

Terahertz Spectroscopy of Graphene and Other Two-Dimensional Materials



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A thesis submitted for the degree of
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In this thesis, two-dimensional materials such as graphene are tested for their suitability for opto-electronic applications using terahertz time domain spectroscopy (THz-TDS). This ultrafast all-optical technique can probe the response of novel materials to photoexcitation, and yield information about the dynamics of the material systems.

Graphene grown by chemical vapour deposition (CVD) is studied using optical-pump THz-probe time domain spectroscopy in a variety of gaseous environments in Chapter 4. The photoconductivity response of graphene grown by CVD is found to vary dramatically depending on which atmospheric gases are present. Adsorption of these gases can open a local bandgap in the material, allowing stimulated emission of THz radiation across the gap.

Semiconducting equivalents to graphene, molybdenum disulphide (MoS_2) and tungsten diselenide (WSe_2), grown by CVD, are investigated in Chapter 5. These members of the transition metal dichalcogenide family show sub-picosecond responses to photoexcitation, suggesting promise for use in high-speed THz devices.

In Chapter 6, an alternative production route to CVD is studied. Liquid-phase exfoliation offers fast, easy production of few-layer materials. THz spectroscopy reveals that the dynamics of these materials after photoexcitation are remarkably similar to those in CVD-grown materials, offering the potential of cheaper materials for future devices.

Finally in Chapter 7, it is shown that carbon nanotubes can be used to make ultrafast THz devices. Unaligned, semiconducting single walled carbon nanotubes can be photoexcited to produce an ultrafast, dynamic THz polariser.

The work in this thesis demonstrates the potential for these novel materials in future opto-electronic applications. THz spectroscopy is shown to be an important tool for the characterisation of new materials, providing information that can be used to understand the dynamics of materials, and improve production methods.

Journal Publications

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- H.J. Joyce, J. Wong-Leung, C. Yong, C.J. Docherty, S. Paiman, Q. Gao, H.H. Tan, C. Jagadish, J. Lloyd-Hughes, L.M. Herz and M.B. Johnston, “Ultra-low Surface Recombination Velocity in InP Nanowires Probed by Terahertz Spectroscopy”, *Nano Lett.*, 12, 5325-5330, 2012
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Contents

1	Introduction	1
1.1	Terahertz Radiation	2
1.1.1	Uses of terahertz radiation	3
1.2	Overview of this thesis	4
2	Experimental Methods	7
2.1	Ultrafast spectroscopy	8
2.1.1	Optical pump-probe spectroscopy	8
2.1.2	Non-linear optics	9
2.1.2.1	Sum-frequency generation	10
2.1.2.2	Second-harmonic generation	11
2.2	Optical-pump terahertz-probe spectroscopy	11
2.2.1	Time-domain spectroscopy	11
2.2.2	Generation of THz radiation	12
2.2.2.1	Optical rectification	13
2.2.3	Electro-optic detection of THz radiation	13
2.3	Experimental setup	15
2.3.1	Double lock-in detection	18
2.3.2	Generation of higher frequency pump pulses	19
2.4	Analysis of data from THz spectroscopy	20
2.4.1	Equilibrium THz conductivity	20

2.4.2	THz Photoconductivity	23
2.5	Physical interpretation of THz photoconductivity	24
2.5.1	Free charge carriers - Drude conductivity	25
2.5.2	Lorentzian conductivity	26
2.6	Other experimental techniques	27
3	Introduction to graphene and two-dimensional materials	29
3.1	Introduction	30
3.2	The structure of graphene	31
3.3	Production of graphene	33
3.3.1	Mechanical exfoliation	34
3.3.2	Epitaxial Growth	34
3.3.3	Chemical vapour deposition (CVD)	35
3.3.4	Wet chemical routes	37
3.4	Terahertz transmission and equilibrium conductivity of graphene . . .	38
3.5	Pump-Probe Spectroscopy	41
3.5.1	Optical Pump–Optical Probe	41
3.5.2	Optical–pump terahertz–probe spectroscopy	44
3.5.3	Theoretical results and THz lasing	53
3.6	Other 2D materials	53
3.6.1	Transition metal dichalcogenides	55
3.7	Carbon nanotubes	58
4	Sensitivity of graphene photoconductivity to environmental gases	61
4.1	Introduction	62
4.2	Sample preparation	63
4.3	Sample characterisation	64
4.3.1	Hall measurements	66

4.4	Terahertz time domain spectroscopy	67
4.4.1	Terahertz Transmission	67
4.4.2	Optical-pump–THz-probe measurements	69
4.4.3	Fluence dependence of photoconductivity	74
4.5	Surface coverage calculations	78
4.6	Discussion	79
4.7	Conclusion	82
5	Ultrafast transient terahertz conductivity of CVD-grown MoS₂ and WSe₂	85
5.1	Introduction	86
5.2	Growth and characterisation	89
5.3	Photoluminescence and THz photoconductivity measurements	90
5.3.1	Monolayer MoS ₂	91
5.3.1.1	Pump energy dependence of THz measurements . . .	94
5.3.2	Monolayer WSe ₂	94
5.3.3	Trilayer MoS ₂	97
5.3.3.1	Reflections in the trilayer data	99
5.4	THz photoconductivity spectra	100
6	Evaluating the photoconductive performance of semiconducting and semi-metal nanoflakes using terahertz time domain spectroscopy	103
6.1	The potential of liquid-phase nanoflake production	104
6.2	THz spectroscopy	108
6.2.1	Pump-Probe Measurements	108
6.2.2	Photoconductivity spectra	111
7	An ultrafast carbon nanotube terahertz polarisation modulator	115
7.1	Introduction	116

7.2	Sample growth and characterisation	117
7.3	Using THz TDS to demonstrate optically activated polarisation . . .	119
7.3.1	Transient polarisation	121
7.3.2	Switch on speed	123
8	Conclusion	127
8.1	Future work	128

List of Figures

1.1	The THz Gap	2
2.1	Electro-optic sampling	14
2.2	Schematic of system used for OPTP-TDS measurements	16
2.3	Principle of OPTP-TDS measurements	18
2.4	Derivation of THz transmission equations	21
3.1	The structure of graphene	31
3.2	Band structure of graphene	32
3.3	Different forms of graphene	36
3.4	Terahertz transmission spectrum of graphene	39
3.5	Optical-pump optical-probe spectroscopy of graphene	43
3.6	An OPTP study of graphite	45
3.7	OPTP of epitaxial graphene	47
3.8	Alternative OPTP study of epitaxial graphene	49
3.9	Temperature dependence of graphene THz photoconductivity	51
3.10	Simulation of stimulated THz emission from graphene	54
3.11	Structure of a TMD monolayer	57
4.1	Characterisation of graphene samples	65
4.2	UV–Visible absorption spectrum of graphene sample	65
4.3	THz transmission spectra of graphene in different gaseous environments	68
4.4	Terahertz spectroscopy of graphene in O ₂	71

4.5	Environmental dependence of pump induced change in terahertz photoconductivity $\Delta E/E_{\text{THz}}$	72
4.6	Photoconductivity spectra of graphene in different environments. . . .	75
4.7	Pump fluence dependence of THz photoconductivity spectra in air . .	76
4.8	Pump fluence dependence of peak THz transmission change in air . .	77
4.9	Estimated surface coverage of atmospheric gases on graphene	79
5.1	Characterisation of transition metal dichalcogenide samples	87
5.2	Photodynamics of monolayer MoS ₂	92
5.3	Fluence dependence of the peak pump induced THz transmission intensity change in monolayer MoS ₂	93
5.4	Fluence dependence of monolayer MoS ₂ photodynamics	95
5.5	Pump energy dependence of monolayer MoS ₂ photodynamics	96
5.6	Spectra of THz and PL pump beams	96
5.7	Photodynamics of monolayer WSe ₂	97
5.8	Comparison of photodynamics in monolayer and trilayer MoS ₂	98
5.9	Removing reflections from trilayer data	99
5.10	THz photoconductivity spectra	101
6.1	Characterisation of nanoflake samples	106
6.2	Ultrafast response of nanoflakes to photoexcitation	109
6.3	Comparison of photodynamics of CVD-grown and liquid-phase exfoliated graphene	110
6.4	Photoconductivity spectra of exfoliated nanoflakes	112
7.1	Characterisation of SWNT dispersion	118
7.2	Selective modulation of THz radiation	120
7.3	Time dependence of THz modulation	122
7.4	Sub-picosecond polariser switch on	124

Chapter 1

Introduction

In the past few decades, progress in electronics has relied upon scaling silicon technology to ever smaller dimensions ^[1]. Further reductions in scale will soon reach a limit imposed by statistical and quantum effects, and difficulties with heat dissipation ^[2]. To continue progress in electronic and opto-electronic applications, new materials and new device concepts are required.

The realisation of two-dimensional materials has opened up a new front in the search for post-silicon materials. Starting with graphene in 2004 ^[3], a wealth of 2D materials have been produced, revealing novel physics and promising exciting technological advances ^[4]. Graphene in particular has sparked the imagination of scientists and the media alike, earning itself the moniker ‘wonder material’ for its remarkably high electronic mobility, immense tensile strength and inherent two-dimensional nature ^[5].

Despite its accolades, pure semi-metal graphene has the severe limitation of having no bandgap ^[1]. For silicon replacement applications, most notably in transistors, a significant bandgap must either be induced in graphene, or a different material found. Fortunately, 2-dimensional semiconducting materials have already been isolated. Molybdenum disulphide, MoS₂, is a ‘semiconducting analogue to graphene’, already showing promise with high on/off ratios in transistor devices ^[6]. MoS₂ is just

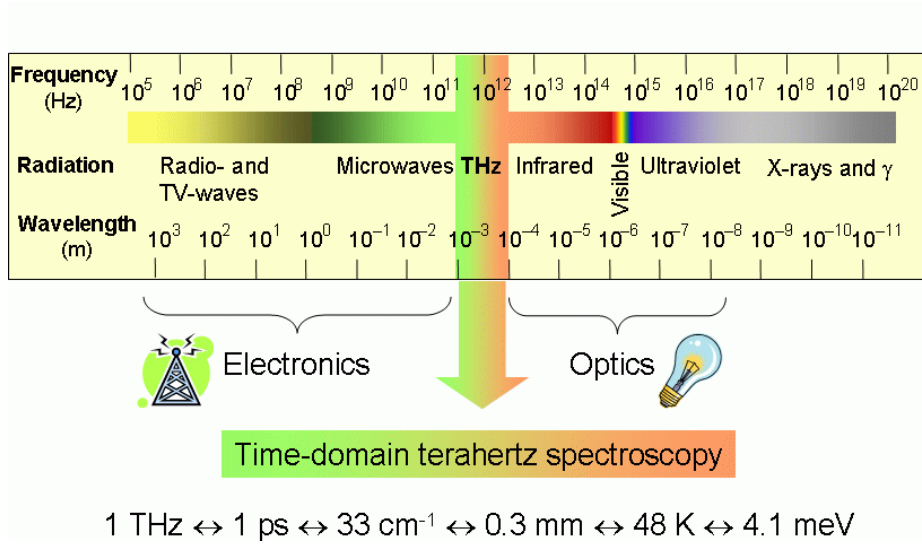


Figure 1.1: The electromagnetic spectrum, indicating the range of the THz gap. Taken from <http://lts.fzu.cz/en/intro.htm>

the first of a wide family of 2D transition metal dichalcogenides to be studied, with the rest of the family offering a broad range of electronic behaviours from insulating to metallic and superconducting properties [7].

