intensity correlation of the pump and probe pulses. Let us address this next by considering two simple Gaussian pulses.

Let the intensity of the pump and probe pulses, $I_p(t)$ and $I_t(t)$, respectively, be describe by Gaussian functions as shown in equation (2.27). Thus, we can write the intensity of the pump and probe pulses, respectively, as

$$I_p(t) = a_p \exp\left(-\frac{t^2}{\tau_p^2}\right), \quad (3.33)$$

$$I_t(t) = a_t \exp\left(-\frac{t^2}{\tau_t^2}\right), \quad (3.34)$$

where a_p and a_t are positive constants and $\tau_p(t)$ and $\tau_t(t)$ are the temporal phases of the pump and probe pulses, respectively. The convolution $G(t)$ (see Appendix A.1) is given by

$$G(\tau) = B \exp\left(-\frac{\tau^2}{\tau_c^2}\right), \quad (3.35)$$

where B is a positive constant and τ_c is the ‘duration’ of the intensity cross-correlation of the pump and probe beams. Thus, substituting equations (3.35) and (3.31) into (3.30), and performing some calculations (see Appendix A.2), we arrive at the solution

$$\begin{aligned} \Delta T(\tau) = & A'_1 \exp\left(-\frac{\tau}{\tau_1}\right) \left[1 - \operatorname{erf}\left(\frac{\tau_c}{2\tau_1} - \frac{\tau}{\tau_c}\right)\right] \\ & + A'_2 \exp\left(-\frac{\tau}{\tau_2}\right) \left[1 - \operatorname{erf}\left(\frac{\tau_c}{2\tau_2} - \frac{\tau}{\tau_c}\right)\right], \end{aligned} \quad (3.36)$$

where erf is the error function. We fit equation (3.36) to the experimental values. Figure 3.4(a) show the impact of τ_c on the $\Delta T(\tau)$. We can observe that the determination of τ_2 is not significantly affected if $\tau_2 \gg \tau_c$. However, that is not the case for τ_1 , since it could be of the order of magnitude of τ_c . In addition, as one can observe in Figure 3.4(b), a variation in τ_1 for the same τ_c also causes a variation in the maximum amplitude of the

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signal. Thus, τ_c should be as small as possible. To do that, one needs to fully compress the pump and probe pulses as much as possible.

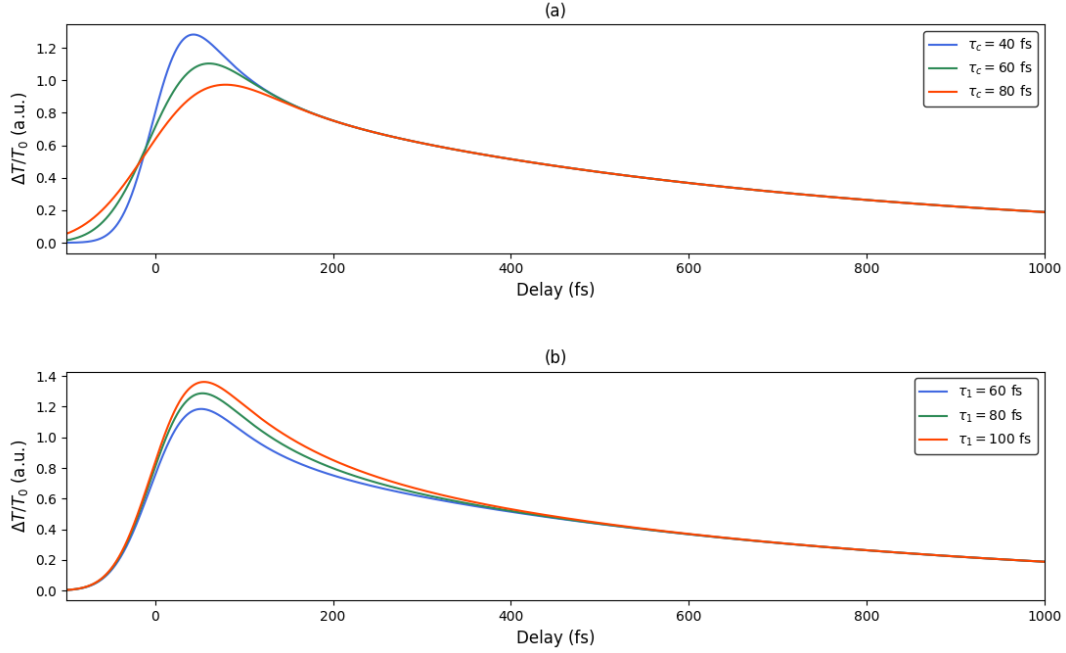


Figure 3.4.: $\Delta T(\tau)$ response for different values of τ_c and τ_1 . (a) Variation of the τ_c for $A_1, A_2 = 0.5$, $\tau_1 = 60$ fs and $\tau_2 = 600$ fs. (b) Variation of τ_1 for $A_1, A_2 = 0.5$, $\tau_c = 50$ fs and $\tau_2 = 600$ fs.

3.4. Key conclusions

We have discussed the theory and applications of ultrafast pump-probe spectroscopy. As a summary, we have listed the highlights of this chapter below.

- (i) Ultrafast optical pump-probe spectroscopy is used to investigate dynamical phenomena on the order of a few picoseconds or less.
- (ii) The pump pulse induces a change in the sample and the probe pulse records the resulting change as a function of the time delay between the pump and the probe itself.
- (iii) In the case of transmission configuration, where we measure the differential transmission of the sample, we can typically study the following responses: ground-state bleaching, excited-state absorption, and stimulated emission.

3. *Ultrafast time-resolved spectroscopy*

- (iv) The study of excited-state absorption or stimulated emission requires a non-degenerate pump-probe system.
- (v) The temporal resolution of a pump-probe experiment is given by the cross-correlation between the pump and the probe pulses (i.e., the cross-correlation of their intensity profiles at the sample plane).
- (vi) The pump-probe signal is described by the convolution between the pump and probe cross-correlation and the sample response (typically a single or a multi-exponential decay function).
- (vii) Some of the direct applications of pump-probe spectroscopy include studying carrier relaxation pathways and timescales in molecular or solid-state materials.

4. Graphene

In this chapter we address graphene, giving a brief overview of its synthesis by chemical vapour deposition. We will also discuss some of its optical properties. Note that we will use the term ‘graphene’ when referring to single-layer graphene and analogues (e.g., bilayer graphene). We will use specific terminology whenever we need to be more specific regarding the graphene ‘type’.



4.1. Introduction

Graphite is a bulk form of carbon with sp^2 hybridisation. It consists of stacked sheets of carbon atoms arranged in a hexagonal lattice. Each of these individual sheets is known as graphene [48–50], as presented in Figure 4.1 (a).

Graphene has a long (and somewhat controversial) history [50–52]. The discovery of the graphite structure dates back to 1924, supported in part by progress in X-ray diffraction technique. The band structure of graphite was developed later in 1947 by Philip Wallace [53] based on the tight-binding approximation, where he considered the properties of a ‘single layer of graphite’. Back then, the definition of graphene did not yet exist, appearing much later [54]. From the theoretical predictions, a single layer of graphite would exhibit an exceptional conductivity, far greater than inter-layer conductivity. Although theoretically predicted as a 2D material, graphene was believed to be thermodynamically unstable [49] and thus difficult to isolate experimentally [52, 55]. Despite this, experimental attempts were made to synthesise it, trying to confirm its presence. In 2004, Andre Geim

4. Graphene

and Konstantin Novoselov succeeded and reported a very simple way to obtain graphene - by micromechanical cleavage [48]. A top-down approach that uses adhesive tape to, step-by-step, separate graphene layers from a piece of bulk graphite until a single one remains. Once synthesised, graphene captured the attention of the scientific community right away. Soon, its outstanding predicted properties were experimentally confirmed. Graphene holds unique properties such as high electrical and thermal conductivity, exceptional mechanical strength and flexibility, and optical absorption in a broad spectral range. It has high biocompatibility and proved to be suitable for chemical functionalisation [56]. Thus, it is a material with potential for many applications in several different fields [57,58]. Regarding optoelectronics, it has been explored for the development of transistors [59], high-speed photodetectors [60], supercapacitors [61], solar cells [62], and biosensors [63].

Theoretical and experimental research in graphene and related materials is still very active. One of the properties that has been currently explored is the graphene layering structure. Layer stacking (meaning the stacking angle and the interlayer distance) can considerably change the electronic properties of graphene [50]. We can refer to this graphene as "twisted graphene", when it presents a structure where the stacked layers are rotated at a specific (known) angle relative to each other.

As part of this work we will study the ultrafast carrier dynamics of graphene. The development of novel and faster electronics relies on these measurements [64,65].

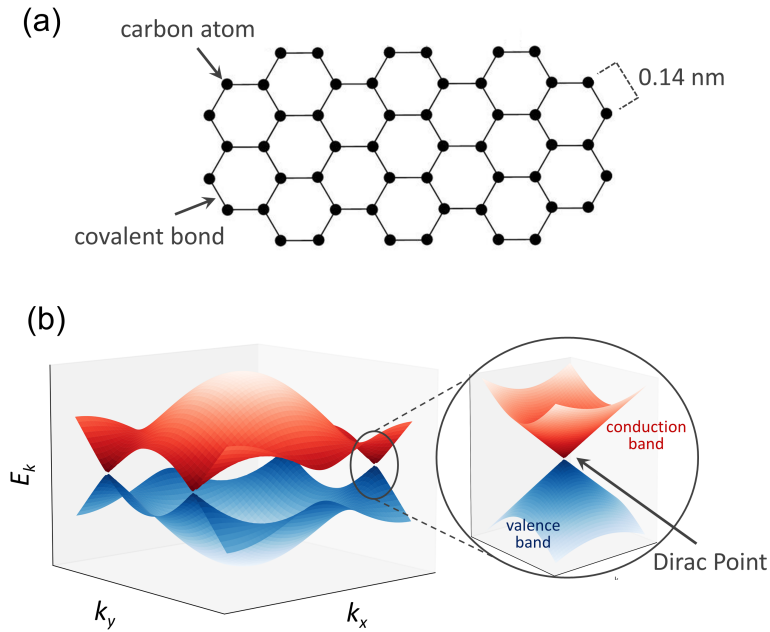


Figure 4.1.: Representation of single-layer graphene (a) crystal structure and (b) band structure and the Dirac cone.

4.2. Graphene synthesis

The effective application of graphene in the development of new devices requires a viable, efficient and, cost-effective way to produce it. In particular, for photonics and optoelectronic applications, high-quality graphene (i.e., low amount of defects in the crystal lattice) is typically required [56, 66–68]. There are several methods [69] by which graphene and graphene derivatives (e.g., multilayer graphene, graphene oxide, reduced graphene oxide, and graphene flakes) can be synthesised, as illustrated in Figure 4.2. Some of these methods are more suitable when looking for ‘pristine’ samples, such as mechanical exfoliation, silicon carbide growth, or chemical vapour deposition (CVD) [69]. By mechanical exfoli-

Table 4.1.: Comparison of different preparation methods of graphene: mechanical exfoliation, SiC thermal decomposition, Reduction of graphene oxide (GO) and CVD. Adapted from [70].

Graphene synthesis	Mechanical exfoliation	SiC thermal decomposition	CVD	Reduction of GO
Advantages	Highly crystalline graphene is obtained by a simple process	It is possible to fabricate devices directly on SiC wafer	Suitable for low-cost and large area production; transfer is easy	Wet process is applicable and suitable for bulk applications
Disadvantages	Small size; shape and layer number are not uniform	Expensive SiC crystalline substrate; graphene transfer is difficult	Use of metal catalysts; usually high temperature is required	Difficult to completely reduce GO; many defects

ation one can have a pristine single-layer graphene, however the method is not suitable for large-scale fabrication [71] and it is mostly used for research purposes. Synthesis by silicon carbide reduction results in high-quality epitaxial graphene, but the production costs are typically high. The CVD [72, 73] is one of the most suitable techniques considering industrial requirements since it has potential for scalability. It offers a good trade-off between graphene quality, yield and reproducibility. Conventional CVD approaches, such as thermal CVD, require high temperature (i.e., on the order of 1000 °C) [70, 74]. Although it allows a large area to be produced, the process can be quite long. It typically requires a temperature ramping time, a long growth time, and long cooling time. Other CVD-based methodologies have been investigated as an alternative for lower temperature synthesis. An alternative technique is the microwave plasma chemical vapour deposition (MPCVD) [75]. This method is represented in Figure 4.3 and was used to synthesise the

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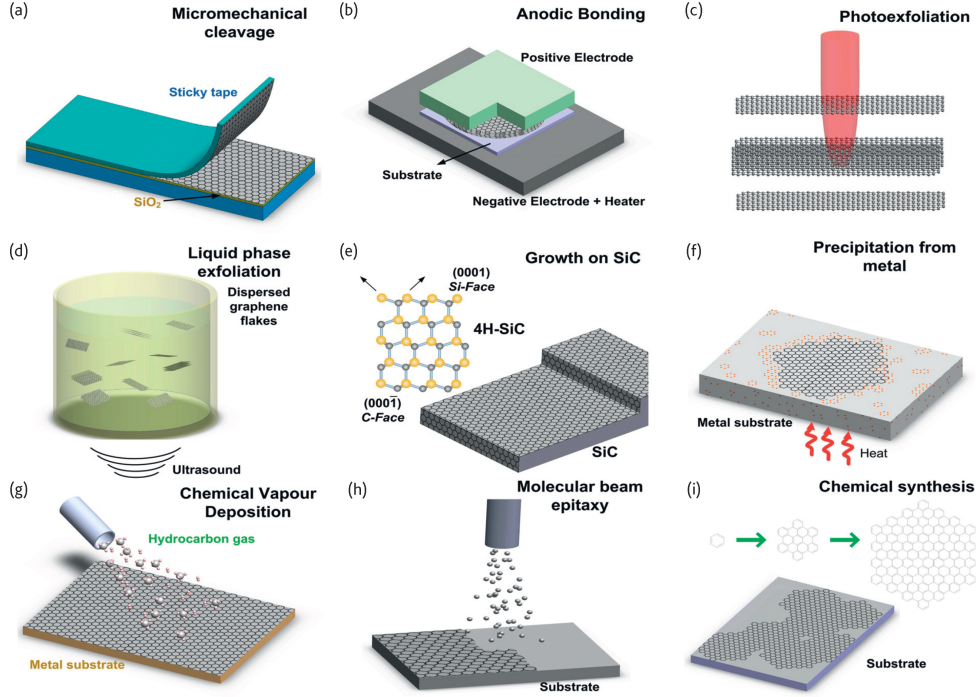


Figure 4.2.: Types of graphene synthesis: (a) micromechanical cleavage; (b) anodic bonding; (c) photoexfoliation; (d) liquid phase exfoliation; (e) growth on silicon carbide; (f) precipitation from metal; (g) CVD; (h) molecular beam epitaxy; (i) chemical synthesis. Graphene samples used in this work were synthesized by CVD as schematically illustrated in (g). Reproduced from [73].

graphene samples studied in this work. Independent of the type, CVD growth conditions are also important for the graphene's domain structure and determines if the graphene is polycrystalline (i.e., with domain boundaries) or single crystalline, as represented in Figure 4.4. The presence of this defect can be estimated, for example, by Raman spectroscopy.

4.3. Methods for structural and morphological characterisation

Raman spectroscopy is one of the most widely used techniques for characterising graphene [77]. It is difficult to find an experimental article related to graphene where this characterisation technique is not present. This analytical technique is non-destructive and allows us to estimate the number of layers from single-layer to few-layer graphene. In the case of few-layer and multilayer, the estimation may not be reliable, particularly if the graphene layers are randomly rotated with respect to each other instead of presenting a typical stacking (see Figure 4.5). Thus, for these cases, Raman results should be combined with data from other techniques, such as UV-Visible spectroscopy. Raman is especially

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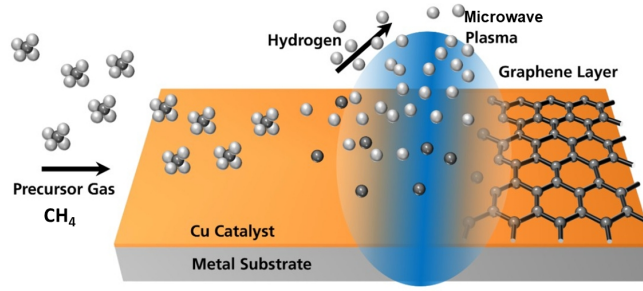


Figure 4.3.: Scheme of the MPCVD synthesis process for graphene. Adapted from (Fraunhofer FEP).

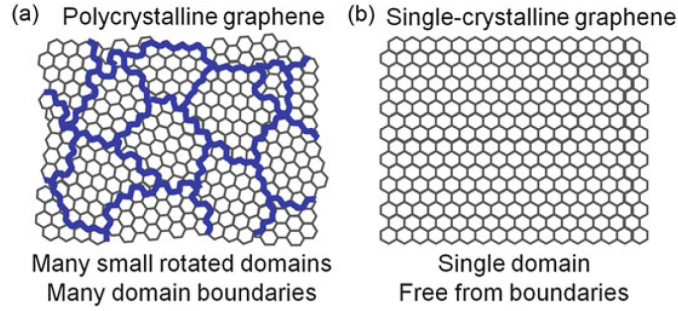


Figure 4.4.: Domain structures of graphene observed for CVD synthesis. (a) Representation of polycrystalline graphene. (b) Representation of single-crystalline graphene. Reproduced from [70].

useful for detecting the presence and the type of defects in the crystal lattice.

Scanning electron microscope (SEM) is useful to investigate the morphology of graphene films. It is particularly useful for detecting wrinkles, small cracks and holes due to damages during graphene transfer to a substrate, such as silicon carbide or quartz. It is used to identify types of defects, such as grain boundaries or absence of atoms in the crystal lattice.

4.4. Graphene optical properties

It is known that a single layer of graphene absorbs around 2.3% of the light in the visible to near-infrared spectrum [79]. This absorption is not influenced by rotation or small lattice defects and thus can be used as a fast and reliable way to quantify the number of layers in graphene samples, as shown in Figure 4.6. The transmission spectrum of graphene is not only relevant to estimate the thickness, it is also useful to estimate the number of generated excited carriers in graphene after ultrashort pulse excitation. If we assume that the system is comprised of graphene and a substrate (e.g., quartz plate) and is considered

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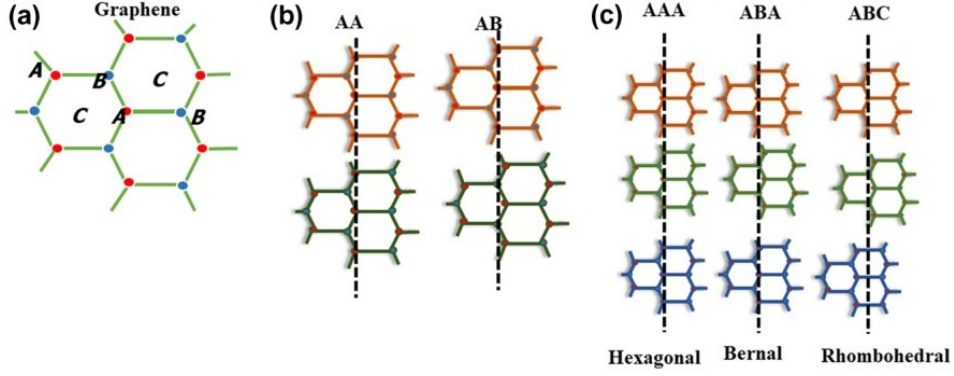


Figure 4.5.: Typical graphene stacking types. (a) Representation of the single-layer structure, A and B denote carbon sites. (b) Bilayer graphene stacking types, (c) Tri-layer graphene stacking types. Reproduced from [76].

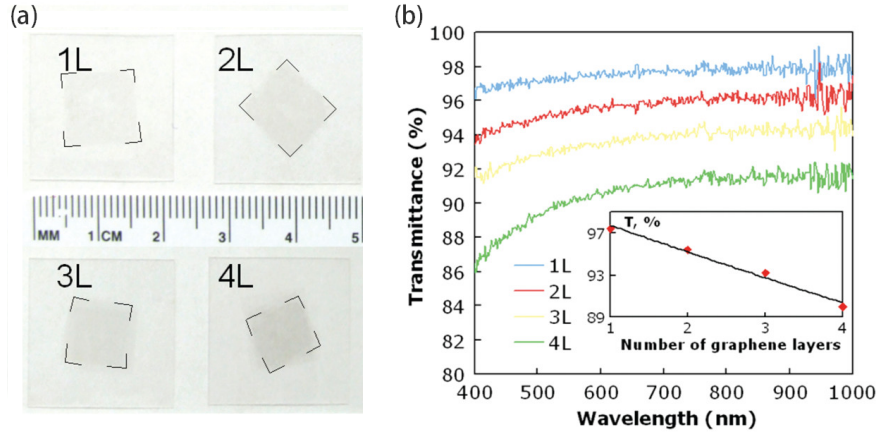


Figure 4.6.: Number of layers estimated by visible-NIR transmission spectroscopy. (a) Graphene samples with n number of layers L. Single-layer (1L), bilayer (2L), few-layer (3L, 4L) graphene. (b) Corresponding transmission spectroscopy. In the inset, the transmission at 550 nm as a function of the number of stacked graphene layers. Reproduced from [78].

a thin film, it can be shown that the transmission spectrum $T(\omega)$ is given by [80]

$$T(\omega) = \frac{S_{g+s}(\omega)}{S_g(\omega)} = |1 + N\sigma(\omega)Z_0 / (n_s(\omega) + 1)|^{-2}, \quad (4.1)$$

where $\sigma(\omega)$ is the optical conductivity, N is the number of layers, $n_s(\omega)$ is the refractive index of the substrate and Z_0 is the impedance in vacuum. The optical conductivity of monolayer graphene is given by

$$\begin{aligned} \Re\{\sigma(\omega)\} &= \frac{4k_B T_a \sigma_q \gamma}{\pi \hbar (\omega^2 + \gamma^2)} \left\{ \ln \left[1 + \exp \left(\frac{E_F^h}{k_B T_a} \right) \right] + \ln \left[1 + \exp \left(\frac{E_F^e}{k_B T_a} \right) \right] \right\} \\ &+ \frac{1}{2} \left[\tanh \left(\frac{\hbar \omega + 2E_F^e}{4k_B T_a} \right) + \tanh \left(\frac{\hbar \omega - 2E_F^e}{4k_B T_a} \right) \right], \end{aligned} \quad (4.2)$$

4. Graphene

where $\gamma = 1/\tau_m$ is the scattering rate, τ_m is the momentum scattering time, k_B is the Boltzmann constant, T_a is the absolute temperature, E_F^e and E_F^h are the electron and hole Fermi energy, respectively, σ_q is the universal quantum conductivity given by

$$\sigma_q = \frac{\pi e^2}{2h}. \quad (4.3)$$

The number of photoexcited carriers at a given wavelength λ can be calculated using

$$N_{\text{ex}}(\lambda) = N_{\text{ph}}(\lambda) \left[1 - 10^{-A(\lambda)} \right], \quad (4.4)$$

where N_{ph} is the number of photons and $A(\lambda)$ is the absorbance of the sample. Thus, integrating equation (4.4) with respect to λ yields the total number of carriers excited by a pump pulse, i.e.,

$$N_{\text{ex,pump}} = \int_{\lambda_1}^{\lambda_2} N_{\text{ph}}(\lambda) \left[1 - 10^{-A(\lambda)} \right] d\lambda \quad (4.5)$$

We will use this result later on Section 7.4.