As well as the advantage of being ultrathin, 2-dimensional materials demonstrate ultrafast behaviour [8]. Today's electronics and optoelectronics are limited to speeds on the gigahertz scale [9]. A push towards terahertz (THz) speeds requires devices based on picosecond or sub-picosecond phenomena. Novel 2D materials must be assessed for their capability of operating at such speeds. Terahertz spectroscopy is a technique well placed for such an assessment [10].

1.1 Terahertz Radiation

The electromagnetic spectrum can be split roughly into two parts based on the method of generating the radiation (see Figure 1.1). At the low energy end of the spectrum, radio waves and microwaves are typically produced by electronic devices, radiating by oscillating electrons. At the other end of the spectrum, waves are generated by relaxation between quantum states in molecules, atoms and nuclei.

Until the last few decades, the border between these two regions formed the ‘terahertz gap’, a region of frequencies between microwaves and the far-infrared that had been difficult to generate. The terahertz region typically covers the frequencies between 300 GHz and 10 THz (1000 μm to 30 μm , or 1 meV to 41 meV). Recent advances have closed the terahertz gap - quantum cascade lasers ^[11], free electron lasers ^[12] and THz generation based on femtosecond laser pulses have allowed access to the THz part of the electromagnetic spectrum ^[10].

1.1.1 Uses of terahertz radiation

Terahertz radiation has applications in a broad range of industries. For communications purposes, THz radiation promises faster, higher bandwidth data links than the microwaves currently used ^[13]. Explosives and drugs have unique THz signatures that can be used to identify them, making terahertz radiation attractive in the security industry ^[14]. For some medical applications terahertz radiation could provide a safer, non-ionising alternative to X-rays ^[15].

All of these applications require cheap, small-scale ways of producing, controlling and detecting terahertz radiation. Methods of modulating and polarising THz radiation, essential to encode information in the THz wave, are particularly few in number. New materials displaying ultrafast responses to electromagnetic radiation, and strong coupling to terahertz radiation are therefore being sought.

Terahertz spectroscopy, perhaps the most prominent application of THz radiation currently, can be used to characterise these new materials ^[8,10]. The comparatively low energy of THz radiation allows it to probe systems without altering them, investigating intraband behaviour, in contrast to more conventional but higher energy forms of optical spectroscopy. This is particularly useful to investigate the cooling of carriers after optical photoexcitation in novel semiconductors, providing information about the speed at which the system relaxes with sub-picosecond resolution.

Terahertz spectroscopy has other advantages over more conventional forms of spectroscopy. As a time domain spectroscopy that measures the variation of a THz electric field as a function of time, all of the phase information in the wave is retained. Thus the complex a.c. conductivity of materials can be measured directly. In the low frequency limit, the THz conductivity measured this way can be considered analagous to the d.c. conductivity, providing information about the material without having to attach contacts.

1.2 Overview of this thesis

This thesis describes the use of THz spectroscopy to investigate the behaviour of photoexcited carriers in 2-dimensional materials, and thus assess them for use in high-speed opto-electronic and THz devices. In Chapter 2, the principles involved in THz time domain spectroscopy and the particulars of the system used for experiments are given, along with derivations of the equations used to convert information about the THz electric field into the conductivity.

The materials to be studied are introduced in Chapter 3. Graphene, transition metal dichalcogenides and carbon nanotubes are described, along with a discussion about spectroscopic measurements previously undertaken on these materials.

Graphene produced by chemical vapour deposition is the subject of Chapter 4. Using optical-pump THz-probe time domain spectroscopy (OPTP-TDS), the THz photoconductivity of the graphene is found to be remarkably sensitive to the presence of atmospheric gases. In the presence of oxygen, the photoconductivity is both a different sign and an order of magnitude larger to the case of graphene in a vacuum.

In Chapter 5, MoS₂ and WSe₂, also grown by chemical vapour deposition, are similarly investigated using OPTP-TDS. The ultrafast nature of the response of these materials to photoexcitation is highlighted, suggesting promise for fast opto-electronic applications.

The potential of an alternative, much cheaper, production method for these materials is investigated in Chapter 6. Nanoflakes of graphene and MoSe₂ produced by liquid-phase exfoliation are examined with OPTP-TDS, revealing similarly ultrafast behaviour to their chemical vapour deposition grown counterparts.

Finally in Chapter 7, a 1-dimensional material is investigated for use as a THz modulator. Carbon nanotubes, which can be considered as rolled up graphene, demonstrate potential for use as an ultrafast, dynamic THz polariser.

Chapter 2

Experimental Methods

The experimental studies in Chapters 4 to 7 use optical-pump terahertz-probe time domain spectroscopy. In this Chapter, the principles underpinning this technique are outlined, including generation and detection of terahertz radiation. The particulars of the experimental system used in Chapters 4 to 7 are detailed, and the equations used to extract THz photoconductivity spectra from time domain data are derived.

2.1 Ultrafast spectroscopy

Terahertz time domain spectroscopy (THz TDS), as used in Chapters 4-7, is part of a wider family of time-resolved spectroscopic techniques. Generally, these methods involve a spectroscopic measurement of a system as a function of time after some perturbation to the system, often provided by a short optical pulse.

In many techniques, such as time-correlated single photon counting (TCSPC) ^[16] and time-resolved microwave conductivity ^[17], high speed electronics are used to detect the change in the system after perturbation. Whilst this has the advantage of utilising electronics which are relatively cheap and easy to implement, the time resolution of such techniques is fundamentally limited by the clock rate of the data acquisition circuit. Current transistor technologies are limited to ~ 500 GHz speeds, preventing the observation of phenomena with picosecond or sub-picosecond scale lifetimes ^[9]. Indeed, one of the frequently touted applications for graphene and other two-dimensional materials is as a high speed transistor, overcoming the current technological hurdle ^[18,19].

2.1.1 Optical pump-probe spectroscopy

In order to overcome the shortcomings of electronically-gated techniques it is necessary to move to optically-gated measurements, where both excitation and detection are performed using ultrashort, synchronised laser pulses. Typically (though not necessarily), a high energy optical pump will be used to photoexcite the system being measured, and a lower energy probe beam used to detect changes within the system resulting from the photoexcitation. The evolution of the system after photoexcitation can be mapped out by varying the optical delay line between pump and probe pulses.

Here, the fundamental time resolution is determined simply by the duration of the laser pulse. In practice, however, experimental considerations limit the achievable resolution - primarily the accuracy of the optical delay line and dispersion and phase-

matching effects resulting from the finite thickness of any non-linear crystals used in the technique.

The strength of such spectroscopic methods therefore depends upon the laser driving the spectrometer. The advent of widely available solid-state lasers producing femtosecond pulses has opened up the study of ultrafast physics, revealing a wealth of information about processes in established materials, and leading the characterisation of new ones. Many techniques require the pumping of non-linear crystals, to produce different pump wavelengths, or, as in the case of THz TDS, to generate the terahertz probe pulse. Therefore the laser must produce both ultrashort and high energy pulses to efficiently drive these processes. For this reason, chirp-pulse amplification regenerative amplifiers are typically used, such as the Spectraphysics Spitfire Pro used for measurements in Chapters 4-7. A general overview of such laser amplifiers can be found in reference 20.

2.1.2 Non-linear optics

The use of non-linear processes was of crucial importance for the measurements performed in later chapters. Such processes allow the generation of THz radiation by optical rectification (section 2.2.2.1) and the production of varied pump frequencies by frequency mixing within non-linear crystals. By utilising the high pulse energy from a regenerative amplifier, we enter a regime in which the polarisation $\mathbf{P}$ of a crystalline material no longer varies linearly with the applied electric field, $\mathbf{E}$ ^[21].

For linear optics we can write the polarisation as

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E}, \quad (2.1)$$

where χ represents the electric susceptibility. Considering only the case of polarisation parallel to the electric field, so that $\mathbf{P}=P_x$, $\mathbf{E}=E_x$, we can include higher order terms in P ,

$$P = P_1 + P_2 + P_3 + \dots = \varepsilon_0(\chi_1 E_x + \chi_2 E_x^2 + \chi_3 E_x^3 + \dots). \quad (2.2)$$

It is the different order susceptibilities, χ_2, χ_3 etc, that give rise to the phenomena useful for THz TDS. The most important of these is the second order term, which allows frequency doubling, optical rectification and the Pockels effect. The second order susceptibility is not present in all materials: inversion symmetry implies that the polarisation would be unchanged under an inversion transformation hence χ_2 can only be non-zero in non-centrosymmetric media. However, in a suitably chosen crystal, coupled with the high energy pulses of an amplified laser, the second order processes can become highly efficient.

2.1.2.1 Sum-frequency generation

Considering the general case of two plane waves of the form $E_i(t) = E_0^{(i)} \cos(\omega_i t)$ incident upon a non-linear crystal where the second order susceptibility dominates, the nonlinear polarisation may be written as

$$P_2(t) = \varepsilon_0 \chi_2 E_1 E_2 = \varepsilon_0 \chi_2 E_0^{(1)} E_0^{(2)} \cos(\omega_1) \cos(\omega_2) \quad (2.3)$$

$$P_2(t) = \varepsilon_0 \chi_2 \left(\frac{1}{2} E_0^{(1)} E_0^{(2)} [\cos((\omega_1 + \omega_2)t) + \cos((\omega_1 - \omega_2)t)] \right), \quad (2.4)$$

making use of the standard trigonometric relation $\cos(u)\cos(v) = 1/2[\cos(u+v) + \cos(u-v)]$. Thus, the second order susceptibility generates two waves with frequencies $\omega_1 + \omega_2$ and $\omega_1 - \omega_2$ respectively. The former, the sum-frequency wave, is useful for generating higher harmonics of the optical pump beam. If, additionally, the ‘phase-matching’ condition is met, namely that the photon momentum of the two incident waves is conserved by the generated wave, efficient sum frequency generation can be achieved. This condition essentially requires the selection of a material with a matching refractive index for both incoming waves and generated wave.

2.1.2.2 Second-harmonic generation

In Chapter 5, the measurements required the generation of the second harmonic of the 800 nm amplified laser beam. This can be considered as a particular case of the above sum-frequency generation, where the two incident waves are identical, and $\omega_1 = \omega_2 = \omega_0$. Hence the generated sum-frequency $\omega_1 + \omega_2 = 2\omega_0$, yielding a 400 nm beam from the 800 nm amplified laser pulse. A crystal of β -BaB₂O₂, known as BBO, can be used to achieve this. In particular orientations of this crystal $n(\omega_0) = n(2\omega_0)$, i.e. the phase-matching condition is met, and so the second harmonic efficiently generated.

2.2 Optical-pump terahertz-probe spectroscopy

Optical-pump terahertz-probe time domain spectroscopy (OPTP-TDS) follows the general principal outlined above for pump-probe spectroscopies. An optical pump pulse is used to photoexcite a sample, and after a delay, a single cycle THz probe used to examine the excitation state. The electric field of this THz pulse can be measured in the time domain, using the technique of electro-optic sampling (Section 2.2.3), which records the full complex spectrum of the THz probe, rather than just the intensity as is typical in optical measurements. Before describing the particulars of the THz spectrometer used for the experiments, the general principles of THz spectroscopy are briefly described.

2.2.1 Time-domain spectroscopy

In conventional optical spectroscopy, the intensity of electromagnetic radiation is measured as a function of frequency. The intensity of an electromagnetic wave is given by the Poynting vector, $\mathbf{S} = \mathbf{E} \times \mathbf{H}$, where $\mathbf{E}$ is the electric field vector and $\mathbf{H}$ the magnetic field vector. At optical frequencies, only the time-averaged Poynting vector can typically be measured. For a plane wave of the form $\mathbf{E}(t, z) = E_0 e^{i(kz - \omega t)}$,

this time-averaged intensity is proportional to $|E_0|^2$, thus all the phase information is lost, and the complex refractive index of the sample cannot be measured.

This problem can be avoided by using the Kramers-Kronig relations, which use the relationship between the electric displacement $\mathbf{D}$ and the electric field $\mathbf{E}$ to extract the full complex refractive index of the material from the intensity measurements [22]. However, this analysis can be complicated, and requires knowledge of either the real or the imaginary part of the refractive index over a large spectral range, which is not necessarily achievable.

Time-domain spectroscopy, such as THz TDS, provides an alternative. By measuring the electric field of the radiation rather than just intensity, the phase of the wave is retained, allowing the complex refractive index (or complex conductivity) to be extracted directly. The analysis required to find the refractive index is presented later in section 2.4.

2.2.2 Generation of THz radiation

Two techniques are common for the generation of THz radiation for THz-TDS - photoconductive emitters [23,24] and optical rectification in non-linear crystals [25]. Photoconductive emitters are particularly useful for systems with low power lasers which cannot efficiently access the second order non-linearities required for optical rectification. A typical switch consists of a pair of metallic electrodes evaporated onto the top of a highly resistive semiconducting substrate, such as semi-insulating GaAs [26]. A large electric field, typically $>1\text{kV/cm}$, is applied across the electrodes. The application of an ultrashort laser pulse generates carriers in the gap between the electrodes, forming a transient dipole under the bias of the electric field that will radiate a range of frequencies of around 1 THz into free space.

2.2.2.1 Optical rectification

With the pulse energies available from a regenerative amplifier, optical rectification in non-linear crystals is easily achieved. When a monochromatic plane wave of the form $E(t) = E_0 \cos(\omega t)$ travels through a non-linear crystal with non-zero second order susceptibility ($\chi_2 \neq 0$), it induces a polarisation [27]

$$P_2(t) = \varepsilon_0 \chi_2 E_0^2 \cos(\omega t) \quad (2.5)$$

$$= \varepsilon_0 \chi_2 E_0^2 / 2 - \varepsilon_0 \chi_2 E_0^2 \cos(2\omega t) / 2. \quad (2.6)$$

The first term of Equation 2.6 is a ‘zero’-frequency polarisation, P_0 . If a broadband ultrashort pulse is used in place of a monochromatic wave, the zero-frequency term will vary in time, and emit a THz electromagnetic pulse, $E_{\text{THz}} \propto \ddot{P}_0$ [28]. Typical crystals for THz generation by optical rectification include zinc telluride (ZnTe), gallium phosphide (GaP) and gallium selenide (GaSe) [10].

2.2.3 Electro-optic detection of THz radiation

The electric field of the THz pulse can be detected using the Pockels effect in certain non-linear crystals [29,30]. The electric field of the THz pulse induces a birefringence in the crystal, which modulates the polarisation of an ultrashort ‘gate’ laser pulse passing simultaneously through the crystal. As the duration of the laser pulse is much shorter than the duration of the single cycle THz pulse (35 fs compared to ~ 1 ps), the terahertz field, and hence the induced crystal birefringence, appear quasi-static to the gate pulse. Thus the gate pulse measures just one point on the THz pulse. Analysing the change of polarisation of reveals the electric field of the THz pulse at that point. By varying the relative time of arrival of the THz and gate pulses, using optical delay stages, the whole THz pulse can be mapped out. This process is represented in Figure 2.1

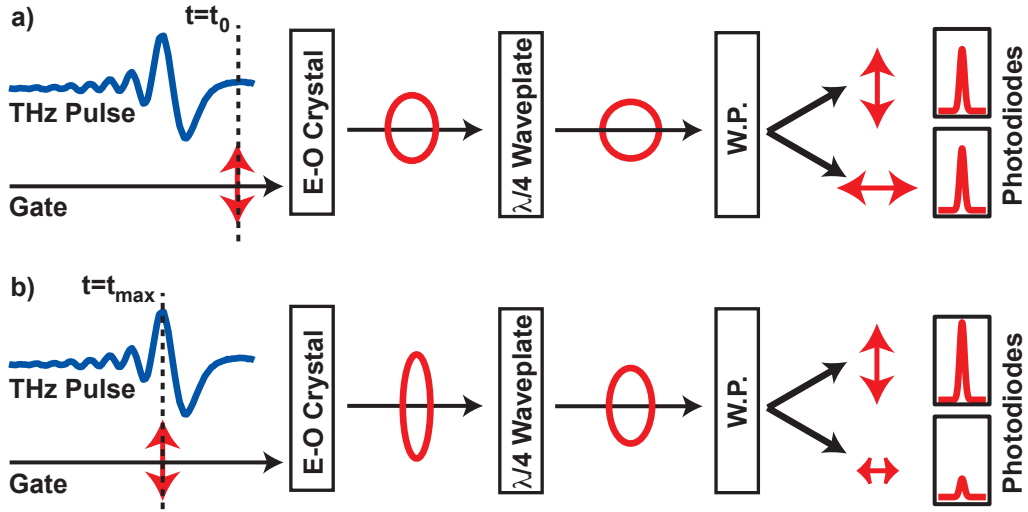


Figure 2.1: THz detection by electro-optic sampling. **a)** In the absence of an electric field, the vertically polarised gate pulse passes through the unaltered electro-optic (E-O) crystal. A quarter-waveplate is set to produce circularly polarised light from this gate pulse. A Wollaston prism (WP) spatially separates the horizontal and vertical components of this light, which is detected by two photodiodes. For circularly polarised light, both components are equal, thus both photodiodes measure the same intensity, and the potential difference between them is $V = 0$. **b)** If the optical delay is set such that the THz pulse and the gate beam overlap in time, here at $t = t_{\max}$, the presence of a THz electric field modifies the birefringence of the electro-optic (E-O) crystal, changing the polarisation of the gate pulse, thus encoding the electric field into the polarisation of the gate. The quarter-waveplate now produces elliptically polarised light, yielding a difference in intensities on the photodiodes which is proportional to the THz electric field.

The change in polarisation of the gate pulse can be measured using a Wollaston prism and a pair of photodiodes. A $\lambda/4$ waveplate is used to convert the linearly polarised gate beam into an elliptically polarised beam. The Wollaston prism spatially separates the linear and horizontal components of this elliptical polarisation, which can be detected by the pair of photodiodes, and the potential difference, V between the photodiodes measured. The photodiodes can be balanced in the absence of a THz electric field by rotating the waveplate to create circularly polarised light, so that the horizontal and vertical components reaching the photodiodes are equal, and so $V = 0$. Thus any change in V in the presence of the THz pulse is proportional to the electric field of the THz pulse.

If desired, the electric field of the THz pulse can be calculated explicitly. Taking V as the potential difference induced across the photodiodes by an instantaneous THz electric field E_{THz} , and V_{max} as the maximum voltage swing measurable during a full rotation of the waveplate, E_{THz} can be extracted from ^[31]

$$\frac{V}{V_{\text{max}}} = \frac{2\pi}{\lambda_{\text{gate}}} dn_{\text{gate}}^3 r E_{\text{THz}}. \quad (2.7)$$

Here, λ_{gate} and n_{gate} are the wavelength of the gate and the crystal refractive index at the gate wavelength respectively, d is the crystal thickness, and r the electro-optic coefficient of the crystal. However, for most measurements only the relative change in terahertz field is required, and so the calculation of the explicit field is not needed.

2.3 Experimental setup

The general principles described above were combined to form the OPTP-TDS system used for measurements in Chapters 4-7.