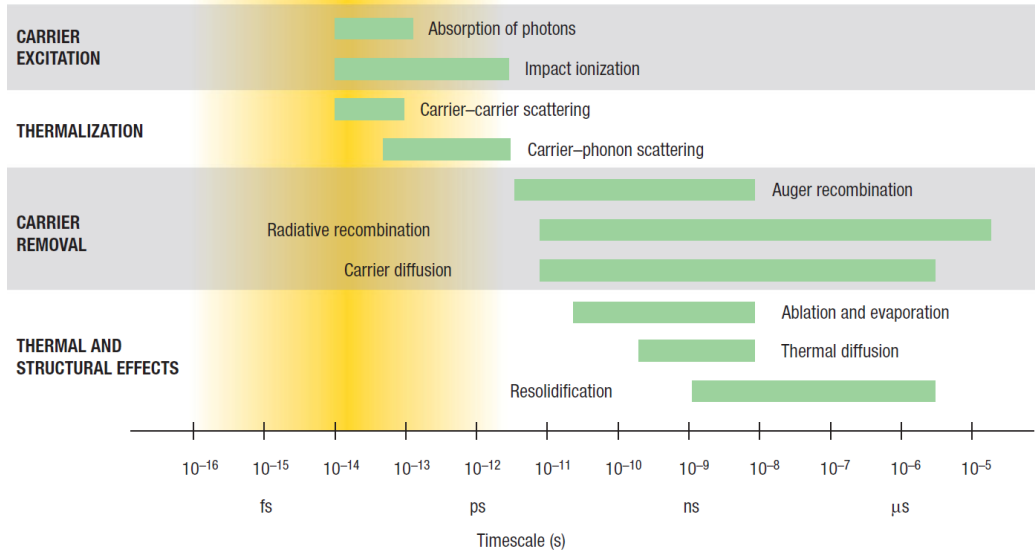


Figure 4.7.: Timescales of different electron and lattice processes in photoexcited solid state materials. The green bar represents an approximate range of characteristic times. In this work we focus on the regime highlighted in yellow. Reproduced from [81].

Graphene has optical ultrafast excitation and recovery responses, that typically happen under the picosecond and femtosecond regime (see Figure 4.7). As illustrated in Figure 4.8, following the excitation by an ultrashort laser pulse (process duration ~ 10 fs), the photo-generated carriers in graphene rapidly thermalise through the process of electron-electron

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scattering (process duration ~ 100 fs). This creates a hot electron distribution, which is characterised by a high electron temperature, while the lattice temperature remains the same. This is followed by energy transfer from the hot electron system to the graphene lattice, through electron-phonon scattering (process duration ≥ 1 ps). Pump-probe spectroscopy is typically used to experimentally study and track this ultrafast non-equilibrium dynamics of carriers in graphene [82]. Dawlaty et al. reported the first pump-probe experimental studies of carrier dynamics in graphene [83]. Several experiments have been performed on single-layer graphene [84, 85], multilayer graphene [86, 87] and other derivatives such as graphene oxide and functionalised graphene [88–91].

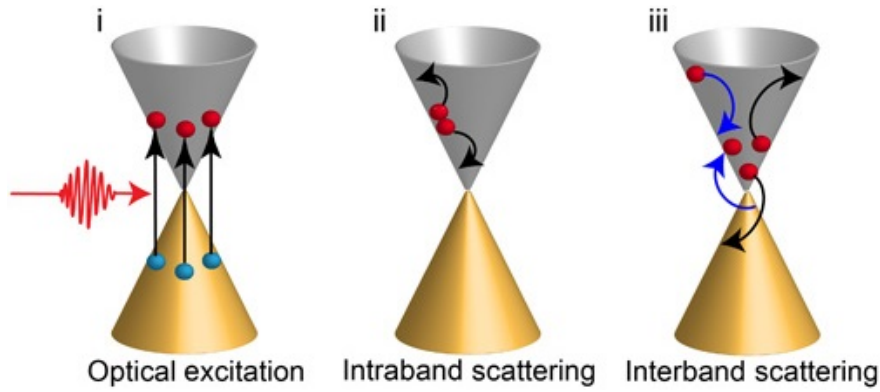


Figure 4.8.: Graphene response to optical ultrafast excitation. (i) Optical excitation of carriers. (ii) Intraband (e-e) scattering. (iii) Interband (e-ph) scattering. Reproduced from [92].

4.5. Key conclusions

This chapter reviewed the structure and properties of graphene, common synthesis methods, and standard characterisation techniques, providing the necessary background for the discussions presented in Chapter 7. We highlight the most relevant aspects below.

- (i) Graphene absorbs light over a very wide spectral range, from UV to far-infrared. In particular, it absorbs around 2.3% of the light in the visible to the near-infrared spectrum.
- (ii) CVD is a bottom-up method of producing graphene. The synthesis involves the deposition of carbon atoms, typically derived from gas precursors such as methane or ethylene, onto a substrate surface where they self-assemble into a graphene layer.
- (iii) Raman spectroscopy one of the most widely used techniques for studying graphene.

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It gives information about its structural properties such as the number of layers, presence of defects or clues regarding the stacking arrangement.

- (iv) Graphene presents an ultrafast response to optical excitation.

5. Materials and methods

This section covers the experimental work details, from the description of the equipment to the methodologies used. It is divided into four main parts: (i) graphene synthesis - where the synthesis of graphene by microwave plasma chemical vapour deposition is described; (ii) materials characterisation - which addresses the analytical techniques used to estimate the composition, structure and morphology of the samples; (iii) ultrafast laser sources - a section that describes the laser system that feeds the custom-built pump-probe setup; and (iv) pulse temporal characterisation - that covers the techniques used for the characterisation of the ultrashort laser pulses, in particular the d-scan technique. Although we provide details regarding the ultrafast laser source, specific details related to the pump-probe setup are not discussed here. This is because the construction of the pump-probe setup was by itself a goal (and a result) of this thesis and thus Chapter 6 is entirely dedicated to it.



5.1. Graphene synthesis

Chemical vapour deposition is a bottom-up method for the production of high-quality graphene [93, 94]. In particular, the microwave plasma chemical vapour deposition (MPCVD) is a technique where a high-purity gas under controlled plasma conditions is decomposed and deposited as a solid phase in a substrate [95]. In this work, the graphene samples were prepared at ‘Instituto de Nanoestruturas, Nanomodelação e Nanofabricação’ (i3N), Physics Department, University of Aveiro (Aveiro, Portugal) by MPCVD on copper

5. Materials and methods

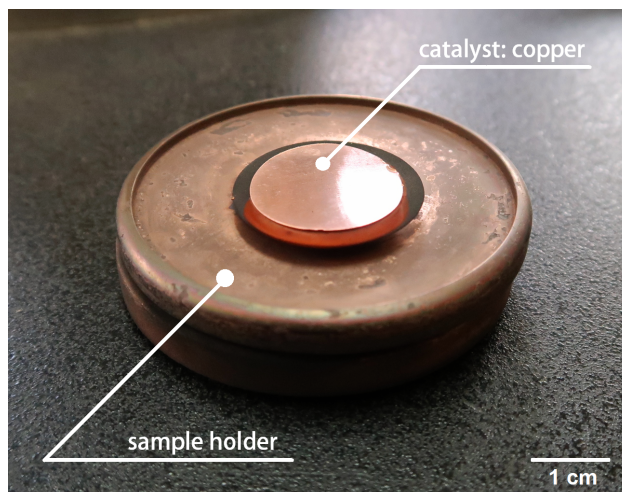


Figure 5.1.: Sample holder with a circular electrolytic copper (Cu) sheet for the synthesis of graphene by MPCVD. Copper was the metal catalyst used in the CVD process.

(Cu) substrates. For the preparation of the substrates, ~ 0.3 mm thick electrolytic Cu sheets were cut into circular pieces of 20 mm diameter, see Figure 5.1. The substrates were mechanically polished, finished with a commercial polishing suspension, and washed under sonication with high-purity acetone followed by high-purity isopropyl alcohol, for 15 minutes in each solvent. This pre-treatment helps to eliminate scratches and to remove oxide from the Cu sheets surface, aspects that otherwise could promote a preferential nucleation site during graphene's growth. The substrates were also oxidized in air over a heat-plate at 350°C for 20 seconds to remove any residual carbon contamination. For the CVD synthesis, the pre-treated Cu sheets were introduced in the chamber of an MPCVD ASTeX AX 6350 6 kW microwave max. power, which is presented in Figure 5.2. The CVD processes were carried out at 1100 W and at 28 Torr with a 4 minutes annealing step and an H_2 flow of 200 sccm. It was followed by the growth phase (or reaction phase) where a 25 sccm CH_4 flow was added to the gas mixture for 30 seconds to form the graphene sample labelled as A, 1 minute to form the sample B and 4 minutes to form the sample C, as schematised in Figure 5.3.

After synthesis, each graphene sample was transferred onto 1 mm thickness fused silica substrate (JGS2)¹, following a standard procedure previously reported [96] using a poly(methyl methacrylate) support layer (average molecular weight 550 000, Alfa Aesar, diluted to 4.5 wt% in anisole) obtained by spin coating. At the end, the prepared graphene samples on silica substrates have a minimum area of 80 mm^2 .

¹Note that this substrate is also referred in the literature as fused quartz JGS2 or quartz glass JGS2.

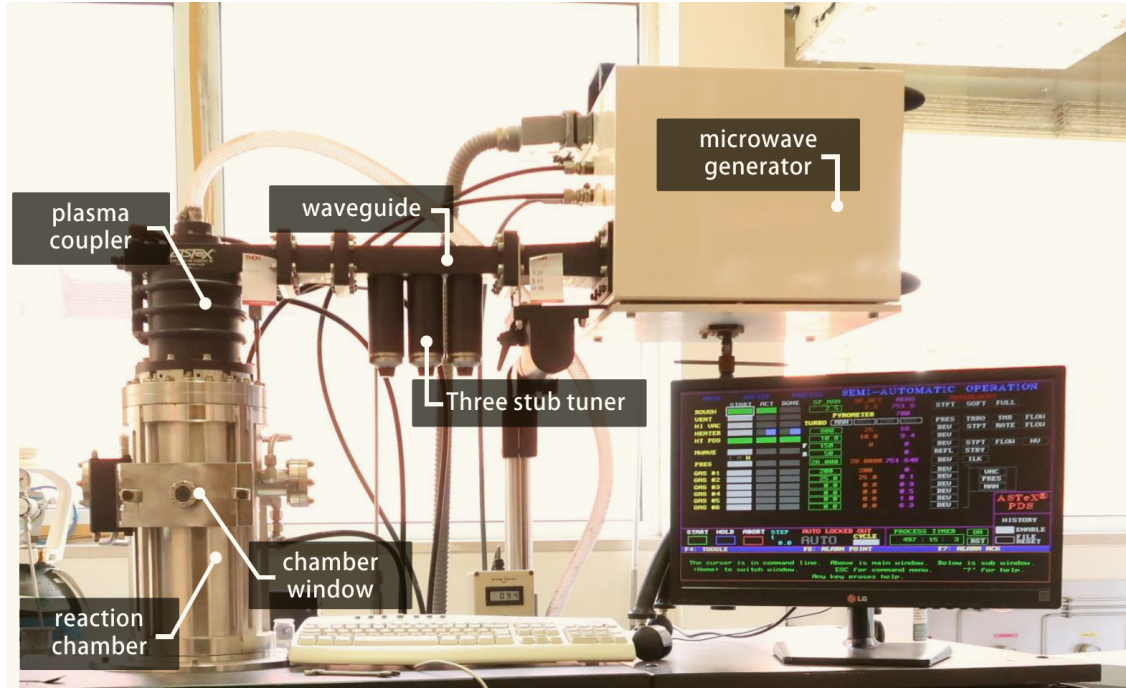


Figure 5.2.: Microwave plasma chemical vapour deposition equipment from i3N.

5.2. Physicochemical characterisation

All the graphene samples were characterised by visible to near-infrared (NIR) absorption spectroscopy and Raman spectroscopy. The analysis were performed at i3N, Physics Department, University of Aveiro (Aveiro, Portugal). The UV-NIR transmittance spectra were collected with a Shimadzu 3600UV spectrophotometer in the range of 200-1200 nm using a resolution of 1 nm. All spectra were corrected to the fused silica reference (fused silica is the substrate where our graphene samples are deposited). The micro-Raman analysis was performed at room temperature on a Jobin Yvon HR800 Raman spectrometer by Horiba, using a He-Cd laser at an excitation wavelength of 441.6 nm. An Olympus optical microscope with a 50 $\times$ objective lens was used to focus the laser beam on the sample and collect the backscattered Raman radiation to be detected by a CCD sensor. Raman spectra in several positions within the graphene area were taken to check the uniformity of the samples. All samples were observed under an optical microscope also to verify uniformity. Additionally, the morphology of the sample C was examined using a TESCAN VEGA 3 scanning electron microscope from i3N operating with an accelerating voltage of 5 kV and a FEI Quanta 400 ESEM FEG from Materials Centre from the University of Porto (CEMUP). For a detailed discussion of the results obtained from all these characterisations, we refer the reader to Section 7.2.

5. Materials and methods

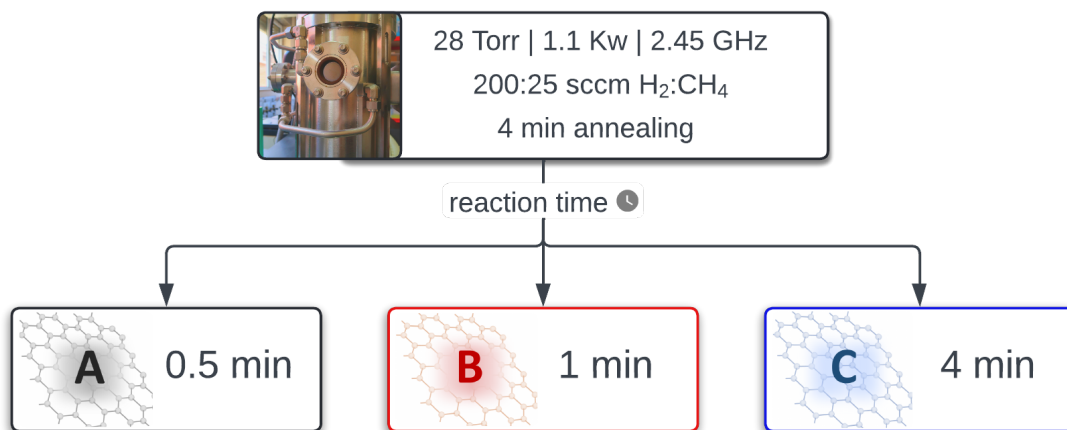


Figure 5.3.: Chemical vapour deposition parameters for the synthesis of samples A, B and C. For clarity, samples A, B, and C will be represented by the colours black, red, and blue, respectively, throughout this thesis.

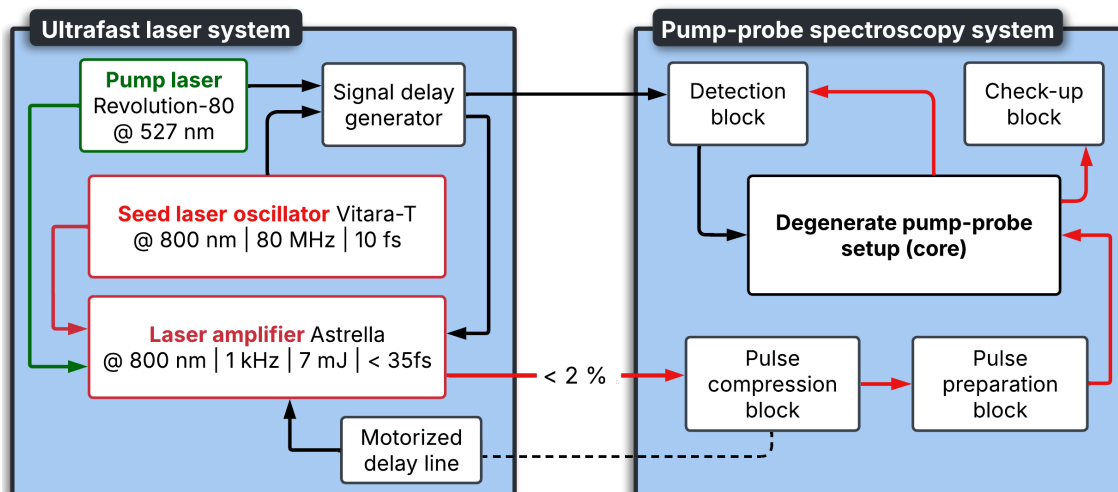


Figure 5.4.: Schematic block diagram representing the commercial system Astrella Ultrafast Laser Amplifier (on the left) and our constructed pump-probe spectroscopy system (on the right). The laser system includes the seed Vitara oscillator, the Revolution pump laser, and the main Ti:Sapphire laser amplifier that drives the pump-probe system. The signal-delay-generator is linked to the pump-probe setup to synchronise with a chopper. Pulse optical dispersion can be controlled by adjusting the motorised delay line or the pulse compression block. Details are given in Section 6.

5.3. Ultrafast laser sources

High-temporal resolution pump-probe spectroscopy relies on the use of ultrafast laser sources capable of generating femtoseconds to attosecond pulses. In this work, the laser system used to feed the custom-built pump-probe setup was a commercially available Ti:Sapphire laser amplifier (Astrella USP, Coherent) [97]. The laser system, schemat-

5. Materials and methods

ised in Figure 5.4, deliveries < 35 fs pulses with an energy of approximately 7 mJ at a repetition rate of 1 kHz and with a central wavelength of about 800 nm. Its spectrum is shown in Figure 5.5. Only a small fraction of the laser power ($< 2\%$) was directed towards the pump-probe setup. Inside the laser amplifier there is grating-based compressor system mounted on a 25 mm stepper motor translation stage. The motor stage can be controlled from the outside (KST201 K-Cube stepper motor controller, Thorlabs) and has a step resolution of about 0.1 μm allowing to pre-compensate for the group delay dispersion introduced by optical components of the pump-probe setup.

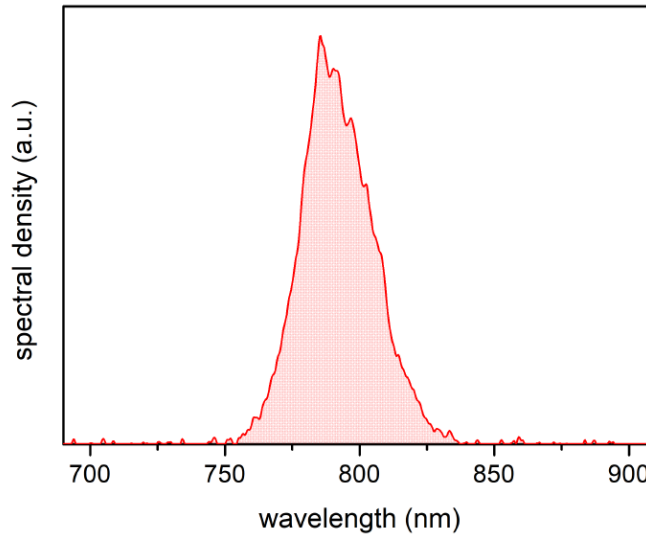


Figure 5.5.: Spectrum of the Astrella ultrafast laser amplifier, the laser source used in the degenerate pump-probe setup. The laser spectrum has a central wavelength of ~ 800 nm and a bandwidth of ~ 35 nm.

5.4. Pulse temporal characterisation

The temporal characterisation of the pump and probe ultrashort laser pulses was performed using the dispersion scan (d-scan) technique. The theory behind this technique is briefly addressed in Section 2.6.3. For the d-scan measurements, the grating system within the Astrella laser amplifier allowed the modification of optical dispersion as needed. In other words, it introduced spectral phase to the pulses to be characterised. This was done by using the KST201 K-Cube stepper motor controller which was connected to the d-scan software. For the SHG of the pump and the probe pulses we used a 100 μm type II BBO crystal. Each beam was focused in the BBO crystal through a 100 mm convex lens and the second-harmonic spectrum was measured using an AvaSpec36-48 spectrometer con-

nected to a single-mode optical fiber. The algorithm of the d-scan was then used for phase retrieval and consequently to estimate the pump and probe pulse durations. Through the information from the d-scan 2D traces, both the pump and the probe laser pulse quality were optimised to yield the best temporal resolution possible at the sample plane inside the pump-probe system. The d-scan software provides also additional information regarding the type of dispersion and the shape profile of the pulses. The results from the d-scan technique were compared to those obtained from a simple intensity autocorrelator. For intensity autocorrelation measurements the pump and probe beams were focused on the same BBO crystal creating a SHG. The probe beam was delayed relatively to the pump beam and the nonlinear signal resulting from the pump and probe temporal overlap was recorded as a function of the temporal delay using a photodiode (PDA100A, Thorlabs). For the results regarding pulse temporal characterisation we refer the reader to the Section [6.1.1](#).

5.5. Key conclusions

We have described the procedure for graphene preparation and characterisation. We also included a description of the femtosecond laser system that feeds our constructed pump-probe setup (which is presented in Chapter [6](#)) and the methods used for pulse duration measurement. As a summary, the key features of this chapter are listed below.

- (i) Graphene samples were prepared through a bottom-up method: microwave plasma chemical vapour deposition.
- (ii) Graphene samples were transferred to a silica glass substrate.
- (iii) The techniques used to investigate the structural properties of graphene were electronic spectroscopy, Raman spectroscopy, and scanning electron microscopy.
- (iv) The laser source feeding the constructed pump-probe setup is a commercial femtosecond laser amplifier delivering >35 fs duration pulses.
- (v) An intensity autocorrelator was applied to estimate the temporal resolution of the pump-probe system.
- (vi) The d-scan technique was also used to characterise the pump and probe pulses.

6. Ultrafast degenerate pump-probe system

In this chapter, we discuss the design and construction of the ultrafast degenerate pump-probe setup. We will explore the system¹ by looking at the specific blocks that compose it, for example, the pulse compressor block and the detection block. We will also address the signal processing and acquisition software. Finally, we performed some tests with the setup.



6.1. The optical system

The primary goal of this thesis was the development of an optical degenerate pump-probe system that could provide information on the ultrafast carrier dynamics in nanomaterials. In particular, we were interested in the study of graphene (Section 7.4). With that in mind and expecting that photoexcited carrier dynamics in graphene have rather fast dynamics² (i.e., on the order of hundreds of femtoseconds [64]), the instrument temporal resolution was in our case an important factor. In what follows, we will see how this optical setup was configured. Note that not all the components were initially proposed for this system. Several trade-offs between the best optical design, the instrument requirements, and the optical components available in the laboratory were made.

The constructed setup is depicted on Figure 6.1 and its main characteristics summarized in Table 6.2. It operates with the Ti:Sapphire laser amplifier (< 35 fs) that is described in

¹Throughout this thesis, we use the terms ‘pump-probe setup’ and ‘pump-probe system’ interchangeably to refer to the same experimental apparatus.

²Here, we are comparing graphene with other nanomaterials in general.

6. Ultrafast degenerate pump-probe system

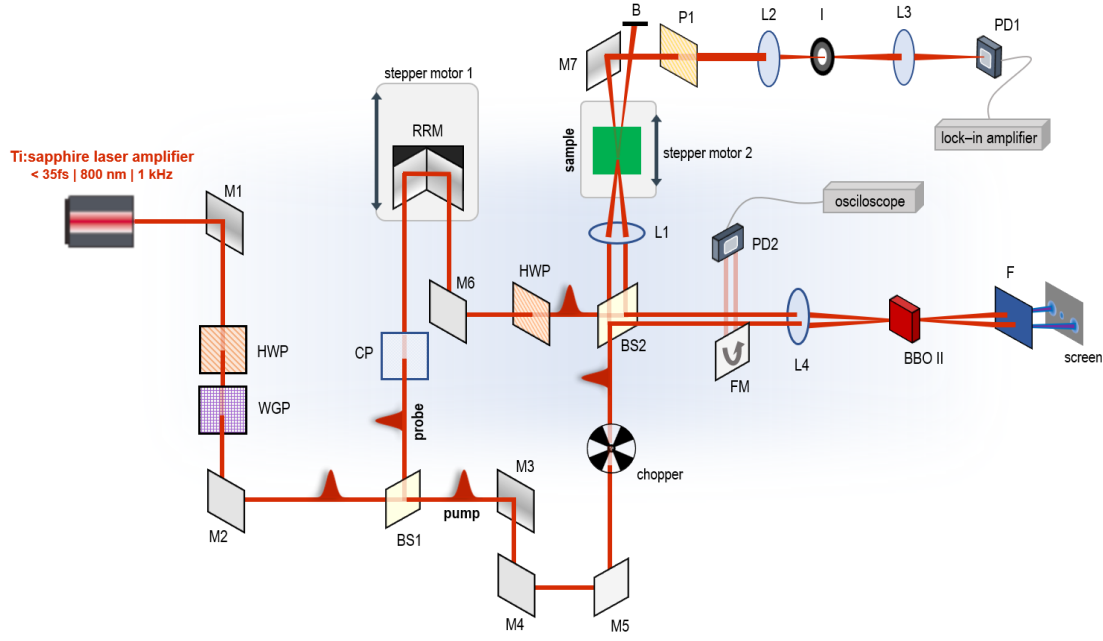


Figure 6.1.: Schematic representation of the custom-built degenerate optical pump-probe setup. A wire grid polariser cleans the polarisation of the ingoing beam. The beam is then divided into two replicas with different intensities, a pump beam (strong) and a probe beam (weak). Through a motorised delay stage, the probe is delayed by a time τ with respect to the pump. Moreover, the pump is modulated at half the repetition rate of the laser beam and the polarisation of the probe is set to be orthogonal to the pump. Both beams are then focused in the sample of interest and the probe is forwarded towards the detector. A polariser and a spatial filter ensure that the probe reaches the detector without the presence of any pump scattered. The transmission of the probe is recorded as a function of the pump and probe delay. Note that, while not shown in the figure, a chopper controller is linked to both the internal reference of the laser system and the lock-in amplifier and a pair of chirped mirrors are positioned before M1. B: blocker; BBO: β -Beta barium borate crystal; BD: beam dump; BS: beam-splitter; CP: compensation plate; F: filter; FM: flip mirror; HWP: half-wave plate; L: Lens; M: mirror; P: Polarizer; RRM: retroreflecting mirror; WGP: wire-grid polariser.

Section 5.3. The setup can be seen as composed by five main blocks: (i) pulse compression, (ii) pulse preparation, (iii) main setup, (iv) probe detection and (v) system check-up, as shown in Figure 5.4. Let us explore the setup and the purpose of each block. To feed the whole pump-probe setup, a small fraction ($< 2\%$) of the laser power is used. The setup begins with a pulse compression block used to compensate for the dispersion that will be introduced along the optical beam path. It consists of a pair of chirped mirrors (DCM7, Laser Quantum) and a pre-compressor system mounted in a stepper motor that is inside the Astrella laser amplifier, which can be controlled from the outside (K-Cube Stepper Motor Controller, Thorlabs). After that, there is a pulse preparation block, which is composed of a half-wave plate (Thorlabs, 600-950 nm) and a wire grid polariser (Thorlabs). As the name says, this block prepares the pulse (i.e., cleans polarization

6. Ultrafast degenerate pump-probe system

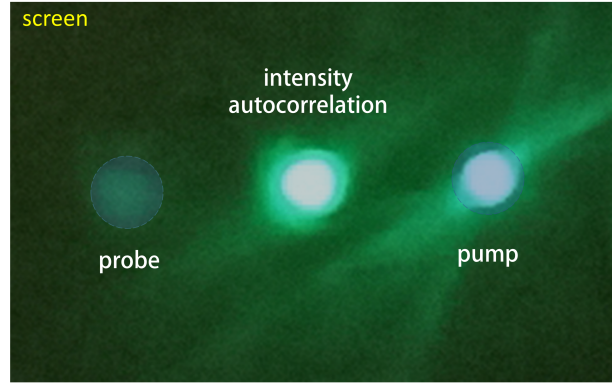


Figure 6.2.: Intensity autocorrelation generated using a type II BBO crystal. On the left is the SHG of the probe beam. On the right is the SHG of the pump beam. In the middle is the intensity autocorrelation as a result of the spatial and temporal overlap of the pump and probe beams. A similar case can be observed on the screen of the pump-probe setup represented in Figure 6.1. When the temporal delay between the pump and probe pulses is close to zero, the intensity autocorrelation can be used to confirm the setup alignment.

and allows power control) before moving into the core of the setup. Our laser output polarisation is mainly horizontal. The half-wave plate will rotate the polarisation while the polariser allows only horizontal polarisation to pass through. Thus, these two components act as a beam attenuator because, by rotating the half-wave plate, one can adjust the power of the transmitted beam while cleaning polarisation. The third block is the core of the pump-probe itself and it resembles a Mach-Zehnder interferometer configuration. A first plate beam splitter (FemtoOptics, 93%) splits the beam into two replicas with different fractions: the most intense, the pump beam ($\sim 93\%$ of the main beam) and the less intense, the probe beam ($\sim 7\%$ of the main beam). The probe is reflected to a high-precision stepper motor stage (model T-NA08A25 from Zaber, 25 mm travel range; microstep size $\approx 0.05 \mu\text{m}$), where a retroreflector mirror is mounted. The polarization of the probe is rotated by 90° (with respect to the pump) by means of a second half wave plate. The pump, after passing through a chopper (MC2000B Thorlabs chopper controller, MC1F10HP chopper blade) and a second beam splitter (Newport, 70% transmission), is non-collinearly focused with the probe beam onto the sample by means of a plano-convex lens (BK7, $f = 100 \text{ mm}$, Thorlabs). The sample is also mounted in another high-precision stepper motor stage (model X-LSM050A from Zaber, microstep size $\approx 0.05 \mu\text{m}$, 25 mm travel range). Therefore, the sample position can be adjust relatively to the spot of the pump and probe beams (which are superimposed exactly at the sample's plane). This is important when analysing samples with different thicknesses. Finally, the fourth block is

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dedicated to detection. The probe beam, after passing through the sample, is sent into a photodiode while the pump is deviated to a beam dump. A polarizer and a spatial filter where placed before the detector to attenuate residual pump scattered light that could reach the detector along with the probe beam. The photodiode is connected to a lock-in amplifier (Stanford Research SR830) that measures the signal at 500 Hz. There is an additional fifth block, that does not have any implication for the instrument itself, which its purpose is to check quickly the setup alignment. Both, the spatial and the temporal alignment are absolutely pivotal in a pump-probe experiment. After the second beam splitter (BS2), the optical arm 1 and the optical arm 2 are ‘equivalent’, although they differ, for example, in the pump and probe power ratios. While arm 1 is dedicated to sample analysis, the arm 2 corresponds to our check-up block. It verifies the temporal and spatial overlap of the beams, by means of intensity autocorrelation technique (see Section 6.1.1). The arm is composed of a plano-convex lens (BK7, $f = 100\text{mm}$, Thorlabs) that focus the pump and probe in a BBO crystal (type II, $100\text{ }\mu\text{m}$) which is followed by a blue filter and a screen. By moving the probe steeper motor, one can confirm the position of the zero delay ($\tau = 0$), i.e., when both pump and probe are temporally overlapped. When the criteria is met, it is possible to observe an intensity autocorrelation on the screen (as shown in Figure 6.2. Moreover, in the arm 2, a flipper mirror is placed that redirects both the pump and probe beams to another photodiode. This is done for two purposes: (i) to evaluate the laser intensity stability before measuring; and (ii) to optimize the phase of the chopper wheel that is modulating the pump pulse (discussed in Section 6.1.2). The main requirements regarding the construction of this setup are summarised in Table 6.1 with the corresponding solution design. Next, we will focus the temporal resolution of this pump-probe setup and later address some aspects related to the $\Delta T(\tau)$ signal detection.

6.1.1. Setup temporal resolution

The accurate determination of the temporal resolution of any ultrafast pump-probe system is crucial³ in order to understand what kind of temporal events it is able to measure. Although one can have an ultrafast laser source feeding the spectroscopy setup, in the end that does not mean that the setup has a high-temporal resolution. As addressed in Section 3.3 the temporal resolution of a pump-probe configuration is given by the cross-

³We will see later in Section 7.4 that knowing the pump-probe system temporal resolution is also important for data analysis / fitting.

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Table 6.1.: Pump-probe setup main requirements and corresponding solution approaches

Requirement	Context / Purpose	Solution design
The pump shall not induce high-order nonlinear effects, neither damage the sample.	Degenerate pump-probe provides information on ground-state bleaching. The determination of decay times can be affected by unexpected nonlinear effects or sample damage, which can lead to misleading results.	(1) Pulse preparation block: it allows power control before the beam enters to the ‘core’ of the setup. (2) The spot size of the pump can be adjusted through the divergence angle of which the pump enters the lens. (3) Appropriated neutral density filters can be introduced in the pump path if necessary. The amount of dispersion introduced by the filters can be compensated in the pulse compression block.
The probe shall be less intense than the pump (approximately one order of magnitude lower).	In a pump-probe system, the probe beam is used to ‘examine’ the sample, which has already been excited by the pump beam. To observe the differential transmission $\Delta T(\tau)$, it is essential that the probe beam does not excite the sample, as this could lead to a continuous depletion of the ground state.	An appropriate beam splitter at the beginning of the setup can easily divide the beam into two replicas with the desired intensity ratio. A 93% - 7% beam splitter was used.
The spot size of the pump should be equal or greater than the spot size of the probe.	For an optimal signal, it is important to make sure that all the sample area that is ‘analysed’ by the probe was previously excited by the pump pulse.	(1) Both beams have similar divergence and pass through the same lens before impinging on the sample. Thus, they have similar spot sizes. (2) The spatial superposition of the beams can be examined using a camera at the sample position. The camera position can be adjust by means of a high-precision stepper motor. (3) Check-up block: the second-harmonic autocorrelation intensity can also be used to evaluate the superposition. It can be observed in a screen in the arm 2 of the setup.
The pump beam should be modulated at half of repetition rate of the laser source.	Ideally, one out of two sequential pump pulses is totally blocked. It ensures a stable signal $\Delta T(\tau)$ and keeps a high SNR.	Use of a chopper in the pump beam. The chopper controller receives a reference signal from the laser system, which is used to produce a half-harmonic. The phase of the chopper wheel can be adjusted. This can be done in the arm 2 of the setup.
The pump should not reach the detector (including pump scattering signal).	Avoid interference effects during detection, especially close to $\tau = 0$ s, where the pump and probe pulses are temporally overlapped. It ensures lower background noise, thus better SNR.	Block the pump beam after the sample and use polarization and spatial filtering.
The pump and probe pulses shall have the same amount of optical dispersion at the sample plane.	Pump and probe pulses should be close to the Fourier-limit, in order to have the best system temporal resolution.	Implementation of a pulse compression block in the setup, which is connected to the laser system.

correlation between the pump and the probe pulses. Remember that ultrashort pulses acquires considerable optical dispersion while propagating, which result in a pulse temporal broadening (see Section 2.4). Our pump and probe beams will acquire optical dispersion during their own optical path until they are spatially overlapped at the sample plane. Thus, if the optical path of the pump and probe beams have optical components with

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Table 6.2.: Characteristics of the degenerate pump-probe setup

Quantity	Value
Pump wavelength, λ_{pump}	800 nm
Pump energy, $\varepsilon_{\text{pump}}$	450 nJ
Probe energy, $\varepsilon_{\text{probe}}$	12 nJ
Pump spot size	$\approx 120 \mu\text{m}$
Pump and probe beam profile	Gaussian
Setup temporal resolution, $\Delta\tau$	$\approx 60 \text{ fs}$
Minimum temporal delay	0.3 fs
Sensitivity	10^{-4}

similar GDD one can compensate both beams equally, until they achieve a Fourier-limited profile. To determine the setup temporal resolution we used, in a first approximation, the intensity autocorrelation technique. The result is shown in Figure 6.3. Assuming

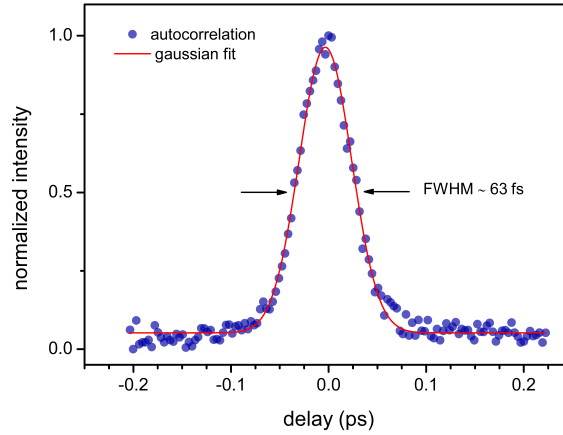


Figure 6.3.: Estimation of the setup temporal resolution through the intensity autocorrelation technique of the pump and probe laser pulses. The measured autocorrelation is depicted by the blue dots and the red line represents the Gaussian fitting. The duration (given by the FWHM) is approximately 63 fs.

a Gaussian profile of the intensity distribution, we obtained a duration of about 63 fs. Although this technique can provide a good estimation of the setup temporal resolution, it has some inherent limitations. We next used the d-scan technique (as experimentally described in Section 5.4) to estimate the pump and the probe durations individually and to yield the best pump-probe temporal resolution possible at the sample plane. Figures 6.4(a-b) and 6.4(c-d) show the measured and retrieved d-scan traces for the pump and probe

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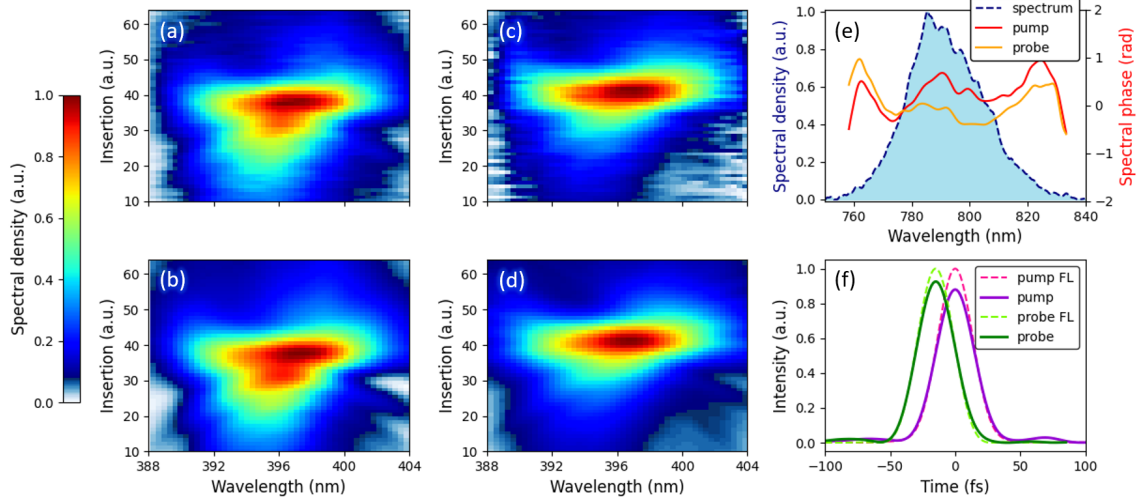


Figure 6.4.: Temporal characterisation of pump and probe pulses using the d-scan technique. (a,c) Measured d-scan traces for the (a) pump and (c) probe beams precisely at the sample position in the pump-probe optical setup. (b,d) Retrieved d-scan traces for the (b) pump and (d) probe pulses with a d-scan RMS error of 1.6 % and 0.7 %, respectively. (e) Spectrum of the laser pulses (dashed line) and spectral phases of the pump (solid red line) and probe pulses (solid orange line). (f) Retrieved temporal intensity profile of the pump (dark green) and probe (purple) pulses derived through Fourier transformation of the spectral domain. Each pulse is normalised relative to its Fourier limit (dashed lines). The probe pulse is shown shifted in time for clarity. The obtained pulse durations (by FWHM) were 34.1 fs and 33.7 fs for the pump and probe pulses, respectively.

pulses, respectively. The corresponding intensity profiles, as depicted in Figure 6.4(f), were derived through Fourier transformation of the spectral domain presented in Figure 6.4(e). The retrieved pulse duration for both the pump and probe pulses was estimated to be 34.1 fs and 33.7 fs, respectively. Therefore, the best temporal resolution of the pump-probe system, given by the FWHM of the pump and probe intensity cross-correlation, is estimated to be on the order of 60 fs.

6.1.2. Signal detection

In the current system, our detection block is composed of a polarizer and a spatial filter (to clean undesirable pump scattering), a photodiode, a chopper controller, and a lock-in amplifier. In a pump-probe experiment, the pump pulse is responsible for driving the sample into a non-equilibrium state through photoexcitation. The probe, delayed by a time τ relative to the pump, ‘examines’ the changes in the transmission, reflectivity, or absorption of the sample. Therefore, it is the probe beam that is detected, not the pump.

Here, the repetition rate of the pump and the probe beams is 1 kHz. Right before hitting the sample, the pump passes through a chopper that modulates the beam at half

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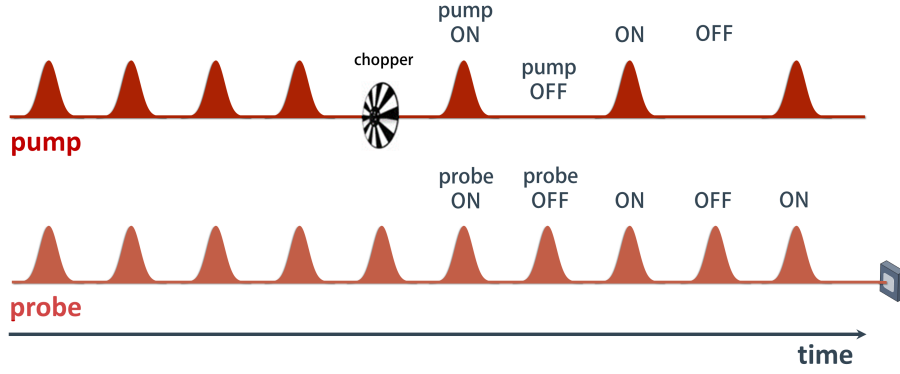


Figure 6.5.: Illustration of the concept of pump beam modulation at half of the repetition frequency for phase-sensitive detection. Initially, both the pump and probe pulses have a repetition rate of 1 kHz. After passing through the chopper, the pump beam will be modulated at 500 Hz, meaning for every two pump pulses, only one will pass. The probe, on the other hand, will not be modulated. The probe pulses passing without the pump being present will not feel any change since the sample is already in an equilibrium state. Thus, the term ‘probe OFF’ is used when no pump pulse has passed, while ‘probe ON’ is used when a pump pulse was present before.

of the repetition rate (i.e., 500 Hz) as schematised in Figure 6.1. Then it interacts with the sample, promoting it to an excited state. Consequently, the sample non-equilibrium state will be modulated by the pump beam at 500 Hz. If the sample transmission, reflectivity, or absorption is changed by the pump beam, these quantities are modulated at that same frequency.

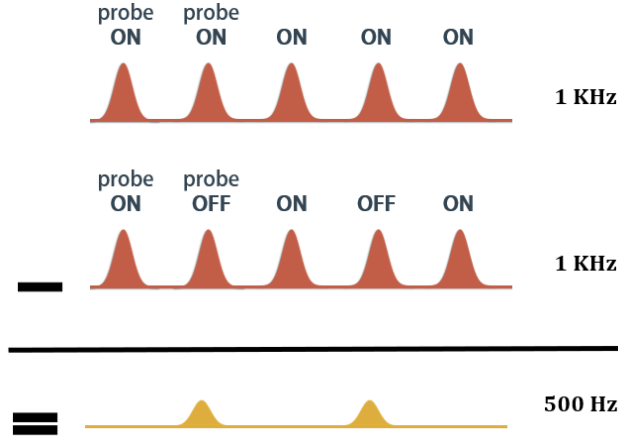


Figure 6.6.: The subtraction of the transmitted probe with and without the pump leads to a 500 Hz signal, the same that the lock-in amplifier filters and amplifies.

We measure the probe beam, that reaches our photodiode at 1 kHz. The photodiode is connected to a lock-in amplifier. What signal should the lock-in amplifier read, 1 kHz or 500 Hz? We are interested in detecting the probe beam that passes through the sample in its non-equilibrium state. Thus, part of the probe beam that reaches the

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photodiode will also have a 500 Hz component due to this interaction with the sample (Figure 6.5). The photodiode will detect the variation of the probe intensity in the presence and absence of the pump (Figure 6.6). That is the signal we want to measure. Thus, the lock-in amplifier should read the 500 Hz signal, which in practice corresponds to $\Delta T(\tau) = T_{\text{pump on}}(\tau) - T_{\text{pump off}}(\tau)$.