The experimental arrangement used for THz time domain spectroscopy is displayed in Figure 2.2. A Spectra-Physics Spitfire Pro Ti:Sapphire regenerative amplifier (800 nm 5 kHz repetition rate, 4 W average power, 35 fs pulse duration) was

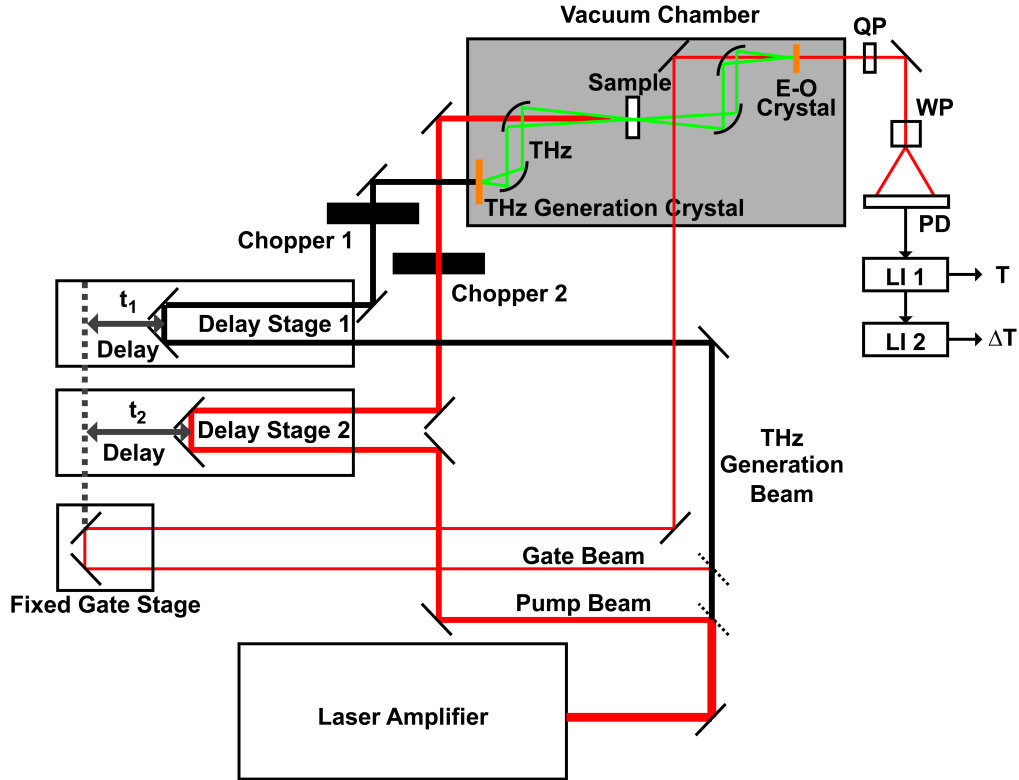


Figure 2.2: Schematic diagram of the apparatus used for THz spectroscopy experiments. The 800 nm output from a Ti:Sapphire regenerative amplifier was used to photoexcite the sample, to generate THz radiation, and to detect the THz electric field by electro-optic sampling. The path length of the pump and THz generation beams could be altered relative to the fixed gate beam, thus varying the time of arrival of the THz and pump pulses at the sample, t_1 and t_2 respectively, relative to the gate pulse.

seeded from a Spectra-Physics MaiTai, and pumped using a Spectra-Physics Empower (20 W).

For the measurements in Chapters 4 and 6, the output of the laser amplifier was split into three beams. A beam of 2.9 W, reduced to 0.29 W with a neutral density filter, was used to photoexcite the sample with a maximum fluence of $180 \mu\text{J}/\text{cm}^2$ incident upon the sample, and a beam width of 2 mm.

The second beam ($200 \mu\text{J}$ per pulse) was used to generate the terahertz probe beam by optical rectification in a 2 mm GaP crystal. The terahertz beam had a width of 0.48 mm at the sample position. The area of the sample probed by the THz beam was much smaller than the area photoexcited by the pump beam; thus the probe measured an area of roughly constant photoexcited carrier density.

The remainder of the amplifier beam ($16 \mu\text{J}$ per pulse) was used as a gate beam for electro-optic sampling of the terahertz field in a $200 \mu\text{m}$ GaP crystal. Using a quarter waveplate (QP) and a Wollaston prism (WP), the gate beam was separated into two spatially resolved polarisation components for detection by photo-diodes (PD), from which the pump induced change in the THz signal can be extracted by two lock-in amplifiers, LI1 and LI2, referenced to optical choppers 1 and 2 respectively. The correct phase of the lock-in amplifiers for each experiment was determined by observing the signal from a reference sample with a well known photoresponse (semi-insulating GaAs).

Variable delay stages in the THz generation and pump beams allowed additional path length to be added to these beams, whereas the gate beam was held fixed. Adding additional path length to the THz generation beam alters the time between the arrival of the THz pulse and the 35 fs gate pulse at the electro-optic (E-O) crystal ($200 \mu\text{m}$ GaP), t_1 . By varying this time, the full dynamics of the THz pulse could be mapped. Alternatively, the time between the pump pulse and the gate pulse, t_2 , could be varied. These measurements are represented in Figure 2.3. In order to measure

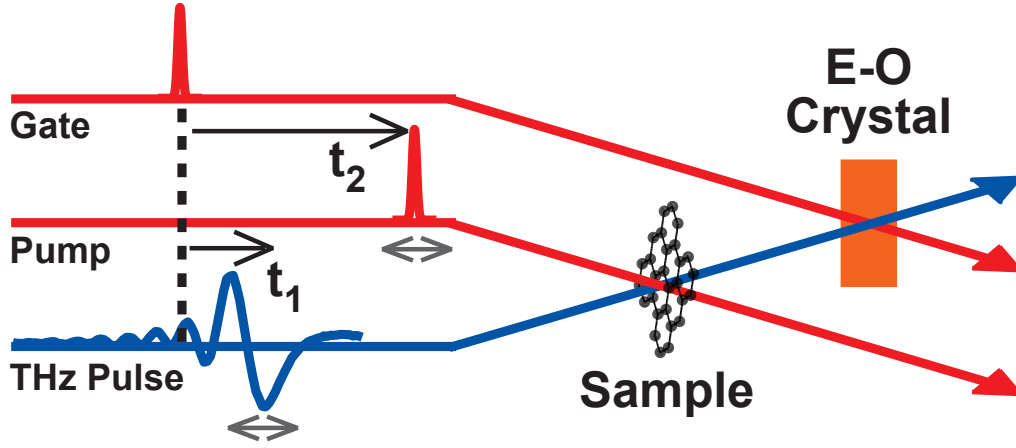


Figure 2.3: Schematic representation of the OPTP-TDS measurements. Varying t_1 allows the electric field, E_{THz} , of the terahertz probe pulse to be sampled in the electro-optic (E-O) crystal. The sample can be probed at different times after photoexcitation by altering t_2 . In this way each part of the THz pulse was probed at the same time after photoexcitation.

the full pump-induced transmission change, as in Figure 4.4, the pump delay time t_2 was set to a fixed value before the THz pulse was measured by varying t_1 . Thus the delay between the pump pulse and the *sampled* part of the THz pulse was constant, avoiding the need for the complicated analysis otherwise required [32]. This data can be Fourier transformed to yield spectral information, as described in the next section.

If the full spectral information is not required, t_1 could be held fixed so that only the peak of the THz field was detected, whilst varying t_2 to reveal an average of the THz response after photoexcitation. This method yielded the temporal evolution seen, for example, in Figure 6.2.

2.3.1 Double lock-in detection

To minimise noise in the signal, a double lock-in detection system was used for signal recovery in OPTP-TDS. Both lock-ins were Stanford Research Systems SR830s. The first was referenced to Chopper 1 in the THz generation beam, set to 2.5 kHz (half the amplifier repetition rate). The output from this lock-in was proportional to the

terahertz electric field, E_{THz} , following from Equation 2.7. The second lock-in was referenced to Chopper 2 in the pump beam, set to 125 Hz. The output from this second lock-in was proportional to the pump-induced change in terahertz transmission, $\Delta E = E_{\text{on}} - E_{\text{off}}$. Thus the change in transmission used in the analysis of THz data in the following section was obtained directly.

2.3.2 Generation of higher frequency pump pulses

A slightly different arrangement was used for the measurements in Chapters 5 and 7. To photoexcite carriers across the bandgap in transition metal dichalcogenides and semiconducting carbon nanotubes, higher pump beam energies than the 1.55 eV fundamental pump from the amplifier were required.

For high energy excitation, the 2.9 W pump beam described in the previous section was frequency doubled in a BBO crystal, as in Section 2.1.2.2, yielding a 3.1 eV (400 nm) pump, with a typical fluence of $100 \mu\text{J}/\text{cm}^2$ at the sample position. The THz generation beam and gate beam were used as above for generation and detection of the THz electric field.

Alternatively, for excitation on resonance with excitons in MoS_2 and the semiconducting carbon nanotubes, variable pump energies were produced using a TOPAS optical parametric amplifier. 3.2 W of the Spitfire amplifier output was used to drive the TOPAS. For the 1.9 eV (650 nm) pump used in Chapters 5 and 7, the output of the TOPAS was 200 mW, producing a fluence of $175 \mu\text{J}/\text{cm}^2$ at the sample position. The remaining output of the Spitfire was used to generate and detect THz radiation, as described above.

The spectra of all pump beam energies used in this thesis can be seen in Figure 5.6.

2.4 Analysis of data from THz spectroscopy

Having measured the transmission of the THz probe through the sample in the time domain, it is useful to convert to the frequency domain, to access the spectroscopic information. For a time domain electric field of the form $\mathbf{E}(t) = E_0 e^{-i\omega t}$, Fourier transforming (using a Fast Fourier Transform algorithm) yields a frequency domain field of the form

$$\tilde{\mathbf{E}}(\omega) = \tilde{E}_0(\omega) e^{-i\omega n d/c}, \quad (2.8)$$

where d is the distance travelled, c is the speed of light and n is the complex refractive index of the medium.

2.4.1 Equilibrium THz conductivity

All of the samples measured in this thesis may be considered as a thin film on a thick substrate, of the type depicted in Figure 2.4. As any reflections within the thick substrate can be removed by windowing the time domain data, substrate reflections are not considered in the following analysis.

Consider a THz wave of the form of Equation 2.8 travelling through medium 1 (usually vacuum), incident normally upon the surface of a reference substrate as shown in Figure 2.4a. For the THz wave transmitted through a region of medium 1 of thickness δ , and substrate thickness d , we may write the electric field as

$$\tilde{\mathbf{E}}_{\text{ref}}(\omega) = t_{13} t_{31} \tilde{E}_0 e^{-i\omega n_1 \delta/c} e^{-i\omega n_3 d/c}, \quad (2.9)$$

where t_{ij} are the Fresnel coefficients for transmission from medium i to medium j at normal incidence, given by ^[21]

$$t_{ij} = \frac{2n_i}{n_i + n_j}. \quad (2.10)$$

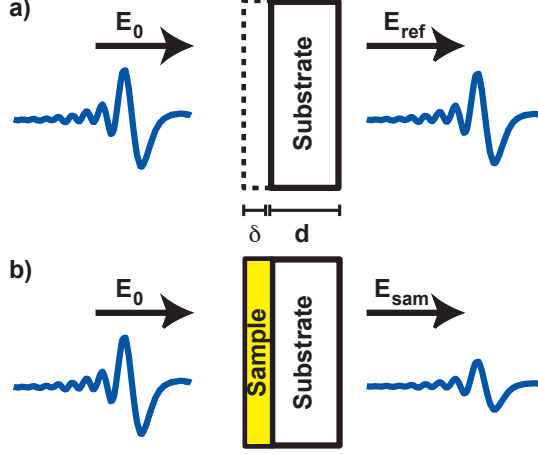


Figure 2.4: A THz electric field passing through a substrate (a), and through a thin film on a substrate (b). Considering the transmission at each interface allows the emerging electric fields to be written as Equations 2.9 and 2.11 respectively.

Similarly, for transmission through both the sample medium 2 of thickness δ and substrate medium 3 of thickness d (Figure 2.4b), we may write the transmitted field as

$$\tilde{\mathbf{E}}_{\text{sam}}(\omega) = t_{12}t_{23}t_{31}\tilde{E}_0e^{-i\omega n_2\delta/c}e^{-i\omega n_3d/c}F_{123}. \quad (2.11)$$

Here, F_{123} accounts for multiple Fabry-Perot reflections within the sample film. Generally, $F_{123} = \sum_{p=0}^p [r_{23}r_{21}e^{i2n_2\omega\delta/c}]^p$. In the thin film limit, however, we can assume infinite reflections (overlapping perfectly in the time domain), hence the Fabry-Perot term becomes

$$F_{123} = \frac{1}{1 - r_{23}r_{21}e^{i2n_2\omega\delta/c}}, \quad (2.12)$$

where r_{ij} are the Fresnel coefficients for reflection from medium i to medium j , given by

$$r_{ij} = \frac{n_i - n_j}{n_i + n_j}. \quad (2.13)$$

Therefore, the transmission through the thin sample, $T(\omega)$, is given by

$$\begin{aligned} T(\omega) &= \frac{\tilde{\mathbf{E}}_{\text{sam}}(\omega)}{\tilde{\mathbf{E}}_{\text{ref}}(\omega)} = \frac{t_{12}t_{23}\tilde{E}_0e^{-i\omega n_2\delta/c}F_{123}}{t_{13}\tilde{E}_0e^{-i\omega n_1\delta/c}} \\ &= \frac{\frac{2n_1}{n_1+n_2} \frac{2n_2}{n_2+n_3}}{\frac{2n_1}{n_1+n_3}} \times \frac{e^{-i\omega\delta(n_2-n_1)/c}}{1 - r_{23}r_{21}e^{i2n_2\omega\delta/c}}. \end{aligned} \quad (2.14)$$

By again considering the limit of thin films we can say $n\omega\delta/c \ll 1$ allowing us to derive the complex dielectric function for the thin film sample

$$\varepsilon(\omega) = n_2^2(\omega) = \frac{i(n_1 + n_3)c}{\omega\delta} \left(\frac{1}{T(\omega)} - 1 \right) - n_1n_3. \quad (2.15)$$

The dielectric function can be related to the complex conductivity σ via Maxwell's equations ^[21], giving

$$\varepsilon(\omega) = \varepsilon_s + \frac{i\sigma}{\varepsilon_0\omega}, \quad (2.16)$$

where ε_s is the low frequency limit of the dielectric function, relevant for frequencies below a phonon resonance. Combining Equations 2.15 and 2.16 yields

$$\sigma(\omega) = \frac{(n_1 + n_3)\varepsilon_0c}{\delta} \left(\frac{1}{T(\omega)} - 1 \right) + i\varepsilon_0\omega(\varepsilon_s + n_1n_3). \quad (2.17)$$

Assuming a very conductive material, the second term in Equation 2.17 can be neglected ^[8], leaving

$$\sigma(\omega) = \frac{(n_1 + n_3)}{Z_0\delta} \left(\frac{1}{T(\omega)} - 1 \right), \quad (2.18)$$

where $Z_0 = 1/\varepsilon_0 c = 376.6 \Omega$ is the impedance of free space. Thus, by measuring the THz electric field passing through the sample and substrate, and the field passing through just the substrate, we can calculate the complex conductivity of the thin film sample.

2.4.2 THz Photoconductivity

For most measurements in this thesis, the change in conductivity induced in a sample by photoexcitation is of interest, rather than the conductivity of the non-photoexcited sample.

In this case, we can consider a thin film on a thick substrate, as depicted in Figure 2.4b and the transmission through the sample and substrate when photoexcited by a pump beam, T_{on} , compared to the transmission through the sample and substrate in the absence of the pump, T_{off} .

Rearranging Equation 2.18 for the case of pump on and pump off respectively yields the equations

$$\sigma_{\text{on}} Z_0 \delta T_{\text{on}} = (n_1 + n_3)(1 - T_{\text{on}}) \quad (2.19)$$

and

$$\sigma_{\text{off}} Z_0 \delta T_{\text{off}} = -(n_1 + n_3)(1 - T_{\text{off}}). \quad (2.20)$$

Subtracting Equation 2.20 from Equation 2.19 gives

$$Z_0 \delta (\sigma_{\text{on}} T_{\text{on}} - \sigma_{\text{off}} T_{\text{off}}) = (n_1 + n_3) \Delta T, \quad (2.21)$$

where ΔT is the change in transmission through the sample because of photoexcitation, $\Delta T = T_{\text{on}} - T_{\text{off}}$.

Assuming only a small change in transmission due to photoconductivity, such that $T_{\text{on}} \approx T_{\text{off}} \sim T_{\text{THz}}$, where $T_{\text{THz}} = (T_{\text{on}} + T_{\text{off}})/2$ yields an equation for the photoinduced conductivity change, $\Delta\sigma = \sigma_{\text{on}} - \sigma_{\text{off}}$

$$\Delta\sigma(\omega) = - \left(\frac{n_1 + n_3}{Z_0 \delta} \right) \frac{\Delta T}{T_{\text{THz}}}, \quad (2.22)$$

where n_1 and n_3 are the refractive indices of the surroundings (usually vacuum, $n_1 = 1$), and substrate respectively, and T_{THz} and ΔT are the outputs of lock-in 1 and lock-in 2 respectively. Thus the pump-induced THz photoconductivity can be extracted from the measured amplitude transmission and change in transmission through the sample and substrate.

Finally, we consider the case of truly 2-dimensional materials, such as graphene, where the thickness δ is difficult to define. In this case, we may consider the 2D conductivity, $\sigma_{2\text{D}}$, measured in Siemens Square (the conductivity equivalent of Ohms per Square). Then we may write

$$\Delta\sigma_{2\text{D}}(\omega) = - \left(\frac{n_1 + n_3}{Z_0} \right) \frac{\Delta T}{T_{\text{THz}}}. \quad (2.23)$$

2.5 Physical interpretation of THz photoconductivity

Photoexcitation of a system will generate a range of quasi-particles, such as free carriers, excitons and plasmons. Due to the low energy of THz radiation, these quasi-particles can be probed directly, and so the THz photoconductivity of the system, $\Delta\sigma$ will contain the signature of the quasi-particles present ^[10]. The quasi-particles excited by an optical probe can therefore be determined by fitting the expected response of quasi-particles to the measured THz photoconductivity spectrum. The derivation of the conductive response of common quasi-particles is described here.

2.5.1 Free charge carriers - Drude conductivity

In many cases the photoexcited electrons and holes can be considered to act as a plasma, free to move within the sample. If particles of charge q and effective mass m^* are non-interacting, and are scattered only by ionic cores which randomise the carrier momentum at a rate $\Gamma = 1/\tau$ [33], the displacement $\mathbf{x}$ of carriers from the equilibrium position in the presence of the THz electric field $\mathbf{E}$ is given by

$$\frac{d^2\mathbf{x}}{dt^2} + \Gamma \frac{d\mathbf{x}}{dt} = \frac{q\mathbf{E}}{m^*}. \quad (2.24)$$

Assuming a THz electric field $\mathbf{E} = \mathbf{E}_0 e^{-i\omega t}$, we can assume an oscillating solution of the form $\mathbf{x} = \mathbf{x}_0 e^{-i\omega t}$. Substituting these solutions into Equation 2.24 results in a displacement

$$\mathbf{x} = \frac{q\mathbf{E}/m^*}{-\omega^2 - i\omega\Gamma}. \quad (2.25)$$

Displacement of N carriers from the equilibrium position generates a polarisation $\mathbf{P}_{\text{disp}} = Nq\mathbf{x}$. Considering the electric displacement vector $\mathbf{D}$ in a linear medium with relative dielectric function ϵ , and allowing for a background polarisation $\mathbf{P}_{\text{back}}$, we may write

$$\begin{aligned} \mathbf{D} &= \epsilon\epsilon_0\mathbf{E} = \epsilon_0\mathbf{E} + \mathbf{P}_{\text{back}} + \mathbf{P}_{\text{disp}} \\ &= \epsilon_0\mathbf{E} + \epsilon_0\chi\mathbf{E} + \mathbf{P}_{\text{disp}}. \end{aligned} \quad (2.26)$$

Using Equation 2.25 in equation 2.26, we obtain an expression for the complex dielectric function

$$\epsilon = 1 + \chi + \frac{Nq^2}{\epsilon_0 m^* (-\omega^2 - i\omega\Gamma)}. \quad (2.27)$$

The dielectric function can be related to the complex conductivity σ using Equation 2.16, giving

$$\epsilon = \epsilon_s + \frac{i\sigma}{\epsilon_0\omega} = 1 + \chi + \frac{i\sigma}{\epsilon_0\omega}, \quad (2.28)$$

where ϵ_∞ is the high frequency limit of the dielectric function. Combining Equations 2.27 and 2.28 yields the a.c. Drude conductivity

$$\sigma_{\text{Drude}}(\omega) = \frac{Nq^2\tau}{m^*(1 - i\omega\tau)} = \frac{\sigma_0}{1 - i\omega\tau}, \quad (2.29)$$

where σ_0 is equivalent to the d.c conductivity of free carriers. Thus by taking the zero-frequency limit of the measured THz conductivity the d.c. conductivity may be found, without needing to attach contacts to the sample.

Despite the many simplifications and assumptions in this model, it has been successfully applied to many systems [8], including graphene, as discussed in Section 3.4.

2.5.2 Lorentzian conductivity

Other quasi-particles are not free, but instead have a restoring force competing with the effect of the applied electric field. Excitons, for example, are bound electron and hole pairs, which experience a restoring force due to the Coulombic attraction between them [21]. Quasi-particles of this type are Lorentzian oscillators, and their conductivity termed a Lorentzian conductivity.

Such systems can be modelled by considering a straightforward extension to the Drude model described above. By adding a restoring force $-\omega_0^2\mathbf{x}$ to the right hand side of Equation 2.24, we find a conductivity of the form

$$\sigma_{\text{Lorentz}}(\omega) = \frac{i\omega A}{\omega^2 - \omega_0^2 + i\omega\Gamma}, \quad (2.30)$$

where A is the amplitude of the Lorentzian oscillator, and ω_0 the frequency at which the system resonates. Lorentzian form conductivities show a resonance peak in the real part of the conductivity, and a change from negative to positive in the imaginary part.