The lock-in amplifier receives an internal reference from the chopper that is modulating the pump at 500 Hz. One thing that has to be carefully configured is the phase of the chopper. The chopper receives a signal from the internal reference of the laser system. Thus, when modulating the pump, it is important that the chopper wheel is synchronised with the laser internal reference signal. This is schematised in the Figure 6.7. When the

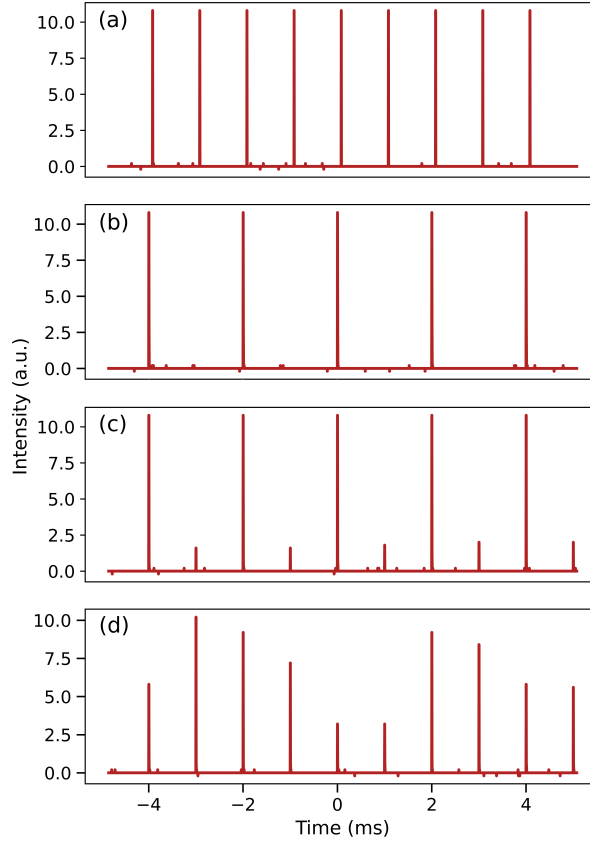


Figure 6.7.: Oscilloscope measurements of the chopped pump beam for different phases. (a) Unsynchronised chopping, leading to a non-modulated beam of 1 kHz. (b) The phase applied to the 500 Hz is synchronised with the pump pulses, meaning that for two pump pulses arriving at the chopper, only one passes, leading to a modulation frequency of 500 Hz. (c) and (d) Partial synchronisation.

chopper wheel is not synchronised with the internal signal, then the pump beam will not be fully modulated at 500 Hz, at least in a large time window.

Imagine now that instead of using a lock-in amplifier, we would: (i) measure the probe

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pulse after passing through the sample in an excited state promoted by the pump pulse; (ii) then we would block the pump and perform the measurement of the probe again. We would then subtract both signals and end up with ΔT . This subtraction will lead to a 500 Hz signal, the same as the one the lock-in amplifier filters (see Figure 6.6). The reason to use the lock-in amplifier instead of this subtraction approach is simply because the signal ΔT is very low in the samples we want to study, i.e., of the order of 10^{-4} of the probe signal, and therefore the extraction of this signal would be very difficult without phase-sensitive detection.

As mentioned in the beginning of this section, in this setup, a polarizer and a spatial filter are part of the detection block. Now the reader might understand better the importance of these components for the detection. We are detecting very low signals at 500 Hz. The pump beam, which is really intense, is at 500 Hz. Therefore, any residual pump scattering that reaches the photodiode will be detected and interfere with the lock-in amplifier measurements. This is particularly relevant close to $\Delta T(0)$, where the pump and probe beams are temporally overlapped. They can interfere with each other and the lock-in amplifier will detect this interference, affecting ΔT . These interference oscillations caused by the pump during the period of the pump and probe beams cross-correlation, is a phenomenon sometimes called as coherent artefact [45]. This is a problem [98] mostly for degenerate pump-probe setups, where colour filters cannot be used. Note, however, that there is another method that could be useful, which is to modulate both beams, as some authors do [83]. In practice, the output signal would be the sum or difference of both modulated frequencies. However, this technique is difficult to implement with kHz beams, since the chopping frequencies have to be $1/2n$ (n is a positive integer) of the original frequency (1 kHz) and thus we would be using frequencies that have more intrinsic noise in the electronic components. Thus, this technique is more relevant when dealing with oscillators (on the order of MHz), where there are no constraints in the chopping frequencies.

6.1.3. Spatial superposition

Figure 6.8 shows the pump and probe beam profiles at the plane where they are spatially overlapped. A Gaussian fit was performed to ensure that the FWHM of the probe was equal or smaller than that of the pump beam. This is important to ensure that all the ‘examined’ sample area by the probe beam was previously excited by the pump beam.

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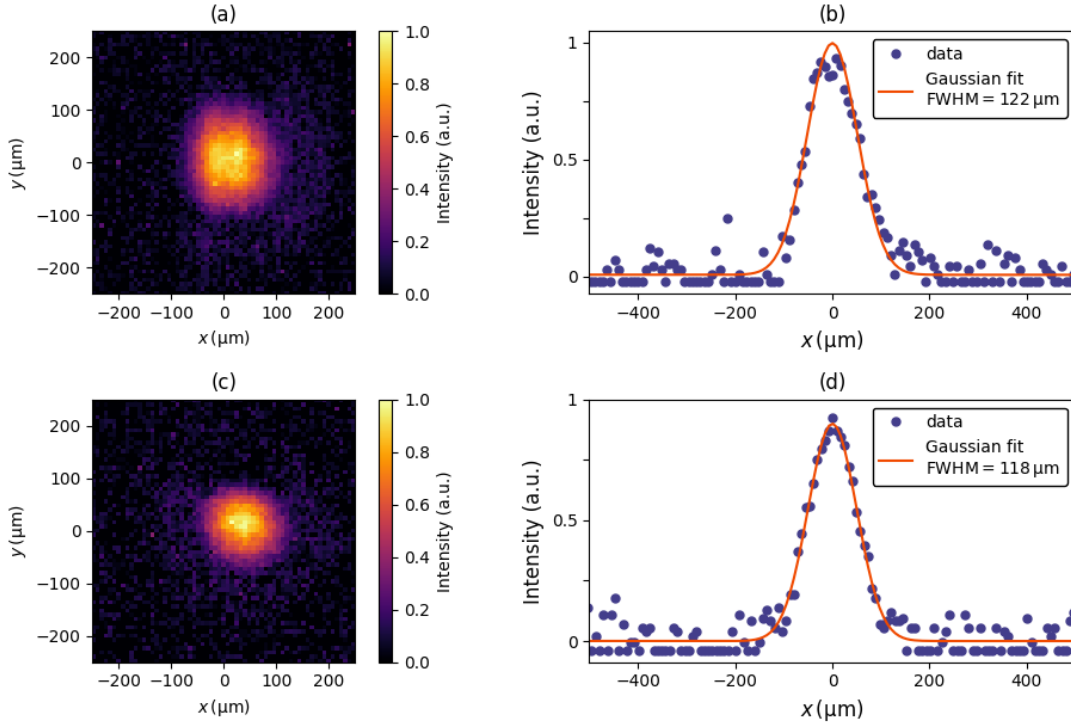


Figure 6.8.: Pump and probe beam profiles when spatially overlapped. (a) Pump beam profile. (b) Cross-section of (a) at $y = 0$ with Gaussian fit. (c) Probe beam profile. (d) Cross-section of (c) at $y = 0$ with Gaussian fit.

Thus, one can improve the signal-to-noise ratio. On the other hand, if the pump pulse is too large compared to the probe, such that it interacts with unintended parts of the sample, it will affect the background noise. A large pump beam area can make it more difficult to separate both beams (pump and probe) before detection. That increases the probability of unwanted pump scattered reaching the detector. Note that if we use lenses, we can play with different pump and probe spots, but if we use, for example, a parabola to focus the beam in the sample, we know that the pump and probe beams have the same radius. Additionally, the estimation of the beam diameter is also important for the estimation of the fluence (or peak intensity) of both beams. Remember that the pump should not induce high-order nonlinear effects or cause sample damage, and at the same time, it should be more intense than the probe beam.

6.2. System control software

A LabVIEW program with graphical user interface (GUI) was developed to control the pump-probe experiment and automatise the data acquisition. Its diagram is represented in Figure 6.9. The program allows the control of the stepper motor stages and the lock-

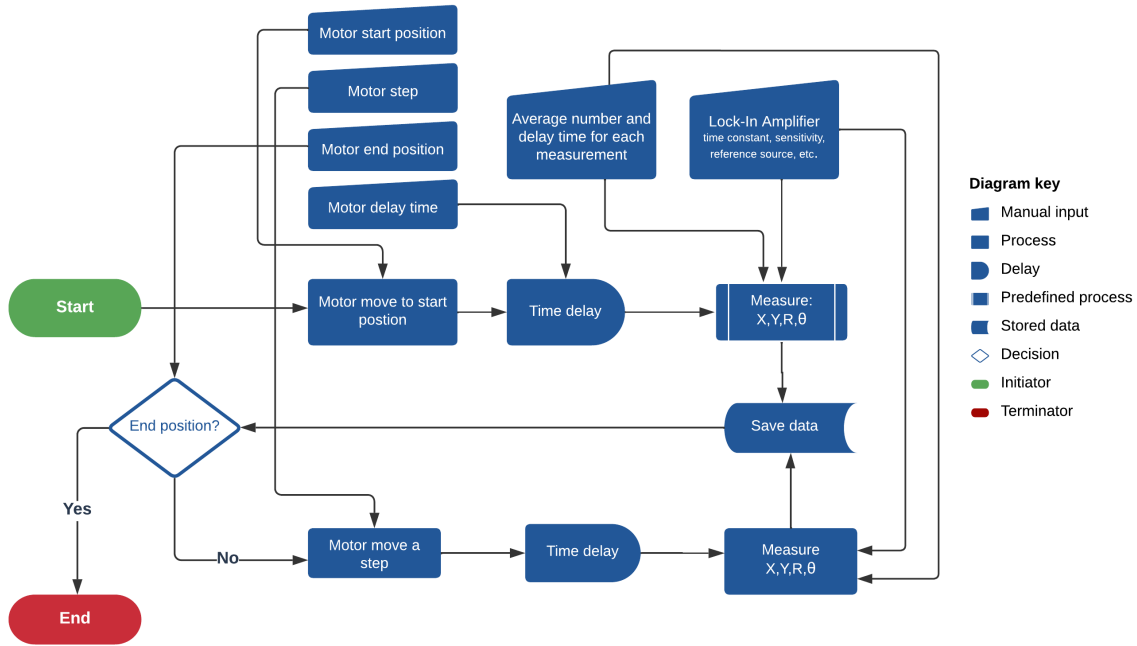


Figure 6.9.: Diagram of the software that controls the pump-probe setup.

in amplifier. Moreover, before starting with the pump-probe experiment, the user can configure the devices and the data acquisition methods. Next, we will discuss the input parameters for the software.

6.2.1. Input parameters

The GUI is divided into five sections as shown in Figures B.1 and B.2 from Appendix B. In the first one, the user can control quantities related to signal processing, namely, the number of means and the waiting time between measurements. In the second section, the user defines parameters related to the lock-in amplifier, for example, the time constant, sensitivity, reference source and phase. The third section is related to the stepper motor responsible for the probe temporal delay. The user can define the initial and final position, the step size, and the time that the experiment should wait before starting measuring. The remaining sections are related to data saving and allows the user to add individual notes about their experiment.

6.2.2. Data acquisition

As schematised in Figure 6.9, the software acquires four quantities from the lock-in amplifier: X , Y , R , and θ . Why do we collect all these data? As we understand from the principles of lock-in amplifiers, the in-phase component X and quadrature component Y

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are related to the polar coordinates, amplitude R and phase θ , by the following relations,

$$X = R \cos \theta, \quad (6.1)$$

$$Y = R \sin \theta, \quad (6.2)$$

$$R = \sqrt{X^2 + Y^2}, \quad (6.3)$$

$$\theta = \arctan\left(\frac{Y}{X}\right). \quad (6.4)$$

Thus, by knowing X and Y we can retrieve R and θ and vice-versa. During the pump-probe measurements these values are constantly displayed in the GUI and the data for all four quantities are saved at the end of the experiment. It seems redundant to collect all this data, and in fact it is. Nevertheless, note that R is always a positive quantity, thus your pump-probe signal $\Delta T(\tau)$ will always appear positive. It could be of interest to look at X to evaluate variations of $\Delta T(\tau)$ signal close to zero. Moreover, the values of Y and θ are important to let the user know when the lock-in is no longer detecting a meaningful signal at 500 Hz, only background noise. We discuss this with examples in Section 6.3 where we present some tests with the pump-probe setup. In the end, since storage is not a constraint, we collected all data, which the software exports at the end of the experiment.

After the probe stepper motor stage moves to the next position ('motor step' in Figure 6.9), there is a waiting time that the user can input ('motor delay time' in Figure 6.9). This waiting time serves two purposes. The first is to avoid vibrations of the motor stage when it finally stops. The second purpose is to wait for the lock-in signal to stabilize, which depends on the input time constant. It is after this waiting time that the software acquires the four parameters X , Y , R , and θ . If the user has selected to perform N averages ($N > 1$), then the software will acquire each parameter N times and will return the average value. In this process, the user can also input a waiting time between each of these N measurements. In the end, in addition to the data files, the software also exports a file with the input parameters used.

6.3. Setup evaluation

Prior to graphene studies, we tested the setup with other available samples, namely a zinc selenide (ZnSe) crystal, a solution of gold nanorods, and a solution of gold nanostars.

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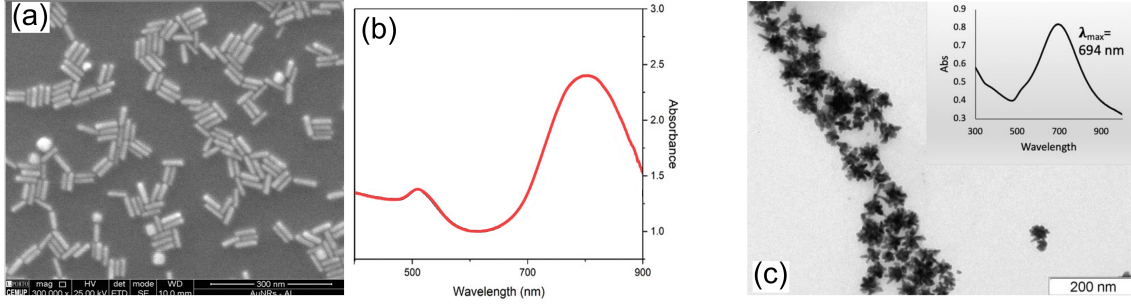


Figure 6.10.: Nanomaterials used for preliminary tests with the pump-probe setup. (a) SEM image of the gold nanorods, reproduced from [99]. (b) Visible-NIR absorption spectrum of the Au nanorods with an absorption band centred at around 800 nm, reproduced from [99]. (c) SEM image of gold nanostars similar to those used in this work, reproduced from [100]. The inset shows the nanostars' visible-NIR spectrum, with an absorption band centred at 694 nm.

Note that, at the time we did these tests, the setup was not yet optimised for the best possible resolution (i.e., the d-scan measurements were performed afterward). With these tests, we aimed to demonstrate that the system is able to analyse different samples, from crystals to nanoparticles dispersed in liquids.

We tested a sample of organic-coated gold nanorods (10x41nm) dispersed in water, which were purchased from Nanopartz (Nanopartz, Loveland, CO, USA). These nanorods (see Figure 6.10) have an absorption band at around 800 nm due to surface plasmon resonance (SPR) [101, 102], making them an interesting material to investigate with our system, which operates with an 800 nm pump wavelength. In nanorods, this absorption band can be tuned toward lower or higher wavelengths according to the nanorod size and morphology [103, 104]. For the time-resolved measurements, a quartz cuvette (1 mm optical path) with the nanorod solution was placed on the motor stage 2 of the pump-probe setup (see Figure 6.1). We used this motor stage to adjust the sample's position relative to the plane where the pump and probe spots were spatially overlapped. Due to the nature of the sample, we had a considerable amount of scattered pump reaching the detector. Thus, a neutral density filter was placed right before the photodetector to eliminate scattering as much as possible. Of course, by doing this, we are also filtering the probe. However, in this case the probe differential signal, $\Delta T(\tau)$, was sufficiently intense. The intensity of the signal will also depend on the concentration of the sample. One of our first results is shown in Figure 6.12(a-b). Since this was simply a test, the response from the sample's background (i.e., only quartz glass cuvette + aqueous solution without

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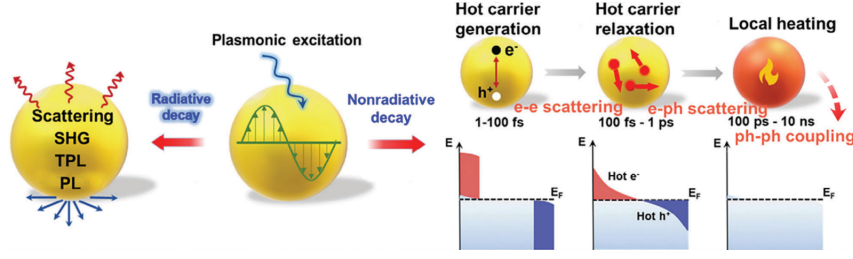


Figure 6.11.: Illustration of radiative and nonradiative surface plasmon decay in plasmonic nanostructures (e.g., gold nanoparticles) after excitation by an ultrashort laser pulse. Adapted from [105]. SHG - second harmonic generation; TPL - two-photon photoluminescence; PL - photoluminescence.

nanorods) was not investigated⁴. Thus, we cannot exclude the presence of background contribution from the measurement presented in Figure 6.12. In this nanorods sample we are measuring the dynamics of the electron-electron and electron-phonon interactions [101, 106], as schematised in Figure 6.11. The electron-electron relaxation is expected to be on the order of hundreds of femtoseconds [106], while the electron-phonon relaxation is longer and expected to be on the order of a few picoseconds [106]. Note that near the delay $\tau = 10$ fs, a second smaller exponential can be observed. We attributed this to some reflection from the probe beam that is being redirected towards the sample.

In Figure 6.12(b) we plotted the values of θ as a function of the delay τ . We can observe that θ is near zero most of the time, as expected. Note, however, that at $\tau < 0$, the value of θ varied significantly. This is because, at $\tau < 0$, the probe pulse reaches the sample before the pump pulse, thus the lock-in amplifier is not measuring any meaningful signal at 500 Hz. For delays near $\tau = 0$ the value of θ also varies (randomly) attributed to the presence of residual pump scattering.

In the same manner, we did experiments with gold nanostars synthesised similarly to those reported in [100]. These nanostars have a large absorption band in the 500-900 nm region (see Figure 6.10). The pump-probe results are shown in Figure 6.12(c-d). Excluding possible contributions from the background and the differences in the solution concentrations, nanostars seem to have a faster relaxation dynamics compared to nanorods, as expected [106]. In Figure 6.12(d) we can observe that θ is ‘well behaved’ from $\tau = 0$ to $\tau \approx 7$ ps, then it starts to vary randomly. We can deduce that after $\tau \approx 7$ ps, the lock-in amplifier is only measuring noise. In other words, when the probe is delayed 7 ps behind the pump, the sample has already recovered from the non-equilibrium state.

⁴However, we tested a fused quartz plate (≈ 1 mm thickness) and we did not observe any time-resolved response under the conditions used.

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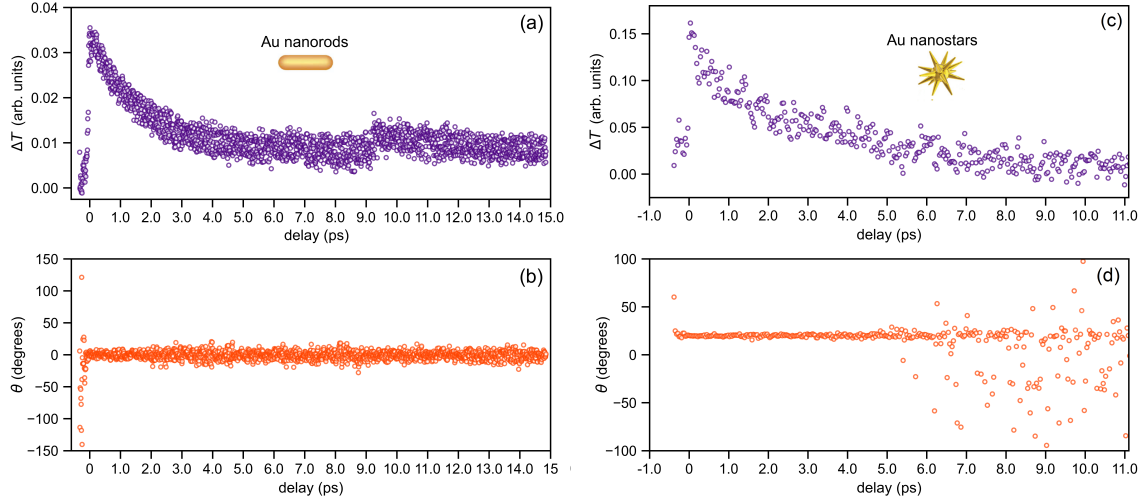


Figure 6.12.: Preliminary tests of the degenerate pump-probe system using gold nanostructures. (a-b) Gold nanorods. In (a) the measurement of the X quantity from the lock-in amplifier, which corresponds to $\Delta T(\tau)$. In (b) the measurement of the corresponding phase θ from the lock-in amplifier. (c-d) Gold nanostars. In (c) the measurement of the X quantity from the lock-in amplifier, which corresponds to $\Delta T(\tau)$. In (d) the measurement of the corresponding phase θ from the lock-in amplifier.

We also tested the setup with an aqueous solution of gold nanoparticles, which we synthesised by liquid pulse laser ablation [107]. However, given the nanoparticles' absorption peak around 520 nm, we did not observe a pump-probe signal. This result allowed us to confidently exclude the presence of false signals arising from experimental artefacts or other origins unrelated to the sample.

Let us look now at the tests with the 1 mm thickness ZnSe crystal. Unlike the previous samples, ZnSe does not have any absorption band around 800 nm. However, if the pump is sufficiently intense, it can interact with the sample through a two-photon absorption [108]. The result for the ZnSe crystal is in Figure 6.13.

These preliminary tests helped to optimise the alignment of the setup, to check its versatility (in terms of the types of samples it could analyse) and its reliability. It also helped to improve the software to control the experiment.

6.4. Data analysis

The most used fitting approach for the analysis of photobleaching processes by pump-probe spectroscopy is the exponential decay. When the instrument temporal resolution is comparable to the temporal response of the sample, this strategy might lead to an overestimation of the relaxation constants. This can happen because of the contribution of the

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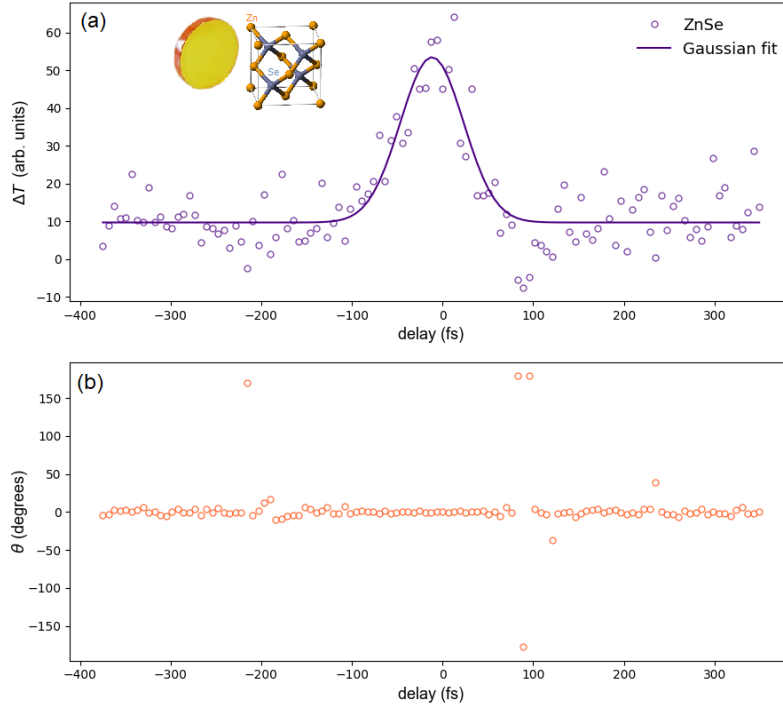


Figure 6.13.: Preliminary tests with a ZnSe sample. (a) Measurement of the X quantity from the lock-in amplifier, which corresponds to $\Delta T(\tau)$. (b) Measurement of the phase θ from the lock-in amplifier. The solid line represents a Gaussian fit with a FWHM of 83 fs.

pump and probe cross-correlation function in a fitting that does not take the instrument response function into consideration. In order to take the instrument temporal resolution into account, we convolute the sample response with the instrument response. The latter is the cross-correlation⁵ between the pump and the probe pulses (which in our case can be described by a Gaussian function). Therefore, let us assume a double exponential decay convoluted with the instrument response (Gaussian function)⁶, which can be written as

$$g(t) = A_1 e^{-\frac{t-t_0}{\tau_1}} \left[1 - \operatorname{erf} \left(\frac{w}{2\tau_1} - \frac{t-t_0}{w} \right) \right] + A_2 e^{-\frac{t-t_0}{\tau_2}} \left[1 - \operatorname{erf} \left(\frac{w}{2\tau_2} - \frac{t-t_0}{w} \right) \right], \quad (6.5)$$

where the time constants τ_1 and τ_2 are the sample carriers fast and slow relaxation times, respectively. A_1 and A_2 are the signal amplitudes, and w is related to the setup temporal resolution and corresponds to the standard deviation of the Gaussian cross-correlation. We will refer to this function as the Gaussian-Double Exponential Decay Convolution (GDEDC), and it will be used in Section 7.4 when analysing the data from pump-probe spectroscopy. Note that, in other to use equation (6.5) it is helpful to know w very well. This is why an accurate estimation of the pump-probe resolution is important.