2.6 Other experimental techniques

Several additional techniques were used during characterisation of the samples to test quality and layer thickness.

UV-Vis-IR transmission spectroscopy was used in Chapters 4 - 7, to determine layer thickness for graphene (Chapter 4 and to observe the onset of exciton absorption in transition metal dichalcogenides (Chapters 5 and 6). Data were taken using a Perkin-Elmer Lambda 9 UV/Vis/NIR spectrophotometer (Chapters 4 and 5), and a Bruker Vertex 80 FTIR spectrometer with a silicon detector (Chapter 6).

Raman spectroscopy was used to identify the number of layers present in graphene and MoS₂. In this technique, inelastic scattering of visible light is used to observe phonons and other vibrations in the system. Monolayer graphene in particular has a usefully unique Raman signature that can be used to identify its presence (see Section 4.3)^[34]. The Raman data in Chapters 4 and 5 were acquired by Lance Li and his group using an NT-MDT confocal Raman microscope system, with laser wavelength 473 nm, power 0.5-1 mW and spot size 0.5 μ m. Raman measurements in Chapter 7 were performed by the group of Valeria Nicolosi at CRANN, Trinity College, Dublin.

Similarly, atomic force microscopy (AFM) was used to further determine the layer thickness in graphene and transition metal dichalcogenides. These images were taken on nominally identical samples using a Veeco Dimension-Icon system, by the group of Lance Li in Taiwan.

Chapter 3

Introduction to graphene and two-dimensional materials

Graphene has proved itself as being unique in terms of fundamental physics, and of particular importance for postsilicon electronics. Research into graphene has divided into two branches, one probing the remarkable electronic and optical properties of graphene, and the other pursuing technologically viable forms of the material. Terahertz time domain spectroscopy (THz TDS) is a powerful tool for both, able to characterise the free carrier response of graphene and probe the inter and intraband response of excited carriers with sub-ps time resolution. In this chapter, THz TDS and related measurements of graphene and other 2D materials are reviewed.

3.1 Introduction

Graphene, a flat monolayer of carbon atoms forming a two-dimensional (2D) honeycomb structure, has been named ‘the simplest complex material’ [35]. It exhibits mobilities in excess of any observed in conventional bulk semiconductors [36], and allows the observation of relativistic quantum mechanics on a condensed matter scale [37], but can be produced using Scotch tape [3]. The first isolation of a monolayer of graphene in 2004 by the now Nobel prize winning Geim and Novoselov transformed the material from a theoretical model, deemed by Landau and Peierls to be unstable at all finite temperatures [38], into a practical reality [3]. Since then graphene has been touted for use as future field effect transistors [39], the replacement for indium tin oxide (ITO) in touch screens [40], electrodes in solar cells [41], and even as anti-bacterial paper [42].

The unique properties of graphene fuel the great enthusiasm for the material. Graphene has shown ballistic transport at room temperature [36] with massless Dirac fermions as the carriers [37], an anomalous quantum Hall effect [43], Klein tunnelling [44], and immense tensile strength [45], to name but a few. However, the electronic properties of graphene, particularly the dynamics of hot carriers, must be understood before graphene can be used for optoelectronic devices [46].

Terahertz Time Domain Spectroscopy (THz TDS) is a method well placed for such studies [10]. This all-optical technique can probe the intrinsic carrier dynamics in the time domain, undisturbed by the influence of contacts that would otherwise have to be attached [47]. Coupled with a higher energy excitation pulse, ultrafast carrier relaxation can be observed with sub-ps time resolution.

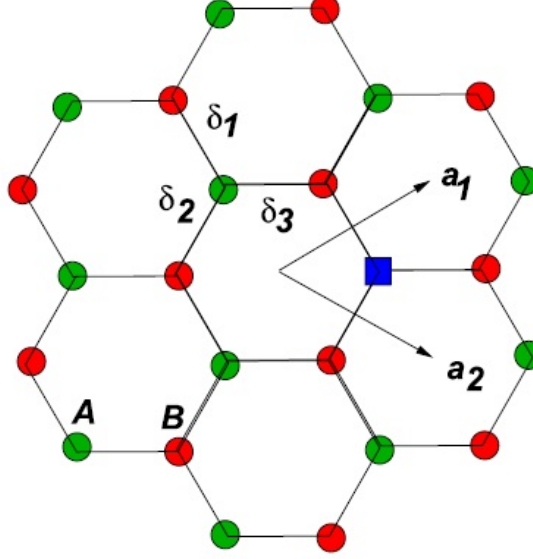


Figure 3.1: Honeycomb structure of graphene showing unit cell vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, and next nearest neighbour vectors δ_i . Taken from [44].

3.2 The structure of graphene

Graphene is composed of carbon atoms in a 2D hexagonal lattice as represented in Figure 3.1, with lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ such that $|\mathbf{a}_1| = |\mathbf{a}_2| = a$, where $a \approx 2.461 \text{ \AA}$. Carbon atoms have 6 electrons each, distributed into the atomic orbitals $1s^2$, $2s^2$, $2p^2$. In graphene, the $1s$ electrons are essentially inert, and the $2s$, $2p_x$ and $2p_y$ orbitals hybridise into three new planar sp^2 orbitals [44]. These orbitals are responsible for the formation of the σ bonds that form the hexagonal structure. There remains one electron from each $2p_z$ orbital, giving one electron per lattice site. It is these electrons that give graphene its unique properties. As can be seen in Figure 3.1, there are two carbon atoms per unit cell, hence two electrons per unit cell. Thus there are two bands: the conduction band and the valance band.

The structure of these bands can be calculated using the tight binding model, for pristine graphene yielding [48, 49]

$$E_{\pm}(\mathbf{k}) = \pm t \sqrt{3 + f(\mathbf{k})}, \quad (3.1)$$

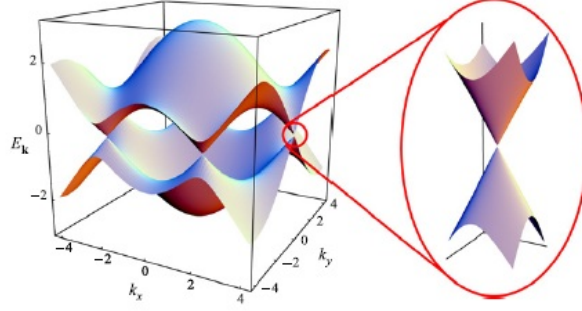


Figure 3.2: Energy spectrum with a zoom in of the bands near the Dirac point. Taken from ^[44].

with

$$f(\mathbf{k}) = 2 \cos(\sqrt{3}k_y a) + 4 \cos\left(\frac{\sqrt{3}}{2}k_y a\right) \cos\left(\frac{3}{2}k_x a\right). \quad (3.2)$$

The resulting energy spectrum for both conduction and valance bands can be seen in Figure 3.2. It can be seen from this figure that there are two momentum values, $\mathbf{K}$ and $\mathbf{K}'$, termed the Dirac points, at which the energy bands meet. Graphene is therefore a zero gap material, or semi-metal. Expanding the dispersion relation (equation 3.1) around these Dirac points produces a linear relationship:

$$E_{\pm}(\mathbf{q}) \approx \pm \hbar v_F |\mathbf{q}|, \quad (3.3)$$

where v_F represents the Fermi velocity, $v_F \approx 10^6 \text{ms}^{-1}$. Equation 3.3 is the ultrarelativistic form of Einstein's equation $E = \sqrt{m^2 c^4 + p^2 c^2}$ with $m = 0$ and $c = v_F$. Thus carriers around the Dirac point are massless fermions, described by the Dirac rather than the Shrödinger equation. These relativistic massless carriers give graphene its uncommon transport properties, such as ballistic transport and half-integer quantum Hall effect. They also allow graphene to be used to further probe the phenomena of quantum electrodynamics ^[38].

3.3 Production of graphene

Graphene is not a uniform term. Each of the various methods of producing graphene yields a product that is distinct, with a drop in mobility being particularly noticeable in the more up-scalable techniques. Thus when comparing spectroscopic investigations, the type of graphene, and its likely form and quality, must be considered. Furthermore, many of the production methods are still in their infancy, with great improvements in quality and domain size of product in recent years. Therefore, two studies on nominally similar graphene could be investigating very different materials.

In the decades preceding the first isolation of graphene, several attempts were made to produce a single layer of graphite, already predicted to have special properties [50]. As far back as 1960, Fernandez-Moran had mechanically exfoliated ~ 15 layers of graphene in a search for electron microscopy support membranes [51]. Iijima used adhesive tape to cleave graphite crystals for the same purpose, foreshadowing Geim and Novoselov's successful method, but then used ethylene dichloride to separate the flakes and leave them in suspension [52]. Other researchers attempted the reduction of oxidized graphite [53], with little success. Later attempts included the use of an AFM cantilever to peel off a single layer, again without success [54].

In the context of these complicated attempts to isolate a monolayer of graphene, the simplicity of Geim and Novoselov's Scotch tape method of producing mechanically exfoliated graphene stands out [3]. Their success in 2004 fuelled both the experimental exploration of graphene, and renewed interest in previously unsuccessful production methods. Epitaxial growth of graphene rapidly followed, and since then the reduction of graphene oxide, liquid-phase exfoliation and chemical vapour deposition have shown promise as large-scale means of producing graphene for technological exploitation.

3.3.1 Mechanical exfoliation

Geim and Novoselov's method used common adhesive tape to apply the weak force ($300 \text{ nN}/\mu\text{m}^2$ [55]) required to overcome the inter-layer Van der Waals interaction in graphite [3]. The resulting pieces of graphite and graphene were transferred to a silicon dioxide substrate, where contrast between the substrate and graphene allows the observation of a monolayer. In this way, pristine mono- and few-layer graphene was isolated, and used to investigate graphene's electronic properties.

Presently mechanical exfoliation yields the best quality graphene, with extremely high mobilities [56,57]. However, its production is time consuming, and not viable on a large scale. In order to make use of graphene's electronic properties in low cost applications, focus has shifted from mechanical exfoliation to chemical methods of production, despite the resulting loss of quality of graphene.

3.3.2 Epitaxial Growth

An early contender to mechanical exfoliation, epitaxial growth of graphene involves the thermal treatment of silicon carbide SiC (0001), resulting in the sublimation of the Si atoms, and a reorganisation and graphitisation of the carbon-enriched surface to form layers of graphene [58]. The observation of graphene's properties on these samples, notably the anomalous quantum Hall effect, led to the initial belief that monolayers of graphene were formed on the SiC surface [59]. However, Raman and STM studies have since shown that this is not the case, and in fact 10-20 layers are produced [60]. This should prohibit the observation of graphene like properties, as graphitic AB stacking breaks the equivalence of the two atoms in the graphene lattice. Fortunately, rotational stacking faults develop during the growth process, which electronically decouple the layers from one another, and so gives the effect, and electronic properties of, a monolayer.

Originally, epitaxial graphene was grown at 1300°C under vacuum [59]. Graphene

prepared in such a way, however, had very limited lateral extension of graphene crystallites, adversely affecting the electronic capabilities of the material. This issue was resolved by the graphitisation of Si-terminated SiC (0001) in a 900 mbar argon atmosphere^[61]. At the higher temperature required for Si to sublime under this condition (1500 °C as opposed to 1150 °C in vacuo), surface diffusion is enhanced such that the surface reorganisation occurs before the graphene is formed. Thus much larger domains of graphene form, with a resulting increase of mobility to 2000 cm²/V s at 27 K. The improvement of domain size using this method can be seen in Figures 3.3a and b. Whilst this mobility seems modest in comparison to mechanically exfoliated graphene, where mobility can exceed 200,000 cm²/V s^[62], it is sufficient to make epitaxially grown graphene useful for field-effect devices, and the nature of the graphene on an insulating SiC substrate allows easy integration into electronic devices. However, there are many defects, non-uniformities and high intrinsic doping in the graphene, limiting the performance of any devices using this production route. Additionally, the system is only quasi-2D, the layers are not entirely decoupled, and cannot be transferred to a different substrate. Thus, other production methods are needed.

3.3.3 Chemical vapour deposition (CVD)

One of the most promising production methods for large-scale technological application of graphene is chemical vapour deposition. It had long been known that CVD of hydrocarbons on transition metal surfaces could produce thin graphitic layers^[65]. Inspired by this, graphene growth using CVD was attempted, using ethylene as the carbon source, and ruthenium as the substrate^[66]. Domains of graphene exceeding 100 μm were formed in this way, but the strong metal-graphene interaction limited both further lateral extension, and carrier transport.

More recently, Bae *et al.*^[63], managed to grow 30-inch sheets of predominantly

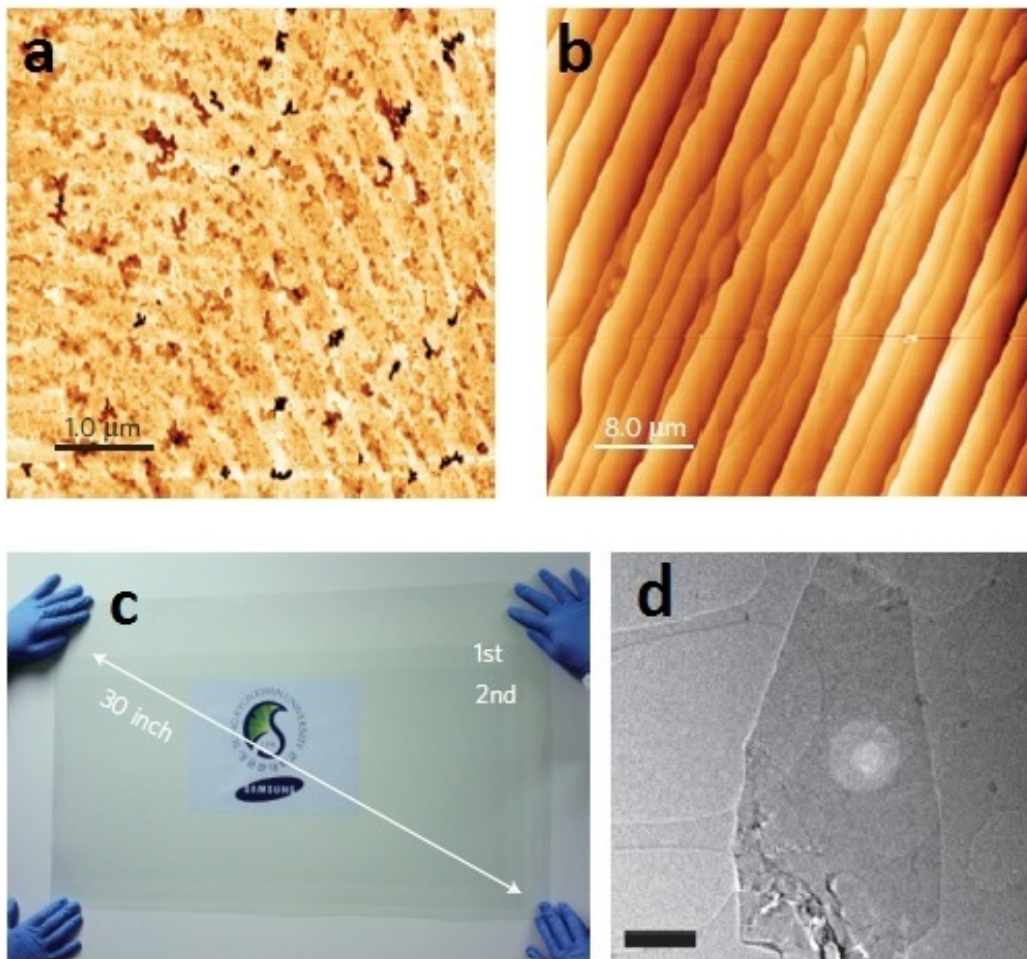


Figure 3.3: **a,b**, AFM images of epitaxial graphene grown **a** in vacuo and **b** in an argon atmosphere. The increased lateral size is clear in **b**. Taken from 61. **c**, 30 inch CVD graphene sheet. Taken from 63. **d**, TEM image of liquid-phase exfoliated monolayer (scale bar 500 nm). Taken from Reference 64.

monolayer graphene on flexible copper substrates (Figure 3.3c), yielding $\sim 125 \Omega$ per square sheet resistance, and 97.4 % transparency. HNO_3 was used to hole dope the sheets even further than the usual p doping found in CVD graphene, lowering the sheet resistance of four stacked graphene layers to $\sim 30 \Omega$ per square, three times less than indium tin oxide (ITO), the material currently used in touch screens. It is thus highly likely that this method will be used to replace ITO electrodes, particularly in view of the limited world supply of indium. Indeed, the same group, working in collaboration with Samsung, have produced an example touch screen device utilising graphene.

Despite these promising results, CVD fabrication remains linked to expensive templates, which are only relevant for high performance applications, such as the devices requiring touch screens [53]. For lower cost, lower performance applications, wet chemical approaches offer an alternative route.

3.3.4 Wet chemical routes

Whereas mechanical exfoliation uses tape to overcome the Van der Waals interaction between graphene layers in high quality graphite crystals, wet chemicals can weaken these interlayer forces by inserting reactants into the interlayer space, and so drive exfoliation [67]. As these methods are carried out in suspension, they can be easily applied to large-scale manufacture. A number of wet chemical processes have so far been shown to yield graphene, including reduction of graphene oxide [67–70], and liquid-phase exfoliation [64, 71–73].

Wet chemical approaches yield graphene with mobilities at least two orders of magnitude smaller than mechanically exfoliated graphene, more impurities, and smaller domain sizes (Figure 3.3d)[71, 74]. However, they are methods in their infancy, and improved results can be anticipated for the future.

3.4 Terahertz transmission and equilibrium conductivity of graphene

It is well known that at visible wavelengths, the absorbance of a graphene monolayer is $\pi\alpha$, where α is the fine structure constant, independent of wavelength, due to a constant optical conductivity of $\pi e^2/2h$ [75]. In the THz regime, however, a Drude absorption peak is expected due to free carriers [76]. This prediction has been tested on both CVD and epitaxially grown graphene, using both THz TDS and far-IR Fourier transform interferometer (far-IR FTIR) spectroscopy [76–79].

Dawlaty *et al.* with epitaxial graphene [77], and Lee *et al.* [76] and Horng *et al.* [78] with CVD grown graphene used FTIR to investigate transmission and hence conductivity in the THz–Far-IR range. These investigations all found the conductivity of graphene to be Drude-like in the THz regime, indicating the dominance of intraband conductivity over interband at low frequencies. A typical result can be seen in Figure 3.4.

Horng *et al.* in particular tested the validity of the predicted Drude behaviour. According to a Drude model, the conductivity should have the form $\sigma = [iD/\pi(\omega + i\Gamma)]$, where ω is the frequency, Γ the scattering rate, and D the Drude weight. For the Dirac fermions in graphene, this has a value $D = (v_F e^2/\hbar)\sqrt{\pi|n|}$, with $v_F = 1.1 \times 10^6 \text{ ms}^{-1}$ the Fermi velocity and $|n|$ the carrier density. This is in contrast to the usual Drude weight in classical materials of $D = \pi n e^2/m^*$, as was derived in Chapter 2.

In order to test this prediction, a gate voltage was applied to the sample to linearly alter the carrier density from the intrinsic hole doping of CVD grown graphene [3]. It was found that at all carrier densities, the measured D was lower than predicted. This difference could be explained by electron-electron interactions, ignored in the Boltzmann transport theory derivation of D . However, one theoretical study investigating this correction predicted a much larger reduction of the Drude weight than

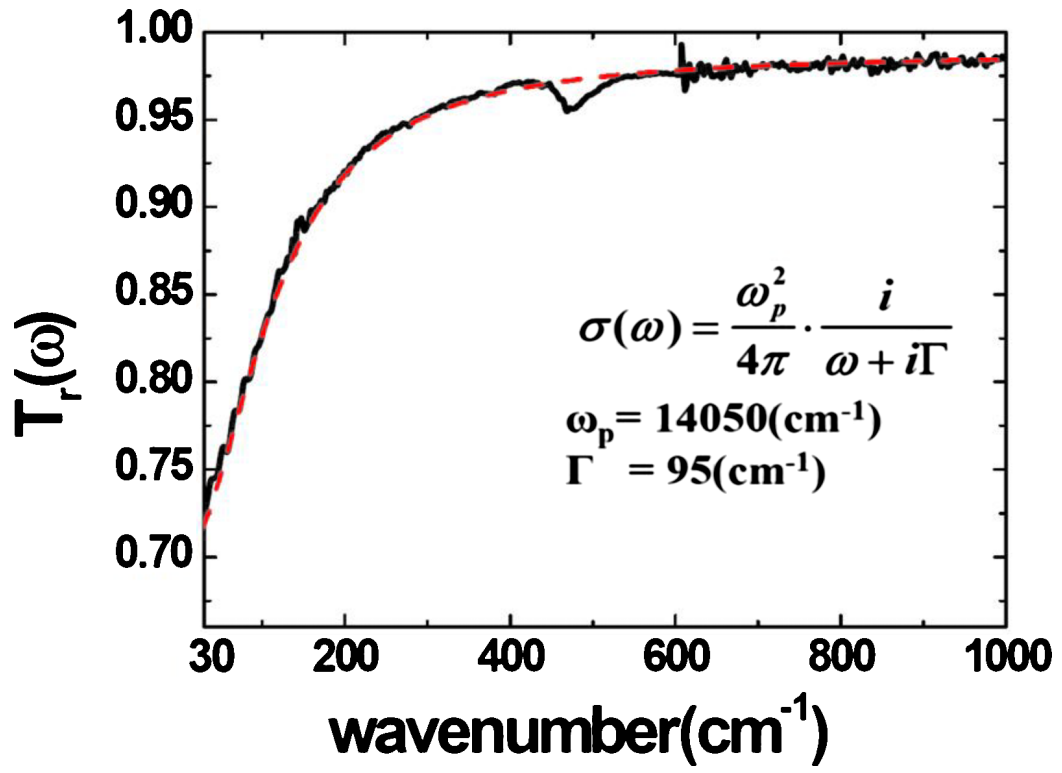


Figure 3.4: Typical transmission spectrum of graphene. The increased absorption at THz wavelengths indicates a Drude type conductivity. At higher wavelengths, the absorption approaches the constant $\pi\alpha$. Taken from Reference 76.

observed by Horng *et al.* Alternatively, defect induced electron or hole localisation could lower the effective free carrier concentration, accounting for the reduced Drude weight. Further investigation is needed to determine the cause of the discrepancy.