⁵See Appendix A.1

⁶See Appendix A.2 and Section 3.3.

6.5. Key conclusions

In this chapter we discussed the construction of the custom-built degenerate pump-probe setup. The main features are enumerated below.

- (i) The system is composed of 4 blocks: pulse compression, pulse preparation, main setup, probe detection, and system check-up.
- (ii) Pulse compression and pulse preparation allow, dispersion compensation and control over power and polarization, respectively.
- (iii) In the detection we used a lock-in amplifier for high-sensitivity detection, which is important when studying thin samples such as graphene.
- (iv) The system works with a pump and probe wavelength centred at 800 nm. It has a temporal resolution of about 60 fs.
- (v) A LabVIEW program was developed to control the pump-probe experiment.
- (vi) Apart from graphene studies, the system was tested with other nanostructures, namely gold nanorods, nanostars, and nanoparticles. One of the objectives was to test the pump-probe setup with samples dispersed in aqueous solutions.

7. Pump-probe spectroscopy of graphene

Graphene is a nanomaterial that has two properties not easily found naturally in a material: a broadband absorption and an ultrafast photoresponse. These characteristics have made graphene an attractive material for the areas of photonics and optoelectronics. In particular, the study and exploitation of hot carrier dynamics in graphene is essential for modern optoelectronic applications, such as the development of high-speed photodetectors. In the previous section, we discussed the construction of a degenerate pump-probe system for ultrafast time-resolved spectroscopy measurements. We used the setup to explore the ultrafast carrier dynamics in few-layer graphene samples. In this chapter, we focus on the presentation and discussion of the results obtained. Firstly, we present the characterisation of the graphene samples by UV-NIR absorption spectroscopy, Raman spectroscopy, and microscopy. Then, we discuss the results from the pump-probe measurements and compare the relaxation dynamics of the different samples. Different approaches for the analysis of the pump-probe data were explored and their advantages and disadvantages are discussed.



7.1. Introduction

Graphene is a nanomaterial that exhibits a broad spectral absorption range and whose photoexcited carriers have ultrafast relaxation times, typically on the order of a few picoseconds or less [64]. This combination makes graphene an attractive material for the development of advanced optoelectronic devices, such as ultrabroadband and high-speed photodetectors [60,109–111], ultrafast electro-optical modulators [112,113], and ultrabroadband

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fast saturable absorbers¹ [57, 117]. Typically, applications related to optoelectronics require ‘high-quality’ graphene - in other words, a crystal with almost no lattice defects. Note that we are discarding here cases where defects are induced on purpose, as in the case of functionalised graphene [118]. Chemical vapour deposition is a bottom-up approach to producing high-quality graphene. As discussed in Section 4.2, there are several types of CVD methods [93], which can be classified on the basis of operation conditions or how precursors are transported. One of the CVD methods is MPCVD, whose advantages were also addressed in Section 4. The MPCVD method is a relatively fast way of producing large-area graphene [119], with potential for low-temperature fabrication, and it has been receiving attention [75, 120].

The chemical, structural, and morphological characteristics of graphene may have an impact on the relaxation decay of its photoexcited carriers. Within the femtosecond regime, one way to experimentally determine the relaxation time of these carriers is through pump-probe spectroscopy. Here, we use the custom-built pump-probe setup (Chapter 6) to study the ultrafast carrier dynamics of graphene samples synthesized by MPCVD. During the synthesis we varied the time of the growth phase, expecting samples with different thicknesses. We labeled them as A for 0.5 minutes growth, B for 1 minute, and C for 3 minutes, as explained in Section 5.1. To characterise the samples we used three main techniques: (i) we first used visible-near IR absorption spectroscopy to detect the number of layers present in the samples; (ii) Raman spectroscopy was mainly used for the detection of defects and their extent; (iii) microscopy was used to check the uniformity of the samples and the quality of the transfer to the fused silica substrate. Then, we analysed the time-resolved spectroscopy results acquired with the pump-probe setup presented in this thesis. We compared the ultrafast relaxation dynamics obtained for the different samples and related them to other characteristics, namely the thickness.

7.2. Sample characterisation

The graphene samples under study (Figure 7.1) were characterised by UV-NIR transmission spectroscopy and Raman spectroscopy according to the description given in Section 5.2.

¹Here, we do not cover the fabrication or the working principles of these optoelectronic devices. We refer readers interested in the topic to the references given in the text and additionally to the following references [114–116].

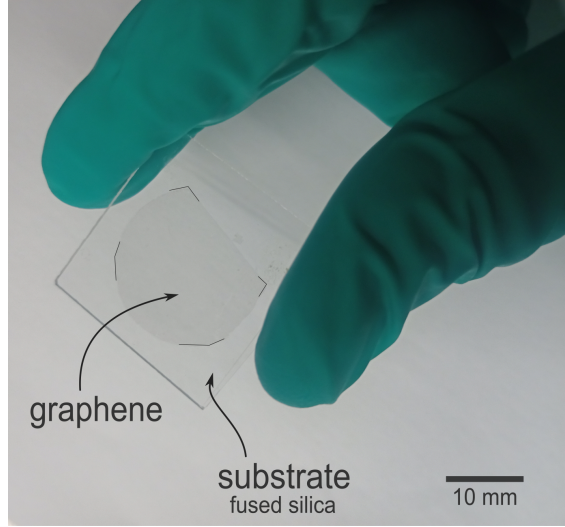


Figure 7.1.: Graphene film deposited on a fused silica substrate. On the image is sample C, which is the easiest to observe with the naked eye.

7.2.1. Visible-NIR absorption spectroscopy

Using visible-NIR absorption spectroscopy, we estimated the number of layers present in the graphene samples. The transmission spectrum of each sample is presented in Figure 7.2. In the spectra, we can observe a band at around 270 nm corresponding to the $\pi \rightarrow \pi^*$ transition of the aromatic π electrons from graphene. Considering 2.3% as the theoretical value of the percentage of absorption per graphene layer in the visible and near-infrared range [79], the transmittance spectra show that samples A, B, and C are made up of approximately 3, 5, and 6 layers, respectively. Consequently, and considering only the number of layers, we refer to these samples as few-layer graphene, following the recommended nomenclature by Bianco et al. [121] and the terminology from the International Organization for Standardization (ISO) as defined at ISO/TS 11665-13:2017 for graphene and 2D materials. Note that, for the estimation of the number of layers, we used the average transmission value for the wavelength range 550 – 800 nm. For sample B, the number of layers varies significantly between 4 and 5, depending on the chosen visible-NIR wavelength range. Specifically, above 720 nm, it approaches 4 layers. Despite this variability, we opted to consider the higher value of 5 layers.

7.2.2. Raman spectroscopy

Here, we use Raman spectroscopy to evaluate the quality of the graphene samples by looking for defects in the crystal lattice. If defects are present, we also aim to analyse

7. Pump-probe spectroscopy of graphene

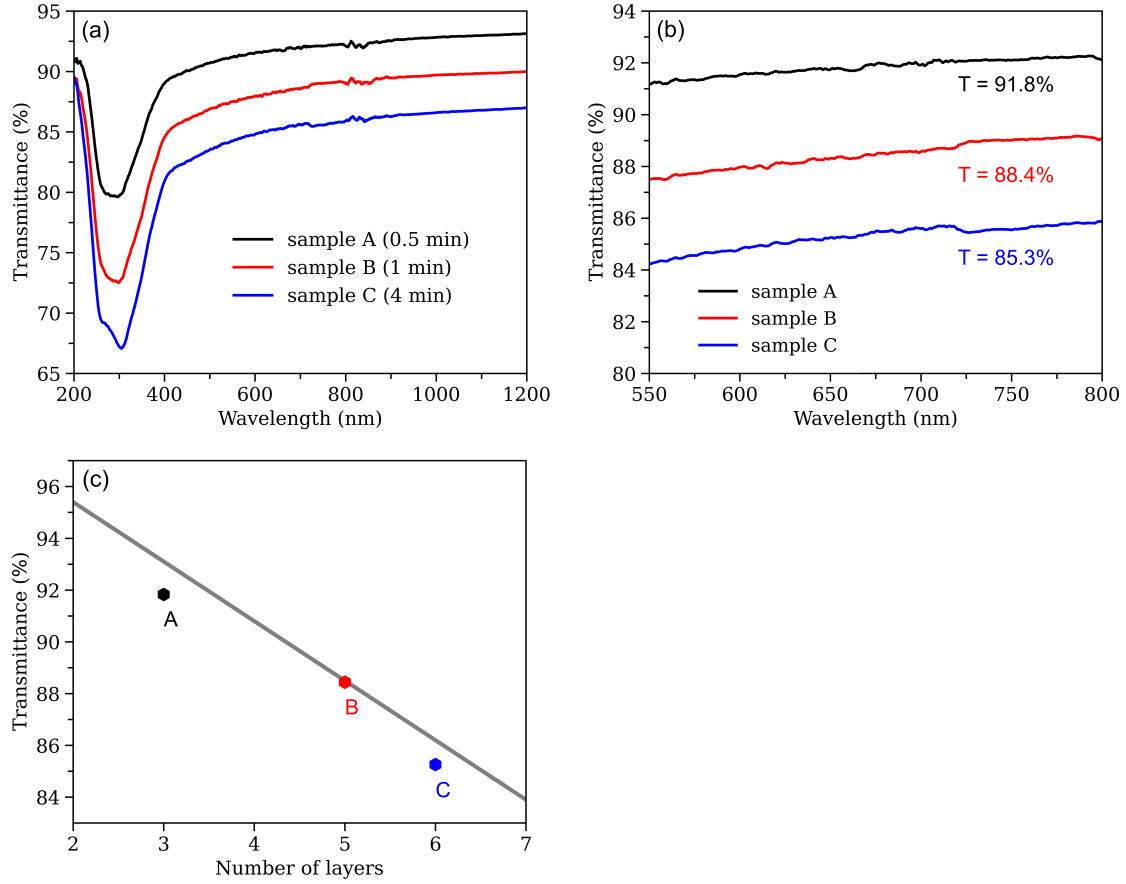


Figure 7.2.: UV-NIR transmission spectra of graphene samples A, B, and C. (a) Transmission spectra in the range of 200–1200 nm. In the legend, the values in parentheses represent the duration of the growth phase during synthesis by MPCVD. (b) Zoom-in of the spectra in the 550–800 nm spectral window. The average value for each transmittance in that range is shown. (c) Transmittance as a function of the number of stacked graphene layers estimated from (b). The grey line corresponds to the theoretical transmittance, considering 2.3% absorption per layer.

their extent. Raman spectroscopy data will also be used to draw conclusions about the sample thickness and will be compared with the results from the visible-NIR absorption spectroscopy.

For each sample (A, B, and C) we collected eight Raman spectra in different positions, and we have selected a representative spectrum of each sample to present in Figure 7.3. In the spectra, we can observe the Raman peaks 2D and G at around 2737 cm^{-1} and 1580 cm^{-1} , confirming the presence of graphene [77]. A D peak is also present at 1367 cm^{-1} , which reveals the existence of defects in the graphene crystal lattice [122]. The most likely contributions for the D peak are (i) the presence of a few C-H groups (due to the molecular hydrogen H_2 used in the synthesis), and (ii) grain boundaries (line defects) from simultaneous nucleation sites at different points, which are difficult to avoid

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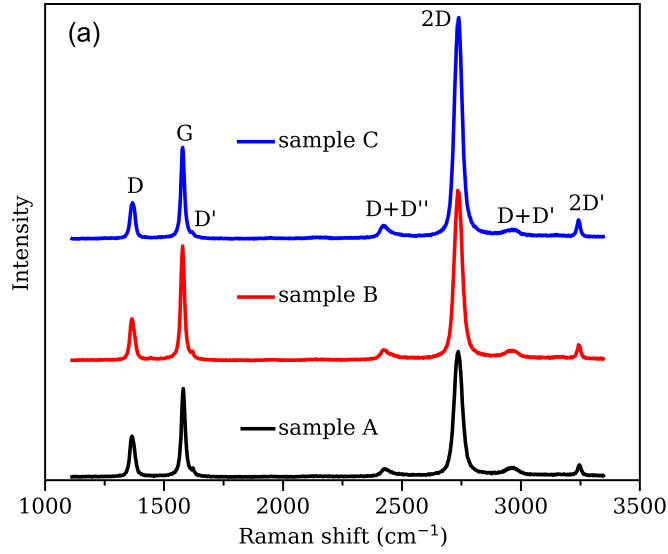


Figure 7.3.: Raman spectra of graphene samples A, B, and C, measured at 441.6 nm (≈ 2.808 eV) in the spectral region 960 – 1860 cm^{-1} . All Raman peaks are identified, including the 2D and G peaks, which are intrinsic resonant modes of graphene.

in a fast bottom-up fabrication process like MPCVD [123]. These three principal Raman peaks, the 2D, G, and D, were fitted using the pseudo-Voigt function [124, 125] that describes the Gaussian broadening of a Lorentz peak and is given by

$$I(s) = A_{\text{pV}} \left[m_u \frac{2}{\pi} \frac{w_{\text{pV}}}{4(s - s_c)} + (1 - m_u) \frac{\sqrt{4 \ln 2}}{\sqrt{\pi} w_{\text{pV}}} \exp \left(-\frac{4 \ln(2)}{w_{\text{pV}}^2} (s - s_c)^2 \right) \right] + I_0, \quad (7.1)$$

where A_{pV} is the amplitude, I_0 is the intensity of the background, s_c is the Raman shift of the peak center, and w_{pV} is the function FWHM. The profile shape factor m_u is 1 for a pure Lorentzian shape. Figure 7.4 plots some of the retrieved values as a function of the sample position, while Table 7.1 provides the average values. We use the notation I_{peak} for the maximum peak height (i.e., peak intensity), Pos_{peak} for the Raman shift of the peak centre (i.e., peak position), and Γ_{peak} for the peak FWHM. The 2D peak is mostly used to determine (at least qualitatively) the graphene layer thickness, i.e., the number of stacked graphene layers. For a single-layer graphene, a typical Raman spectrum presents a sharp 2D peak with a profile close to Lorentzian, but for an increasing number of layers, this peak starts to broaden and some shoulders might appear. This happens when layers are in a conventionally stacking order, like AA or AB [73, 126]. However, when the stacking order is not conventional - in other words, the arrangement of graphene layers deviates from the common configuration found in graphite - this spectral broadening is not obvious [127–129]. We hypothesized this is the case for the samples under study. The

7. Pump-probe spectroscopy of graphene

Table 7.1.: Raman characterisation of graphene samples A, B, and C. Average peak intensity, position, and FWHM for the Raman peaks I_{2D} , I_D , and I_G estimated from the pseudo-Voigt fitting. Average intensity ratio I_D/I_G and crystallite size L_a . All values are presented with the corresponding standard deviation.

Fitted Parameters		Samples		
		A	B	C
Intensity (a.u.)	I_{2D}	2492 (231)	3236 (113)	4189 (683)
	I_G	1710 (504)	2077 (584)	1975 (415)
	I_D	911 (91)	859 (52)	854 (227)
Position (a.u.)	Pos_{2D}	2737.2 (0.4)	2737.0 (0.3)	2736.6 (0.6)
	Pos_G	1580.7 (0.7)	1579.1 (0.5)	1579 (1)
	Pos_D	1367.1 (0.3)	1366.9 (0.3)	1367.5 (0.4)
Peak FWHM (a.u.)	Γ_{2D}	41 (1)	39.6 (0.5)	39.7 (0.9)
	Γ_G	19.4 (0.7)	18.0 (0.5)	18.2 (0.7)
	Γ_D	19.4 (0.7)	24.7 (0.4)	25.2 (0.4)
Intensity ratio	I_D/I_G	0.6 (0.2)	0.4 (0.1)	0.4 (0.1)
Crystallite size* (nm)	L_a	17 (6)	22 (7)	22 (8)

(*) estimated using equation 7.2

average value of Γ_{2D} is similar for the three samples, suggesting that the graphene layers are not conventionally stacked but relatively rotated by an arbitrary angle. Since Γ_{2D} cannot be used to evaluate the number of layers, we now look at the 2D peak intensity. When we look at I_{2D} , we can see a clear difference between samples. The I_{2D} increases from sample A to sample C. This happens across the sample area, as demonstrated in Figure 7.4(a), and confirms the results obtained from the visible-NIR spectroscopy. In some sample positions, a strong G peak (i.e., comparable to or more intense than the 2D) was observed. Kim et al. [129] reported a similar Raman feature for bilayer graphene with a twisted stacking angle of about 10° measured using a 633 nm wavelength laser, which is far from the one used in this work (i.e., 442 nm). However, in their study, they estimated that for lower wavelengths, this angle is close to 13° .

The intensity ratio of the D peak to that of the G peak (I_D/I_G) can be used to estimate the graphene crystallite size [130, 131], L_a (also known as the degree of graphitization). We adopted the expression by Cançado et al. [131] to determine L_a , which is given by

$$L_a = \frac{C}{E_t^4} \left(\frac{I_D}{I_G} \right)^{-1} \quad (7.2)$$

7. Pump-probe spectroscopy of graphene

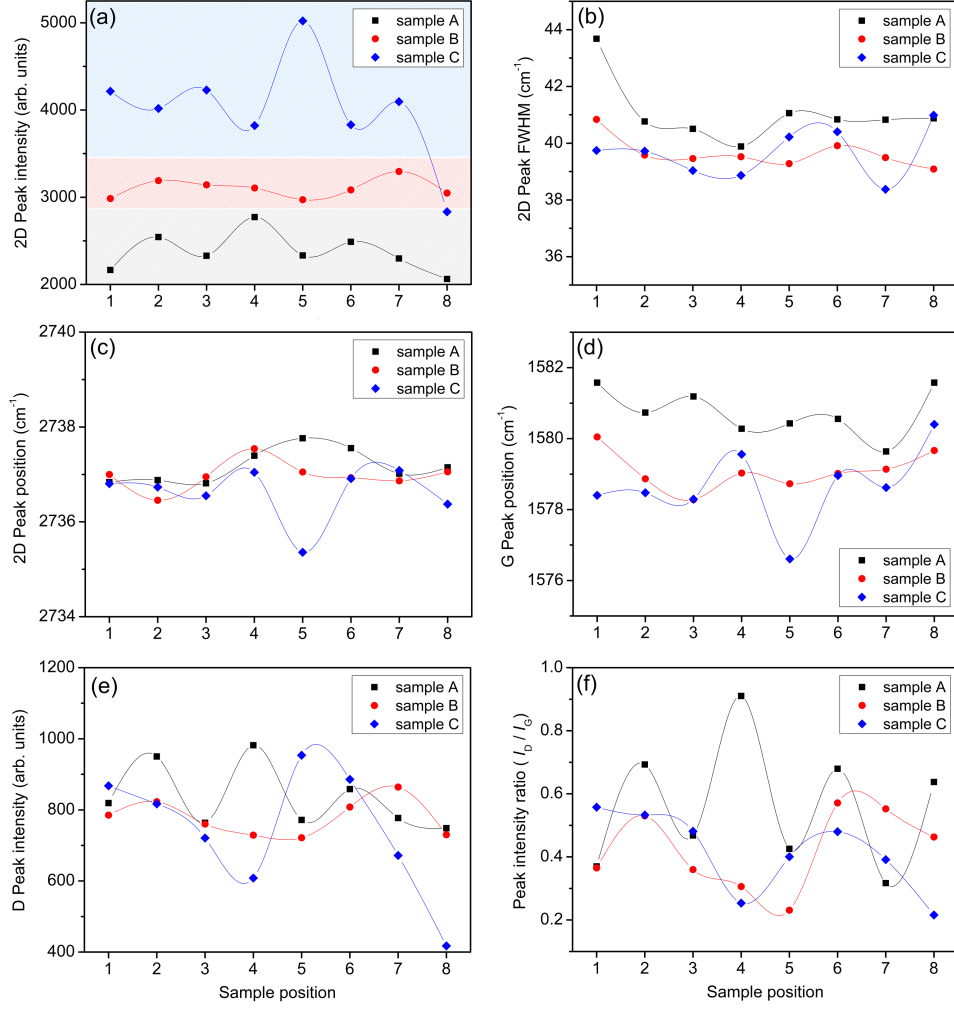


Figure 7.4.: Parameters of the Raman peaks as a function of the measurement position within graphene samples A, B, and C. (a) Values of the 2D peak intensity. The background colour is used to highlight the differences between the samples. (b) Values of 2D peak FWHM. (c) Values of 2D peak position. (d) Values of the G peak position. (e) Values of the D peak intensity. (f) Values of the I_D/I_G intensity ratio.

where E_l is the excitation energy in eV and C is equal to $560 \text{ nm} \cdot \text{eV}$. As shown in table 7.1, the average crystallite size was revealed to be slightly smaller for sample A compared to samples B and C, which had similar values. Considering that the samples have similar characteristics with the exception of number of layers, we use this as a factor of differentiation between them. Next, the pump-probe will allow us to experimentally investigate if differences in the carrier dynamics are observable.

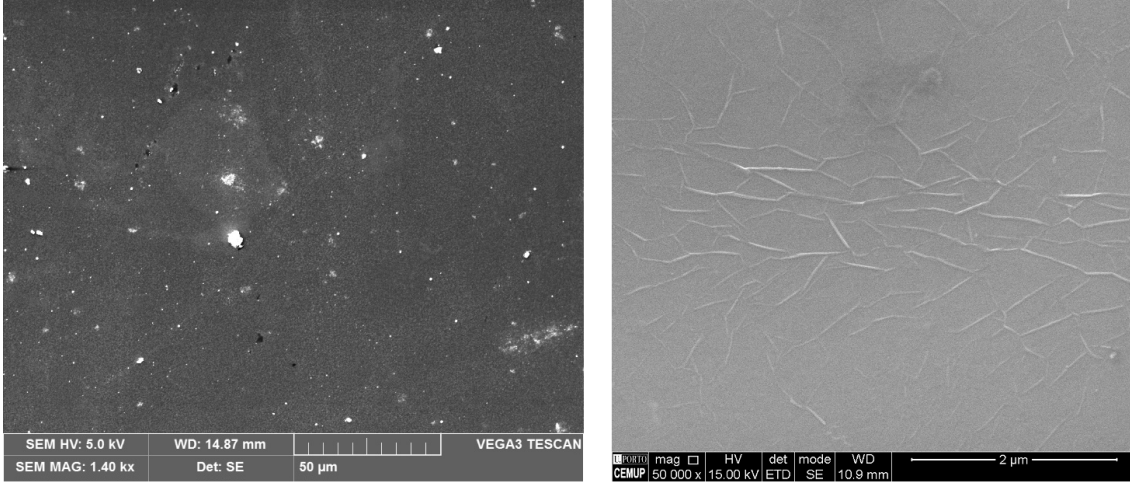


Figure 7.5.: Scanning electron microscopy images of sample C. Left: image with a 50 μm scale bar. Right: image with a 2 μm scale bar.

7.3. Microscopy analysis

The analysis from both scanning electron microscopy (Figure 7.5) and optical microscopy shows that the graphene exhibits a consistent coverage. It is a nearly continuous film, with no large² islands or large holes where the underlying substrate is visible. Although not represented here, it is worth noting that the limiting corners of the graphene samples were damaged, resulting in gaps where the underlying fused silica could be observed. This damage extended up to ~ 1 mm from the corners of the graphene toward the centre. We excluded these areas from our time-resolved spectroscopy measurements.

7.4. Carrier dynamics

After the structural and morphological characterisation of the graphene samples, we will analyse the results from time-resolved spectroscopy and draw conclusions about their carrier relaxation dynamics. In particular, we want to explore the following question: does the number of layers affect the carrier relaxation dynamics of few-layer graphene? In the data analysis, we will use and compare three fitting strategies: a double exponential decay convoluted with a Gaussian function (GDEDC) (i.e. convoluted with the instrument response function), a double exponential decay (DED) fitting only, and the Maximum Entropy Method (MEM) fitting. Unlike the other functions, the MEM fitting strategy does not assume in advance the number of components present within the relaxation

²By ‘large’ we mean a few hundred micrometers.

7. Pump-probe spectroscopy of graphene

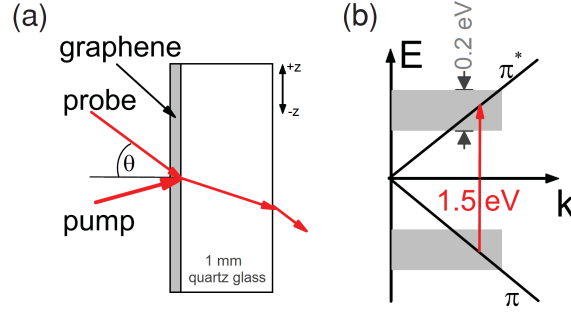


Figure 7.6.: Illustration of graphene in the pump-probe experiment. (a) Few-layer graphene deposited on quartz. The sample can move along the z -axis, therefore different regions of the sample can be analysed. The probe beam hits the surface at an angle θ . (b) Representation of pump excitation. Linear band structure of graphene with the pump and probe optical transitions (red arrow). Adapted from [84].

curve. Comprehensive details regarding the formulation of the MEM algorithm can be found in references [132–134]. We will compare our results to those from the literature, for experiments with graphene under similar conditions to those used in this work.

During the pump-probe measurements, the graphene carriers were optically excited from their equilibrium distribution by the pump pulse as represented in Figure 7.6. Consequently, the probe transmission, $\Delta T/T_0$, changed through time as a result of the carrier redistribution and can be expressed as [84]

$$\frac{\Delta T(\hbar\omega, t)}{T_0} \approx -a_0 \left[\Delta f_e \left(\frac{\hbar\omega}{2}, t \right) + \Delta f_h \left(-\frac{\hbar\omega}{2}, t \right) \right], \quad (7.3)$$

where a_0 is the graphene linear absorption coefficient and $\Delta f_{e,h}(\hbar\omega, t) = f_{e,h}(\hbar\omega, t) - f_{e,h}(\hbar\omega, 0)$ is the difference between the distribution function $f_{e,h}(\hbar\omega, t)$ of electrons and holes at time t and the distribution function $f_{e,h}(\hbar\omega, 0)$ before excitation. Typically, the excited carriers thermalize through carrier-carrier scattering within a ~ 150 fs window [64, 135]. After thermalization, the hot carriers undergo a cooling process to the lattice temperature. In this process, the hot carriers lose most of their energy to the optical phonons within 1 ps or less after photoexcitation [135–137]. In this study, we did three pump-probe measurements in different locations³ for each graphene sample. Under the experimental conditions used, the density of photoexcited carriers was calculated to be on the order of 10^{14} cm^{-2} per layer, estimated using equation 4.4, according to [80, 138]. The differential transmission, $\Delta T/T_0$, as a function of the probe delay for our graphene

³Our measurements were in the center of the graphene sample. We discarded the regions close to the edges. The three measurement positions within the sample were separated by at least of 1 mm, which is greater than the pump spot size used (120 μm).

7. Pump-probe spectroscopy of graphene

samples A, B, and C is shown in Figure 7.7. From the fittings, which we will discuss

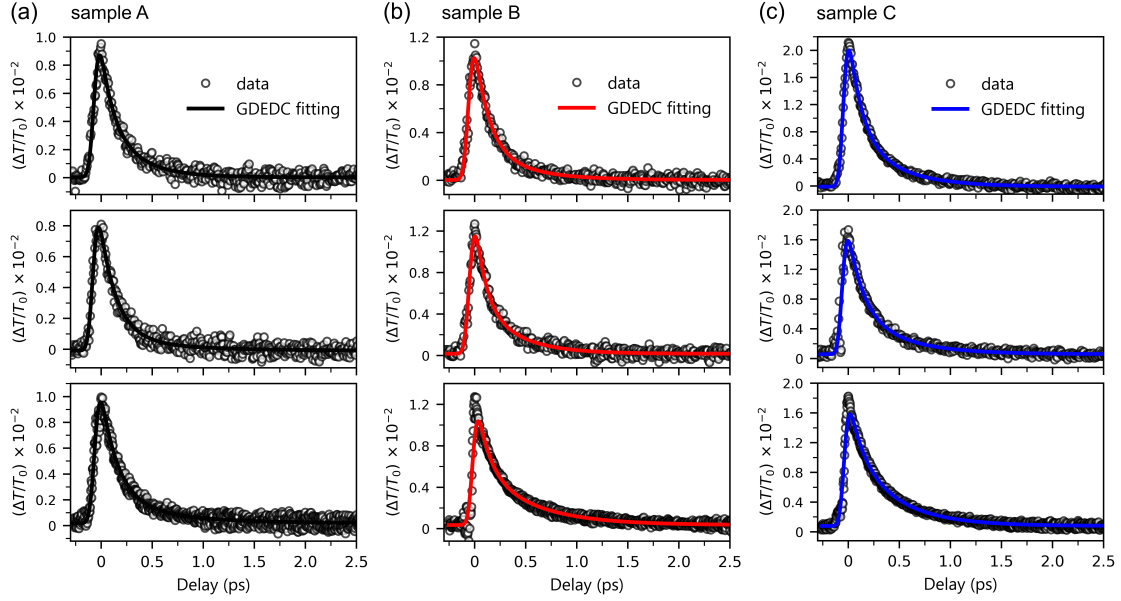


Figure 7.7.: Experimental pump-probe curves for samples A, B and C, respectively from right to left. The circles represent the experimental data and the solid lines represent the GDEDC fitting. GDEDC - Gaussian and Double Exponential Decay Convolution.

next, we observed that the graphene carrier relaxation dynamics consists of two distinct decay times, as expected. We can also observe that the maximum value of $\Delta T/T_0$ is proportional to the number of layers. When applying the GDEDC fitting⁴, see Figure 7.7, we observed a fast recovery constant that falls within the range of 0.12 to 0.15 ps attributed to carrier thermalisation. The slower time constant, due to carrier cooling, was found to vary between 0.4 to 0.5 ps. These results, summarised in Table 7.2, are the average of three measurements taken at different locations in the sample and thus reflect both the uncertainty related to the experiment and variations within the samples. Considering the values from the GDEDC fittings, there is no evidence that the temporal relaxation dynamics of the samples is different. When applying the DED fitting, see Figure 7.8, the retrieved relaxation times increased slightly, in particular τ_2 . From the DED fitting we obtained a τ_1 on the order of 0.15 to 0.18 ps and τ_2 varied between 0.6 to 0.7 ps. If we take a look at the values in Table 7.2 it seems that from the DED fitting, τ_1 increases slightly from A to C. However, these differences fall within the standard deviation. Moreover, the values of τ_2 from sample A present the highest standard deviation, reflecting the lower SNR from the measurements. This is the sample with the lowest number of layers and it was the most ‘difficult’ to measure because its signal was lower compared to B and C

⁴All decay times and residuals from the GDEDC, DED, and MEM fittings are in Appendix C.

7. Pump-probe spectroscopy of graphene

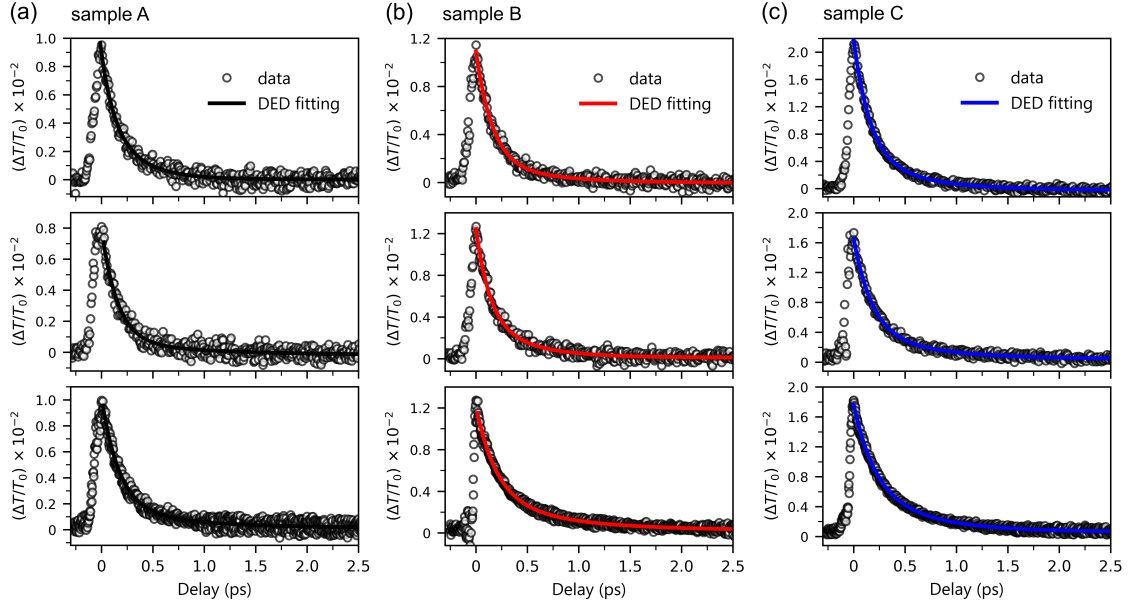


Figure 7.8.: Experimental pump-probe curves for samples A, B and C, respectively from right to left. The circles represent the experimental data and the solid lines represent the DED fitting. In this fitting only the data starting from probe delay = 0 ps was considered for the fit. DED - Double Exponential Decay.

samples. To sum up, considering the results from the DED fittings, there are no significant differences between samples. Although the retrieved values from the GDED and DED fittings are different, they are not too discrepant. In the end, both approaches lead to the same conclusion: no significant differences were found between samples. Similarly to GDED and DED, no significant variation was observed between samples A to C when applying MEM analysis (Figure 7.9). A two-way analysis of variance (ANOVA) was conducted (with a 95% confidence interval) to test for differences in the mean of the relaxation times between samples and between the fitting models. If, on the one hand, we found no evidence of differences in the relaxation times between the graphene samples, on the other hand, the ANOVA shows we cannot ignore that there are differences between the fitting approaches for τ_1 . Figure 7.10 shows the maximum transmission after photoexcitation plotted for several pump fluences. It was verified that the maximum value of $\Delta T/T_0$ was proportional to the pump fluence, excluding the presence of undesired high-order nonlinear effects. Moreover, the pump pulse energy (~ 450 nJ at 1 kHz) used is below the estimated threshold damage for graphene [139–141]. Note, however, that this threshold is dependent on the pulse repetition rate, which here is on the order of the kHz. For ultrabroadband oscillators operating at the typical 80 MHz, additional thermal effects might be present, and thus, this threshold is lower.

7. Pump-probe spectroscopy of graphene

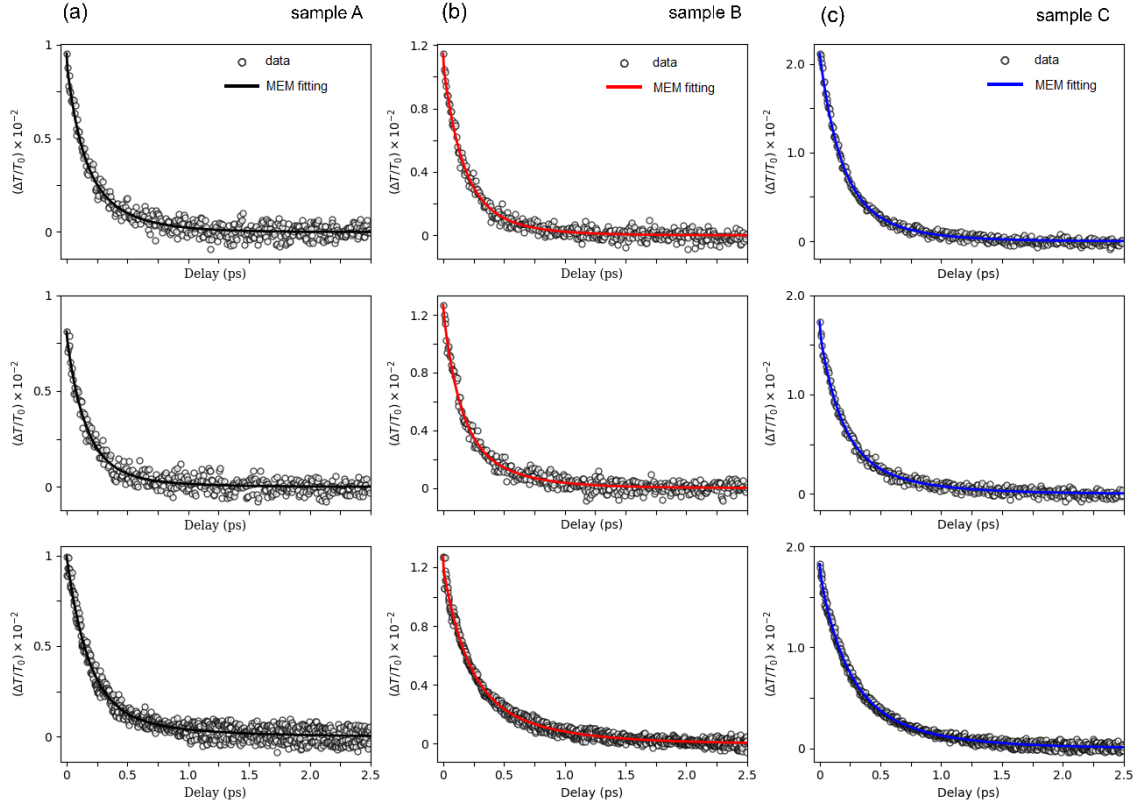


Figure 7.9.: Experimental pump-probe curves for samples A, B and C, respectively from right to left. The circles represent the experimental data and the solid lines represent the MEM fitting. MEM - Maximum Entropy Method

Previous experimental degenerate pump-probe studies have reported changes in the carrier dynamics with the number of layers [142]. The opposite was also reported for optical phonon cooling in multilayer graphene [142]. Graphene samples come in ‘many flavours’, they can have different density and type of defects, different number of layers, different stacking order, different interactions with the substrate, etc. Thus, comparison in the literature can be challenging. In this work, we were assuming that our samples have similar characteristics, with the number of layers being the only variable. However, from Raman spectra we found that in our samples, the graphene layers seem to be disposed relative to each other by an arbitrary rotation angle and thus apparently decoupled. We also do not know precisely the kind of defects present in the crystal lattice, but we know that their presence is similar among the samples. Table 7.3 provides an overview of degenerate pump-probe spectroscopy studies on graphene at around 800 nm. Therefore, similar to the experimental conditions used in this work. From this summary of the literature, we can see that the values for τ_2 can vary from around 0.4 to 2.5 ps. The values obtained in this work are close to those reported by Breusing et al. [84] for a single-layer exfoliated

7. Pump-probe spectroscopy of graphene

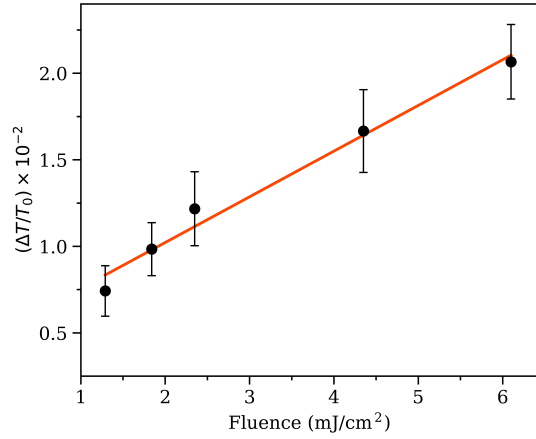


Figure 7.10.: Maximum value of $\Delta T/T_0$ after photoexcitation plotted as a function of the pump fluence. Data from sample C. The orange line represents the linear fitting, showing that under the conditions used high-order nonlinear effects are negligible.

Table 7.2.: Ultrafast relaxation times for graphene samples A, B, and C. The fast τ_1 and slow τ_2 relaxation times were obtained from the GDEDC, DED, and MEM fittings of the pump-probe differential transmission curves. The results are shown as a mean of three measurements done in different positions at the centre of the graphene samples. All values are presented with the corresponding mean standard deviation

Decay time	Fitting	Sample A	Sample B	Sample C
τ_1 (ps)	GDEDC	0.15 ± 0.02	0.12 ± 0.02	0.135 ± 0.008
	DED	0.15 ± 0.03	0.17 ± 0.03	0.18 ± 0.03
	MEM	0.15 ± 0.03	0.16 ± 0.03	0.18 ± 0.03
τ_2 (ps)	GDEDC	0.5 ± 0.2	0.43 ± 0.07	0.44 ± 0.02
	DED	0.7 ± 0.3	0.6 ± 0.1	0.62 ± 0.07
	MEM	0.5 ± 0.2	0.5 ± 0.1	0.54 ± 0.07

graphene.

In conclusion, our pump-probe results suggested that there are no differences in the carrier relaxation times between the samples under study. This study also shows that other parameters should be taken into account, such as the unconventionally stacked configuration of our graphene layers. Therefore, our hypothesis is that the observed ultrafast relaxation times of the samples under study are identical as a result of the random stacking angle.

7.5. Key conclusions

Having explored the carrier dynamics of few-layer graphene in this chapter, we conclude with the following remarks:

7. Pump-probe spectroscopy of graphene

Table 7.3.: Reported carrier relaxation dynamics in graphene by degenerate pump-probe spectroscopy for excitation wavelengths between 780-830 nm. N_{layers} - number of graphene layers; D peak - presence of a D peak on graphene Raman spectra; Excitation - pump and probe central wavelength; Resolution - temporal resolution of the experiment; F_{pump} - pump fluence; τ_1 - fast relaxation time; τ_2 - slow relaxation time; APCVD - ambient-pressure chemical vapour deposition; SiC - silicon carbide; TCVD - thermal chemical vapour deposition. (*Laser pulse duration. **Temporal resolution of the experiment, estimated from the convolution of the 7 fs pump and probe pulses. [†]Attributed to optical phonon lifetime.)

Sample	N_{layers}	Raman D peak	Excitation (nm)	Resolution (fs)	F_{pump} ($\mu\text{J}\cdot\text{cm}^2$)	τ_1 (ps)	τ_2 (ps)	References
Epitaxial graphene on SiC	6	yes	780	85*	160	0.12	1.4	[83]
	12				170	0.07	1.7	
	12				110	0.07	1.7	
	37				126	0.07	0.4	
Epitaxial graphene on SiC	55	yes	780	100*	15	-	2.55 [†]	[136]
	16						2.5 [†]	
	2						2.55 [†]	
APCVD graphene on quartz	2	yes	780	100*	15	-	2.5 [†]	[136]
Exfoliated graphene on muscovite	1	no	830	10**	200	0.14	0.8	[84]
TCVD graphene on soda-lime glass	1	yes	800	100*	8	-	1.25	[85]
					18		1.3	
					25		0.1	
					29		0.2	
					33		1.3	

- (i) From electronic spectra we conclude that our graphene samples A, B, and C have 3, 5, and 6 layers, respectively.
- (ii) From Raman spectra we conclude that the quality of the samples is similar, with comparable defect densities.
- (iii) From Raman spectra we also conclude that layers are apparently decoupled due to the narrow 2D peak of the Raman spectra.
- (iv) SEM micrographs revealed small points of defects in graphene and also some wrinkles. The graphene layers seem to be uniform over a large area.
- (v) The relaxation dynamics of the few-layer graphene samples after excitation at around 1.55 eV is described by a bleaching recovery composed of an electron-electron relaxation time between 120-180 fs and an electron-phonon relaxation time below 1 ps.
- (vi) Three methods were applied to data analysis. Although the values obtained from the

7. *Pump-probe spectroscopy of graphene*

fittings varied, they all suggest that there are no differences in the carrier dynamics between samples.

- (vii) Under the experimental conditions used, the time constants were shown to be independent of the sample thickness.
- (viii) In practice, if the temporal response of graphene is thickness-independent (within the few-layer regime) it means we can improve the efficiency of graphene-based devices without compromising their temporal resolution.

8. Conclusions and perspectives

In this section, we draw the overall conclusions of the work presented in this thesis. The work was mainly divided into two parts, the construction of the femtosecond optical pump-probe setup and the exploitation of few-layer graphene ultrafast carrier dynamics. We also reemphasize the relevance of ultrafast time-resolved measurements in the fundamental research of nanoscience and technological applications. Based on the results of this work, we also discuss short- and long-term future research perspectives.



Custom-built ultrafast pump-probe setup

An optical degenerate pump-probe setup, in transmission geometry, was constructed and implemented in the framework of this thesis. The instrument is mainly intended for femtosecond time-resolved spectroscopy of nanomaterials. It is a tool for tracking their ultrafast dynamics, e.g., lifetime of charge carriers and associated relaxation pathways, providing a deeper understanding of their structure-function and morphology-function interplay. Thereby, the technique contributes to the rational design of nanomaterials, enhancing their efficiency in optoelectronics, catalytic, or biomedical applications.

Details on the pump-probe setup design, optical requirements, and construction were given. Currently, the instrument is driven by a < 35 fs commercial Ti:Sapphire laser amplifier (800 nm, 1 kHz), and its temporal resolution is around 60 fs. It is worth highlighting that the system combines three relevant features:

- (i) High temporal resolution: The setup works with the highest temporal resolution possible, constrained only by the ultrafast laser source (i.e., the Fourier-limited pulse

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width). This was successfully implemented by using a pulse compression block that compensates for optical dispersion. Thus, the setup can be easily adapted to work with other sources, such as ultrabroadband laser oscillators (e.g., pulse duration < 7 fs).

- (ii) High signal-to-noise ratio: The setup can detect very small signals, as low as 10^{-4} , when compared to the probe signal at 1 kHz. A lock-in amplifier, associated with a synchronized mechanical chopper, filters out signals at half the repetition rate, providing a good signal-to-noise ratio.
- (iii) Automation: The instrument is automated and the user can define several setup parameters according to experimental needs, for example, the step delay between the pump and the probe pulses (motor steps), the duration of the experiment, or the position of the sample under study. The ability to control the delay gives more flexibility when studying a wide range of relaxation dynamics, from ultrafast to relatively slow processes. Moreover, the precise positioning of the sample is particularly important when analysing samples with different thicknesses.

The system was successfully tested with nanomaterials: gold nanostructures in aqueous solution and graphene deposited on transparent substrates. In the case of graphene, we proposed to explore the influence of its thickness (in other words, the number of layers) on the relaxation dynamics.

Carrier relaxation dynamics in few-layer graphene

The second goal of this work was to experimentally investigate the impact of sample thickness on the carrier dynamics of few-layer graphene samples. We found that graphene with 3, 5, and 6 layers, showed similar decay time constants. The carrier bleaching recovery presented a first relaxation time around 150 fs and a second, slower, relaxation time on the order of 500 fs. The former is associated with carrier-carrier scattering while the latter is associated with carrier-phonon scattering processes. These temporal decays were obtained by applying different fitting strategies, namely, double exponential decay, double exponential decay convoluted with the instrument response function and the maximum entropy method, which has the ability to discern the decay components without assuming their number in advance. Although with small differences that fall within the associated

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uncertainty, the results of the three fittings converged. The results suggested that, under the experimental conditions used and within the few-layer regime, the carrier relaxation dynamics is independent of the sample thickness. Nonetheless, we interpreted this result carefully since characterisation from Raman spectroscopy suggested that the graphene layers could be randomly oriented relative to each other, and consequently decoupled. Taking this into account, we hypothesized that the observed thickness-independence is a consequence of the graphene interlayer spacing and arrangement. Additional experimental studies need to be done to test this hypothesis. Thus, our results leave the influence of twisted layers on the ultrafast dynamics of graphene as an open question.

One could be asking, what are the practical implications of the findings of this work. We found that one can have a slightly thicker graphene material without significantly compromising its ultrafast response. While graphene's ultrafast dynamics is essential for high-speed optoelectronics, due to its fast excitation and recovery, its ultrathin nature can turn difficult to achieve a reasonable device efficiency. Thus, based on our results, the requirement of single-layer graphene may not be necessary when addressing devices response time. In practice, we can use a sample with more layers obtaining a signal enhancement, without compromising the device temporal performance. Moreover, this could be an advantage when one needs to functionalize graphene.

Future research perspectives

As for the short-term future directions of this research, we intend to turn the degenerate pump-probe system into a non-degenerate one. This would be done with a white light continuum probe and would require adding a different detection block. Options include a monochromator before the detector, or the use of a spectrometer. A non-degenerate pump-probe setup with a broadband probe is more versatile, allowing the study of more materials and molecular systems with complex pathways. It provides information within a wide-range spectral mapping. Other processes, apart from photobleaching, can be followed, such as the case of excited state absorption. Regarding graphene, we aim to study the impact of layer twisting on its carrier relaxation dynamics. This study is, of course, strongly dependent on a fabrication method that would enable control of this feature. To the best of our knowledge, the study of the bilayer and few-layer graphene carrier relaxation dynamics as a function of the layer stacking angle has not yet been explored, despite the

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growing interest in the recent field of twistronics in 2D materials.

The study of carbon-based materials has received continuous attention considering the development of the next generation of electronics, energy storage devices, and sensors. Foresight Portugal 2030, for example, has carbon-derived materials (carbon fibres, carbon nanotubes, graphene) and polymers at the centre of the new techno-economic system, either in terms of structural or functional materials [143]. To contribute to new developments, we intend to use the pump-probe system to conduct ultrafast time-resolved studies on different graphene-based materials, including graphene oxide, graphene quantum dots and functionalised graphene (e.g., can pump-probe be used to confirm/identify different functionalization?).

Finally, we also aim to use pump-probe to study the ultrafast carrier dynamics of gold-based nanostructures as a function of shape and size for tailored biomedical applications.

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Appendix

A. Cross-correlated and convoluted functions

A.1. Cross-correlation of two Gaussian functions

Let A and B be two ultrashort pulses characterised by their intensity profiles $I_A(t)$ and $I_B(t)$, respectively. The intensity profiles are given by:

$$I_A(t) = A_0 \exp\left(-\frac{t^2}{\tau_A^2}\right), \quad (\text{A.1})$$

$$I_B(t) = B_0 \exp\left(-\frac{t^2}{\tau_B^2}\right), \quad (\text{A.2})$$

where A_0 and B_0 are positive constants related to magnitude of the intensity profile and $\tau_{A,B}$ are related to the pulse width (duration) through the FWHM, i.e. $\text{FWHM}_{A,B} = 2\sqrt{\ln(2)}\tau_{A,B}$, as defined in Section 2.2. The cross-correlation of both functions, $I_A(t)$ and $I_B(t)$, is given by

$$G(\tau) = I_A(t) \otimes I_B(t) = \int_{-\infty}^{+\infty} I_A(t) I_B(t + \tau) dt, \quad (\text{A.3})$$

$$G(\tau) = A_0 B_0 \int_{-\infty}^{+\infty} \exp\left(-\frac{t^2}{\tau_A^2}\right) \exp\left(-\frac{(t + \tau)^2}{\tau_B^2}\right) dt. \quad (\text{A.4})$$

We can use the convolution theorem, that states

$$\mathcal{F}_t \{I_A(t) \otimes I_B(t)\}(\omega) = \tilde{I}_A(\omega) \tilde{I}_B^*(\omega), \quad (\text{A.5})$$

where $\tilde{I}_A(\omega)$ and $\tilde{I}_B(\omega)$ are the Fourier transform of $I_A(t)$ and $I_B(t)$, i.e.

A. Cross-correlated and convoluted functions

$$\mathcal{F}_t \{I_{A,B}(t)\}(\omega) = \tilde{I}_{A,B}(\omega) = \int_{-\infty}^{+\infty} I_{A,B}(t) e^{-i\omega t} dt, \quad (\text{A.6})$$

and $(*)$ denotes the complex conjugated of $\tilde{I}_B(\omega)$. Therefore, we have

$$G(\tau) = \mathcal{F}_\omega^{-1} \left\{ \tilde{I}_A(\omega) \tilde{I}_B^*(\omega) \right\}(t), \quad (\text{A.7})$$

where $\mathcal{F}_\omega^{-1}$ is the inverse Fourier transform given by

$$\mathcal{F}_\omega^{-1} \left\{ \tilde{I}_A(\omega) \tilde{I}_B^*(\omega) \right\}(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{I}_A(\omega) \tilde{I}_B^*(\omega) e^{i\omega t} d\omega. \quad (\text{A.8})$$

Substituting the equations (A.9) and (A.10)

$$\tilde{I}_A(\omega) = A_0 \tau_A \sqrt{\pi} \exp \left(-\frac{\omega^2 \tau_A^2}{4} \right), \quad (\text{A.9})$$

$$\tilde{I}_B^*(\omega) = B_0 \tau_B \sqrt{\pi} \exp \left(-\frac{\omega^2 \tau_B^2}{4} \right), \quad (\text{A.10})$$

into (A.7) and performing the calculations, we find that

$$G(t) = A_0 B_0 \frac{\sqrt{\pi} \tau_A \tau_B}{\sqrt{\tau_A^2 + \tau_B^2}} \exp \left(-\frac{t^2}{\tau_A^2 + \tau_B^2} \right). \quad (\text{A.11})$$

If we define the constant G_0 as

$$G_0 = A_0 B_0 \frac{\sqrt{\pi} \tau_A \tau_B}{\sqrt{\tau_A^2 + \tau_B^2}}, \quad (\text{A.12})$$

and the temporal width parameter τ_c as

$$\tau_c = \sqrt{\tau_A^2 + \tau_B^2}, \quad (\text{A.13})$$

we can rewrite equation (A.11) as

$$G(t) = G_0 \exp \left[-\frac{t^2}{\tau_c^2} \right]. \quad (\text{A.14})$$

Therefore, the cross-correlation of the two Gaussian pulses, A and B , yields also a Gaussian function, $G(t)$, with a FWHM given by

A. Cross-correlated and convoluted functions

$$\text{FWHM}_G = 2\sqrt{\ln 2} \tau_c \approx 1.6651 \tau_c. \quad (\text{A.15})$$

Since τ_A and τ_B are related to FWHM of the pulses A and B , respectively, through

$$\text{FWHM}_{A,B} = 2\sqrt{\ln 2} \tau_{A,B} \approx 1.6651 \tau_{A,B}, \quad (\text{A.16})$$

we can rewrite equation (A.13) as

$$\tau_c = \frac{1}{2\sqrt{\ln 2}} \sqrt{\text{FWHM}_A^2 + \text{FWHM}_B^2}. \quad (\text{A.17})$$

As a result, the FWHM of $G(t)$ is related to FWHM_A and FWHM_B through

$$\text{FWHM}_G = \sqrt{\text{FWHM}_A^2 + \text{FWHM}_B^2}. \quad (\text{A.18})$$

For the particular case where $\tau_A = \tau_B$, equations (A.13) and (A.18) become

$$\tau_c = \sqrt{2} \tau_A, \quad (\text{A.19})$$

$$\text{FWHM}_G = \sqrt{2} \text{FWHM}_A. \quad (\text{A.20})$$

A.2. Convolution of a double decay exponential with a Gaussian function

Consider a double exponential decay response function $h(t)$ and a Gaussian function $G(t)$, respectively given by

$$h(t) = A \exp\left(-\frac{t}{\tau_1}\right) + B \exp\left(-\frac{t}{\tau_2}\right), \quad (\text{A.21})$$

$$G(t) = G_0 \exp\left[-\frac{t^2}{\tau_c^2}\right], \quad (\text{A.22})$$

where τ_1 and τ_2 are fast and slow decay times ($\tau_2 > \tau_1$) and τ_{ac} is related with temporal width of the pulse. The convolution of both functions is given by

$$C(t) = h(t) * G(t) = \int_{-\infty}^{+\infty} h(\tau) G(t - \tau) d\tau. \quad (\text{A.23})$$

A. Cross-correlated and convoluted functions

Applying the expressions for $h(t)$ and $G(t)$ and using the distributivity property of the convolution, we get

$$\begin{aligned} C(t) = & AG_0 \int_0^{\infty} \exp\left(-\frac{\tau}{\tau_1}\right) \exp\left[-\frac{(t-\tau)^2}{\tau_c^2}\right] d\tau \\ & + BG_0 \int_0^{\infty} \exp\left(-\frac{\tau}{\tau_2}\right) \exp\left[-\frac{(t-\tau)^2}{\tau_c^2}\right] d\tau, \end{aligned} \quad (\text{A.24})$$

where the lower limit of integration was set to zero since the exponential decay function has a domain $[0, \infty]$. Each of the integrals in equation (A.24) is the convolution of a single exponential decay function with a Gaussian function. Thus, we can split this convolution $C(t)$ into two, i.e.,

$$C(t) = AG_0 C_1(t) + BG_0 C_2(t), \quad (\text{A.25})$$

where

$$C_1(t) = \int_0^{+\infty} \exp\left(-\frac{\tau}{\tau_1}\right) \exp\left[-\frac{(t-\tau)^2}{\tau_c^2}\right] d\tau, \quad (\text{A.26})$$

$$C_2(t) = \int_0^{+\infty} \exp\left(-\frac{\tau}{\tau_2}\right) \exp\left[-\frac{(t-\tau)^2}{\tau_c^2}\right] d\tau. \quad (\text{A.27})$$

Both integrals are similar and, therefore, we will just be performing the calculations for one of them. Let us define $\alpha = 1/\tau_1$ such that

$$C_1(t) = \int_0^{+\infty} \exp\left[-\frac{(t-\tau)^2}{\tau_c^2}\right] \exp(-\alpha\tau) d\tau. \quad (\text{A.28})$$

Using the exponential property of product of powers, we can rewrite the exponent in the following manner:

$$-\frac{(t-\tau)^2}{\tau_c^2} - \alpha t = -\frac{1}{\tau_c^2} \left(\tau - t + \frac{\alpha\tau_c^2}{2} \right)^2 - \alpha t + \frac{\alpha^2\tau_c^2}{4}. \quad (\text{A.29})$$

Substituting equation (A.29) into equation (A.28), we get

$$C_1(t) = \exp(-\alpha t) \exp\left(\frac{\alpha^2\tau_c^2}{4}\right) \int_0^{+\infty} \exp\left[-\left(\frac{\tau - t + \frac{\alpha\tau_c^2}{2}}{\tau_c}\right)^2\right] d\tau. \quad (\text{A.30})$$

A. Cross-correlated and convoluted functions

To solve this integral we will use the chain rule. First, we define¹

$$\tau(\xi) = \tau_c \xi + t - \frac{\alpha \tau_c^2}{2}, \quad (\text{A.31})$$

such that

$$\exp \left[- \left(\frac{\tau - t + \frac{\alpha \tau_c^2}{2}}{\tau_c} \right)^2 \right] = \exp \left(-\xi^2 \right). \quad (\text{A.32})$$

Using the chain rule

$$\int_{x_1}^{x_2} f(x) dx = \int_{\xi_1=g^{-1}(x_1)}^{\xi_2=g^{-1}(x_2)} f(g(\xi)) \frac{dg(\xi)}{d\xi} d\xi, \quad (\text{A.33})$$

we have that

$$\int_0^\infty \exp \left[- \left(\frac{\tau - t + \frac{\alpha \tau_c^2}{2}}{\tau_c} \right)^2 \right] = \tau_c \int_0^\infty \exp \left(-\xi^2 \right) d\xi, \quad (\text{A.34})$$

where

$$\xi(t) = \frac{\tau - t + \frac{\alpha \tau_c^2}{2}}{\tau_c}. \quad (\text{A.35})$$

Substituting equation (A.34) into (A.30), we obtain

$$C_1(t) = \tau_c \exp(-\alpha t) \exp \left(\frac{\alpha^2 \tau_c^2}{4} \right) \int_0^\infty \exp \left[-\xi^2 \right] d\xi. \quad (\text{A.36})$$

The error function erf is defined as

$$\text{erf}(y) = \frac{2}{\sqrt{\pi}} \int_0^y e^{-x^2} dx. \quad (\text{A.37})$$

Thus, using equation (A.37) and equation (A.35), we can write equation (A.36) as

$$C_1(t) = \frac{\sqrt{\pi}}{2} \tau_c \exp(-\alpha t) \exp \left(\frac{\alpha^2 \tau_c^2}{4} \right) \left[\text{erf} \left(\frac{\tau - t + \frac{\alpha \tau_c^2}{2}}{\tau_c} \right) \right] \Big|_0^\infty. \quad (\text{A.38})$$

Calculating the limits, we obtain

$$C_1(t) = \frac{\sqrt{\pi}}{2} \tau_c \exp(-\alpha t) \exp \left(\frac{\alpha^2 \tau_c^2}{4} \right) \left[1 - \text{erf} \left(\frac{\tau_c}{2\tau_1} - \frac{t}{\tau_c} \right) \right]. \quad (\text{A.39})$$

¹Note that the inverse function is given by: $t^{-1}(\xi) = \frac{\xi - \tau + \frac{\alpha \tau_c^2}{2}}{\tau_c}$

A. Cross-correlated and convoluted functions

By doing the same steps for $C_2(t)$, we can now finally write the convolution of equation (A.24)

$$\begin{aligned} C(t) = & A' \exp\left(-\frac{t}{\tau_1}\right) \left[1 - \operatorname{erf}\left(\frac{\tau_c}{2\tau_1} - \frac{t}{\tau_c}\right)\right] \\ & + B' \exp\left(-\frac{t}{\tau_2}\right) \left[1 - \operatorname{erf}\left(\frac{\tau_c}{2\tau_2} - \frac{t}{\tau_c}\right)\right], \end{aligned} \quad (\text{A.40})$$

where we defined constants A' and B' respectively as

$$A' = AG_0 \frac{\sqrt{\pi}}{2} \tau_c \exp\left(\frac{\tau_c^2}{4\tau_1^2}\right), \quad (\text{A.41})$$

$$B' = BG_0 \frac{\sqrt{\pi}}{2} \tau_c \exp\left(\frac{\tau_c^2}{4\tau_2^2}\right). \quad (\text{A.42})$$

B. Custom-built GUI

Screenshots of the custom-built GUI that controls the pump-probe system, collects, and saves experimental data.

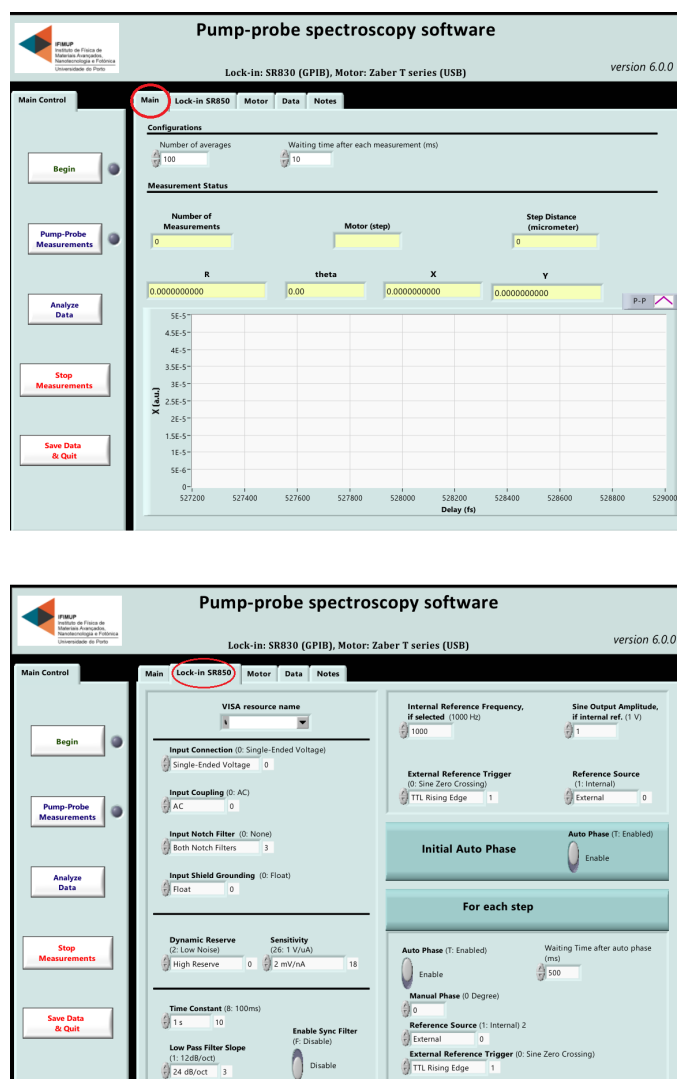


Figure B.1.: Screenshots of the custom-built GUI: ‘Main’ tab (top) and ‘Lock-in’ tab (bottom).

B. Custom-built GUI

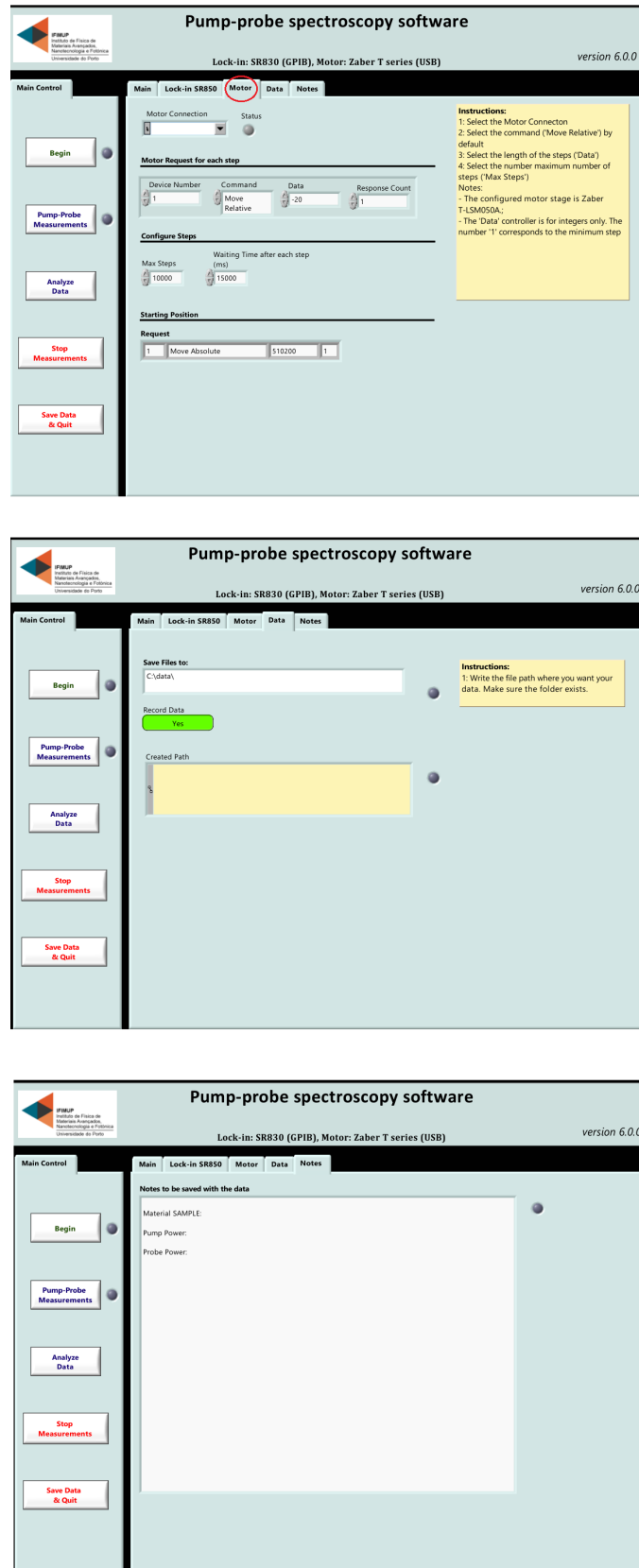


Figure B.2.: Screenshots of the custom-built GUI: 'Motor' tab (top), 'Data' tab (middle) and 'Notes' tab (bottom).

C. Decay times and residuals

In Tables C.1 and C.2: decay times τ_1 and τ_2 obtained from all fittings (GDEDC, DED, MEM) for samples A, B, and C. Three measurements (#1, #2, #3) were taken per sample at different positions. The mean values of these decay times are reported in Table 7.2 of Section 7.4. In Figures C.1, C.2, C.3, C.4, C.5, C.6: residuals of the pump-probe data fittings, DED, GDEDC and MEM presented in Section 7.4 for samples A, B and C.

Table C.1.: All values of the ultrafast relaxation time, τ_1 , for the graphene samples A, B and C obtained from the GDEDC, DED and MEM fittings

Decay time		τ_1 (ps)		
Fit function		GDEDC	DED	MEM
Sample A	#1	0.12	0.12	0.12
	#2	0.16	0.16	0.15
	#3	0.16	0.17	0.18
Sample B	#1	0.14	0.16	0.15
	#2	0.10	0.14	0.13
	#3	0.12	0.19	0.19
Sample C	#1	0.13	0.16	0.16
	#2	0.13	0.18	0.18
	#3	0.14	0.19	0.20

C. Decay times and residuals

Table C.2.: All values of ultrafast relaxation time, τ_2 , for the graphene samples A, B and C. Values obtained from the GDEDC, DED and MEM fittings

Decay time		τ_2 (ps)		
Fit function		GDEDC	DED	MEM
Sample A	#1	0.32	0.32	0.35
	#2	0.64	0.96	0.45
	#3	0.61	0.81	0.68
Sample B	#1	0.43	0.67	0.38
	#2	0.36	0.45	0.41
	#3	0.50	0.73	0.61
Sample C	#1	0.42	0.57	0.46
	#2	0.46	0.69	0.55
	#3	0.43	0.58	0.61

C. Decay times and residuals

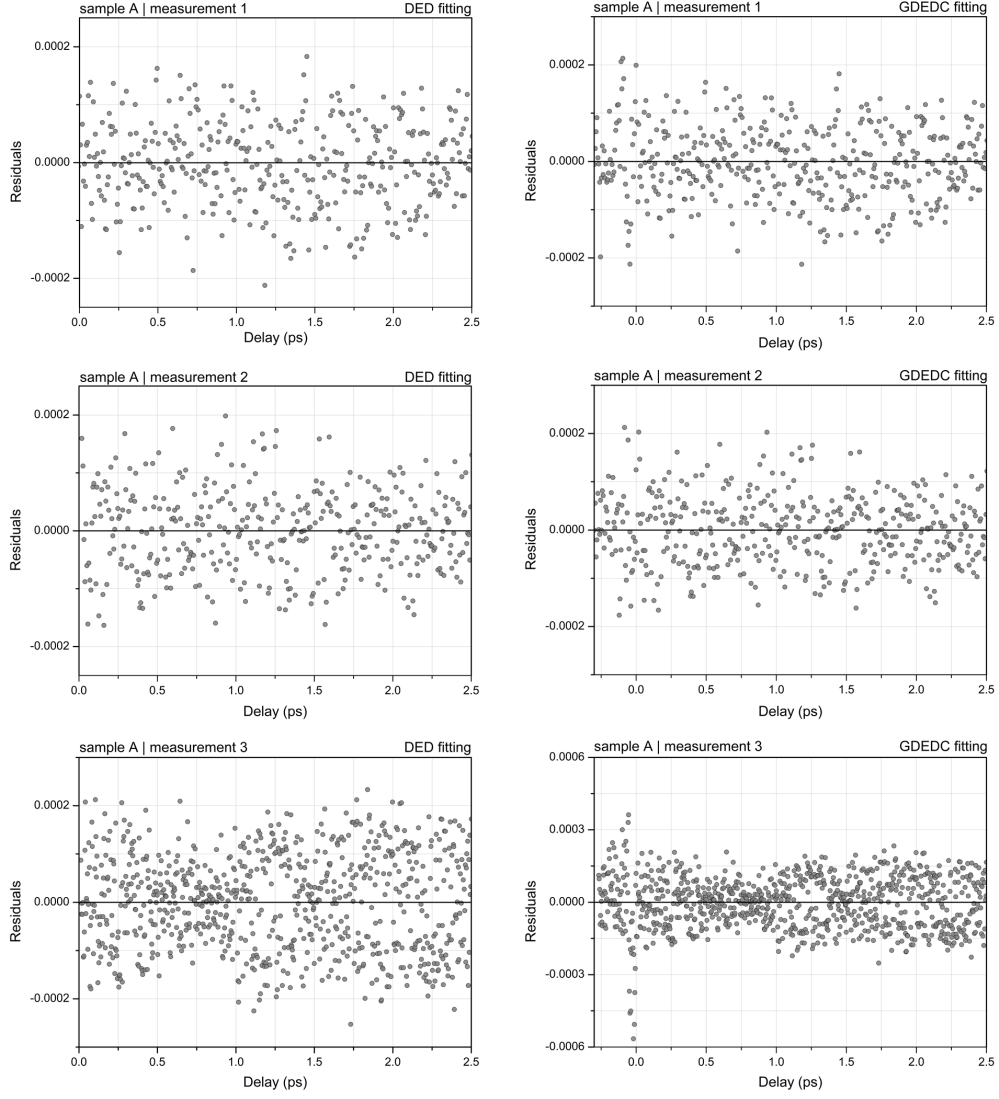


Figure C.1.: Residuals of the data fittings GEDC and DED presented in Section 7.4 for sample A.

C. Decay times and residuals

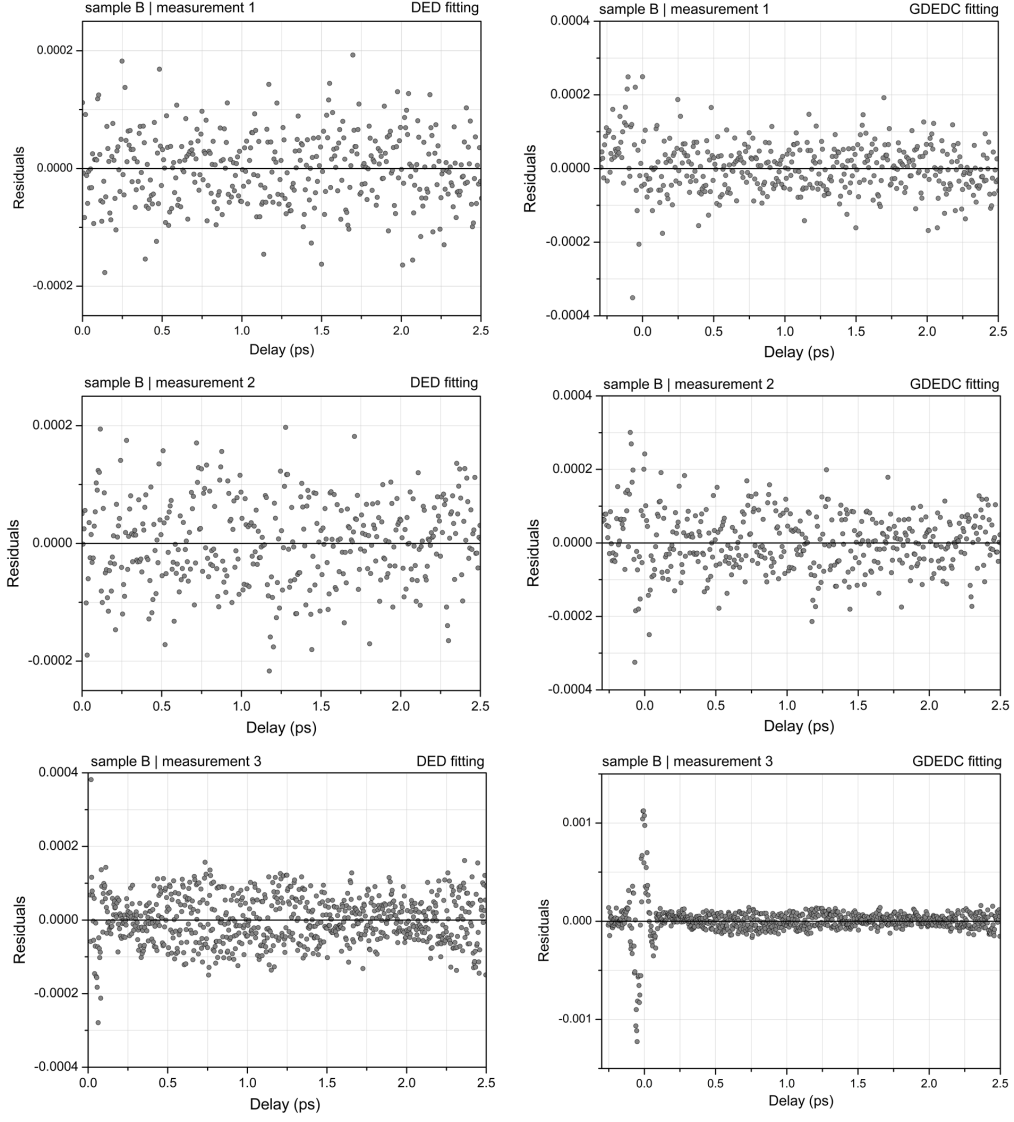


Figure C.2.: Residuals of the data fittings GDEDC and DED presented in Section 7.4 for sample B.

C. Decay times and residuals

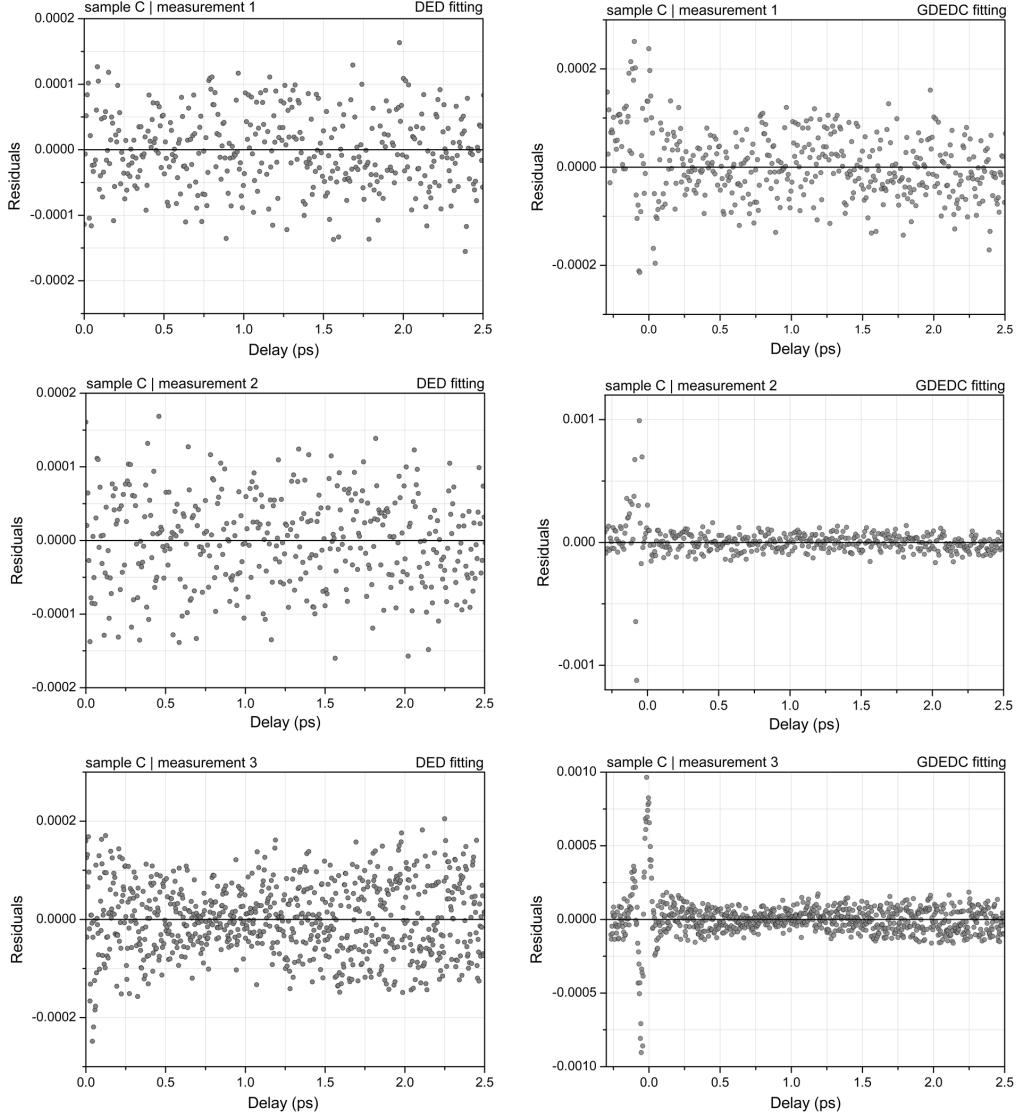


Figure C.3.: Residuals of the data fittings GDEDC and DED presented in Section 7.4 for sample C.

C. Decay times and residuals

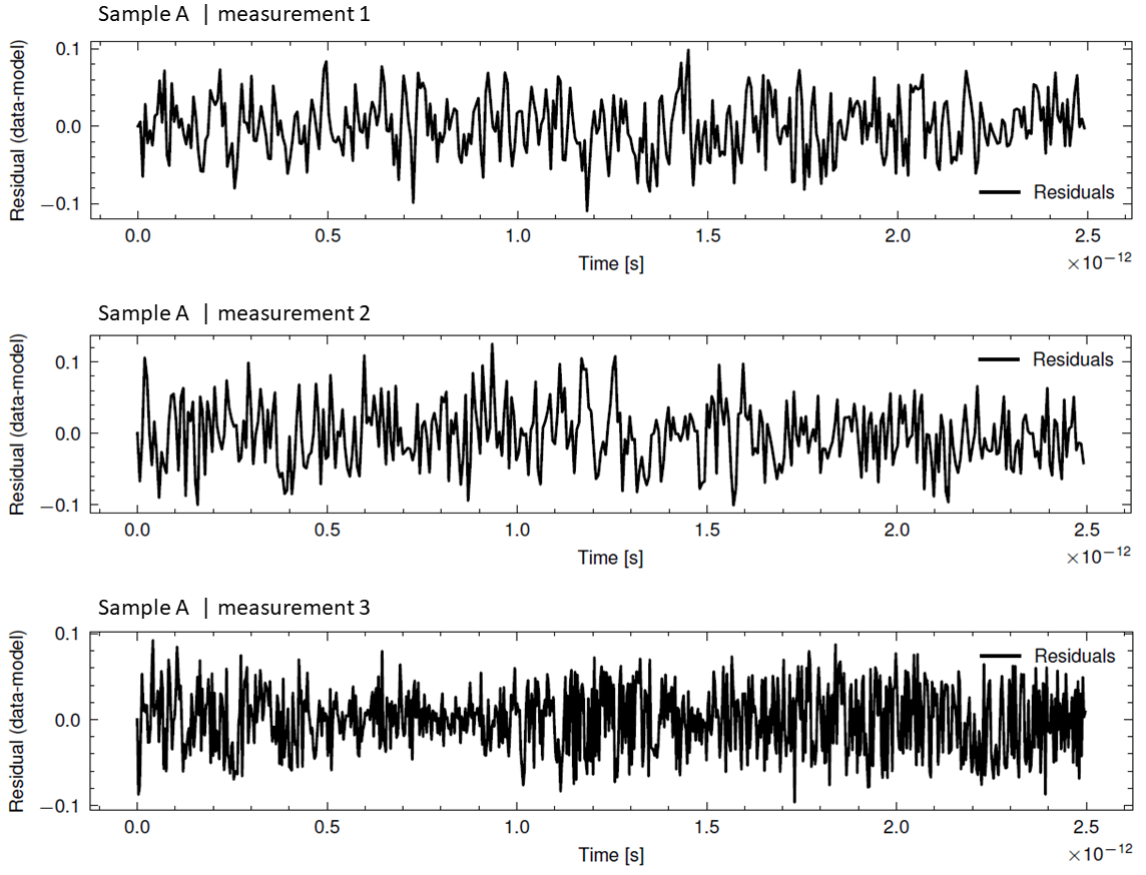


Figure C.4.: Residuals of the MEM data fitting presented in Section 7.4 for sample A.

C. Decay times and residuals

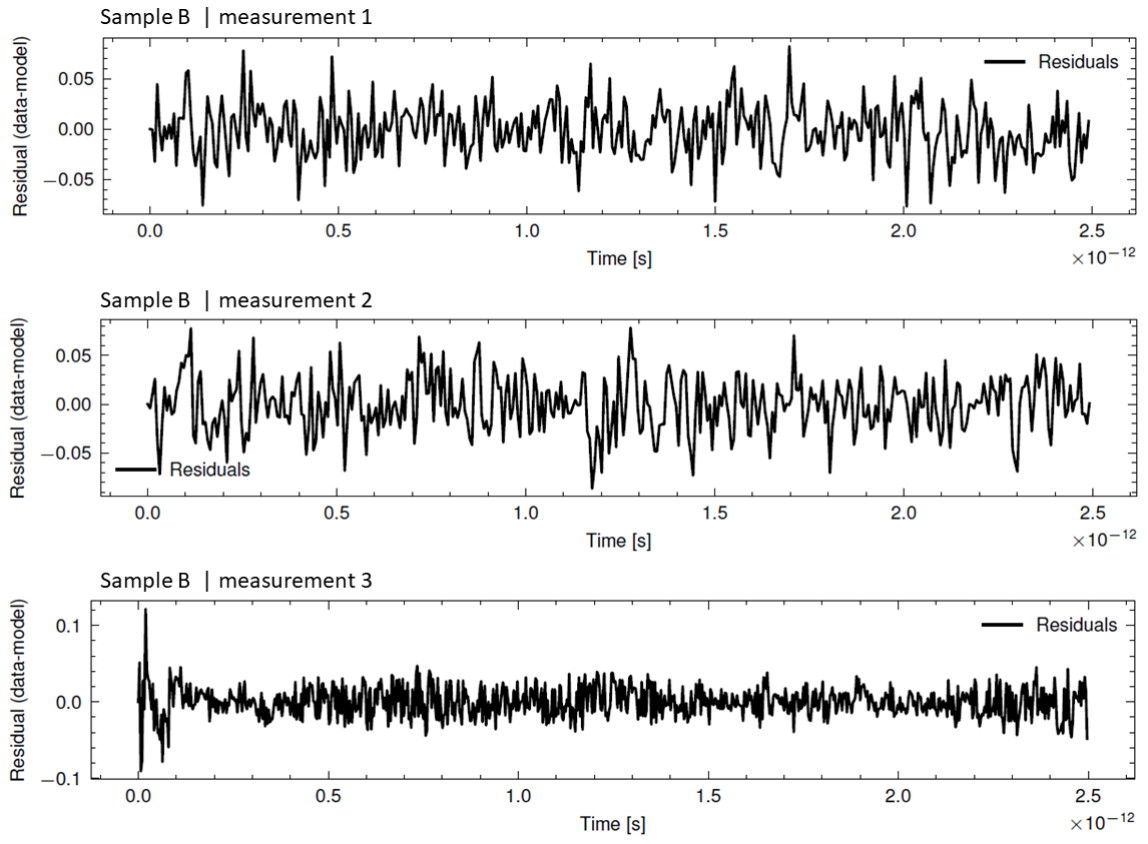


Figure C.5.: Residuals of the MEM data fitting presented in Section 7.4 for sample B.

C. Decay times and residuals

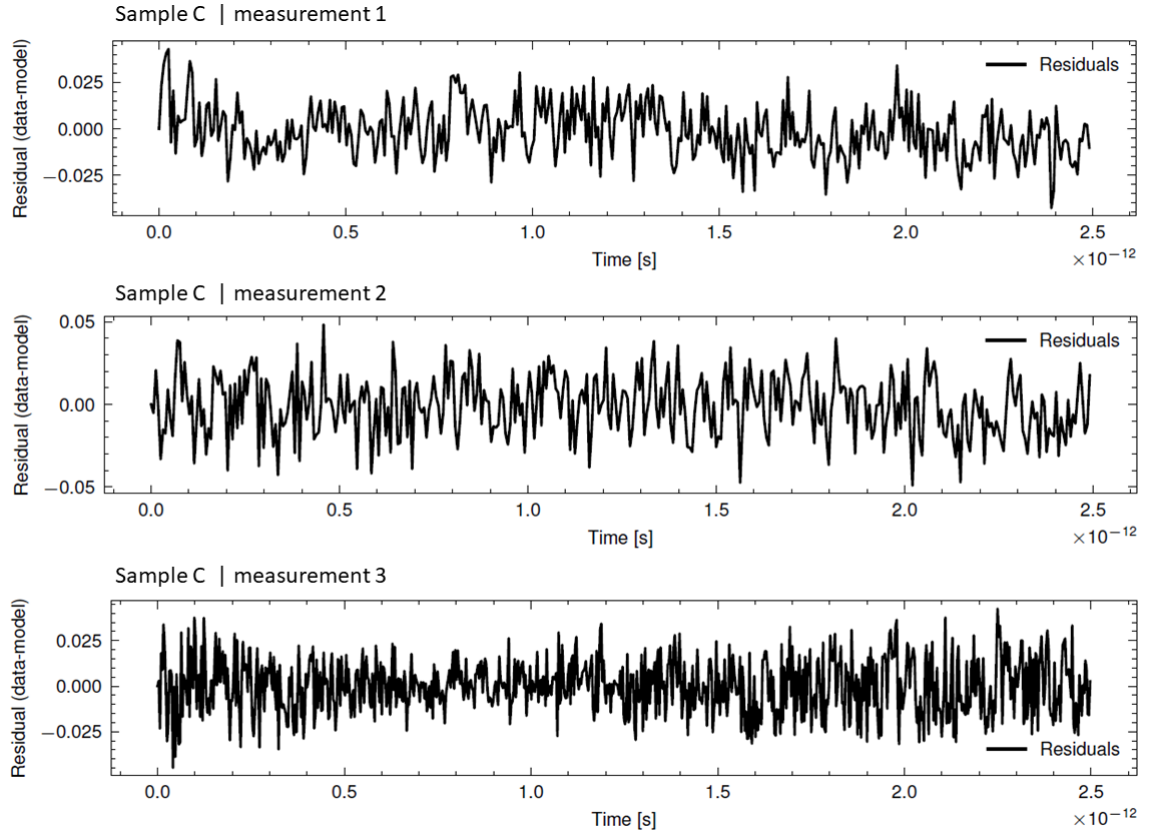


Figure C.6.: Residuals of the MEM data fitting presented in Section 7.4 for sample C.

Publications

Publications within the scope of this thesis:

Observation of thickness-independent ultrafast relaxation times in MPCVD few-layer graphene

Tânia M. Ribeiro, T. E. C. Magalhães, B. Kulyk, A. F. Carvalho, S. Nilsson, H. Feuk, A. J. S. Fernandes, F. Costa, P. T. Guerreiro, H. Crespo
Carbon 232, 119700 (2025)

In preparation: Nonlinear and ultrafast spectroscopy studies of gold nanostructures in aqueous solution

Tânia M. Ribeiro, T. E. C. Magalhães, P. T. Guerreiro, H. Crespo

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Awards:

Roger Kelly Award

Roger Kelly Award under the Rising Stars category (3rd year of PhD and postdoctoral researchers) at the 8th Venice International School on Lasers in Materials Science (SLIMS) in Italy. It recognizes the best research poster and presentation.