In addition to these FTIR measurements, Tomaino *et al.* used THz time domain spectroscopy to map the carrier dynamics of a large area CVD sample on a silicon substrate with $> 90\%$ monolayer coverage [79]. THz transmission through the sheet as a function of position was measured, and used to deduce the local sheet conductivity, σ_s . They measured an inhomogeneity in σ_s of between 1.7×10^{-3} and 2.4×10^{-3} S, which they ascribed to variations in doping level. These conductivity values are 30 times greater than the constant conductivity at optical wavelengths, suggesting intraband transitions dominate the conductivity, in agreement with FTIR studies. This hypothesis was confirmed by an agreement between the THz conductivity and dc conductivity measured using a four probe technique. This work highlighted the benefits of using THz spectroscopy as a contactless probe of conductivity.

A Fourier transform of these THz TDS results yielded the frequency dependent transmission through the sample. Tomaino *et al.* found a flat, featureless response up to the experimental bandwidth of 2 THz, suggesting the probe frequencies were well below the Drude roll-off frequency, in contrast to the FTIR measurements described above.

In a further THz TDS study on CVD-grown graphene, Maeng *et al.* used a gate voltage to modulate the carrier density, similarly to Horng *et al.* [80]. The optical conductivity was again found to be spectrally flat, with the magnitude of conductivity related to the carrier density. When the Fermi level was tuned to be close to the Dirac point, so that carrier density was minimal, the conductivity was observed to be independent of n at room temperature. Away from the Dirac point, however, the optical conductivity varied as $\sqrt{n}$. Both of these observations can be explained within a Drude framework, in the two separate regimes of low and high carrier density.

Additionally, chemical doping using viologen ^[81] was used to reduce the p-type doping of the CVD-grown graphene, and shown to have an identical effect to modulation of the carrier density by applying a gate voltage.

There has been little investigation of the discrepancy between these spectrally flat THz TDS results and the FTIR measurements. A further FTIR study by Choi *et al.* on both mono and multilayer epitaxially grown graphene samples indicated that the Drude roll-off frequency for monolayer samples was higher, and the conductivity drop much smaller than for the multilayer sample ^[82]. Thus the quality of the sample potentially effects the observed conductivity form.

3.5 Pump-Probe Spectroscopy

An alternative form of spectroscopy, pump-probe spectroscopy, allows the time domain investigation of excited carrier dynamics. An understanding of the ultrafast relaxation dynamics of carriers in graphene is essential for designing new graphene-based optoelectronic devices ^[83]. An optical pump pulse (usually $\lambda \sim 800\text{nm}$) is used to photoexcite the sample, and a weaker probe pulse is subsequently used to map the cooling of these hot carriers with sub-ps resolution by comparing the transmission of the probe beam with and without the excitation pulse. By using a THz probe, the ultrafast relaxation dynamics of low energy carriers near the Dirac point can be studied. However, most work so far has used higher energy IR probes, and so we briefly review these studies here.

3.5.1 Optical Pump–Optical Probe

The first studies of graphene using this method used the then new epitaxial growth method for producing samples. Dawlaty *et al.* investigated samples with between 6 and 37 layers of epitaxial graphene, using a 780 nm pump and probe beam ^[84]. They found that upon excitation, probe transmission increased rapidly (photo-induced

bleaching) due to state blocking, followed by a relaxation on two distinct exponential time scales, as seen in the bottom section of Figure 3.5. A first, fast relaxation time of 70-120 fs was followed by a slower time of 0.4-1.7 ps. The first time scale was attributed to the equilibration of the photoexcited carrier populations by carrier-carrier intraband scattering. A subsequent thermalisation by carrier-phonon scattering was attributed to the longer time constant. A schematic of this relaxation can be seen in top section of Figure 3.5.

Later works used a longer wavelength probe, but found broadly similar results to Dawlaty *et al.*, differing only in the interpretation of the cooling mechanisms. Newson *et al.* studied mechanically exfoliated graphene of varying layer number [85]. A similar two time constant decay was found, with the longer time scale attributed to a mixture of carrier-phonon and carrier-carrier scattering. Additionally, it was found that the results were similar for 1-3 layers of graphene. For more the 3 layers, however, the second time constant was found to lengthen, highlighting the importance of inter-layer interactions. Hale *et al.* [86] and Wang *et al.* [83] observed the familiar two time constant decay on exfoliated and CVD grown graphene respectively, but interpreted the longer decay as a bottleneck in cooling due to anharmonic decay of hot optical phonons. Ruzicka *et al.* demonstrated that the diffusion coefficients in epitaxially grown graphene and reduced graphene oxide (RGO) differed by only a factor of two ($1.1 \times 10^4 \text{ cm}^2 \text{ s}^{-1}$ and $5.5 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ respectively) [87]. This is an encouraging result, considering the low cost of RGO fabrication. Other than this result, however, there have been few direct comparisons between different types of graphene.

Optical pump-probe spectroscopy can yield important information about carrier dynamics. However, the high energy probe can study only interband transitions. To investigate the intraband response, terahertz (THz) length radiation is preferable [46].

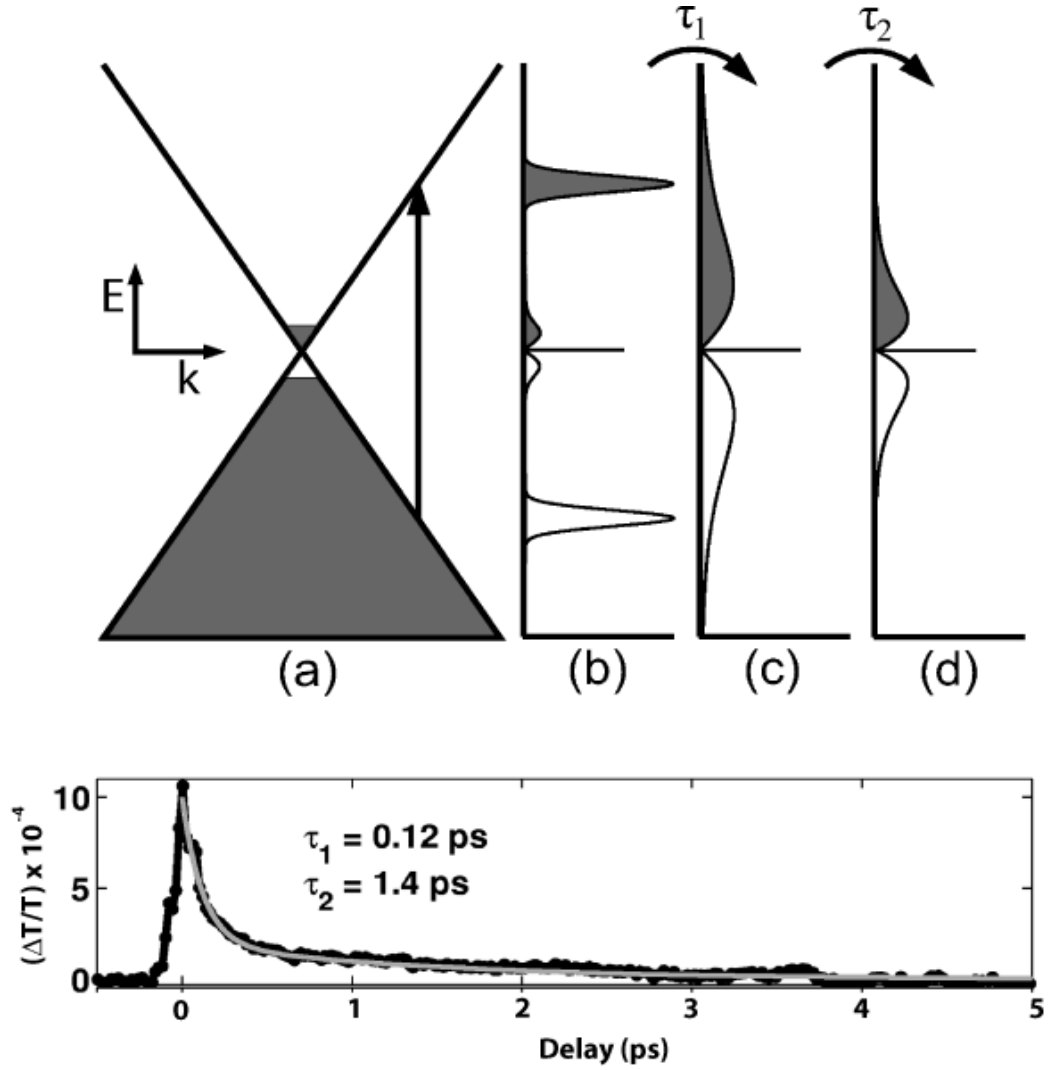


Figure 3.5: **TOP a**, Band structure of graphene showing effect of optical pump. **b**, Distribution of carriers immediately after pump. **c**, Equilibration of carriers by carrier-carrier scattering. **d**, Subsequent cooling of hot carrier distribution by carrier-phonon scattering or recombination. **BOTTOM** Typical transmittivity transient seen in optical pump-probe experiments. Decay is characterised by two time constants, τ_1 and τ_2 . Taken from Reference 84.

3.5.2 Optical-pump terahertz-probe spectroscopy

Due most likely to the relative novelty of THz techniques ^[88], even fewer investigations have utilised a THz rather than optical or IR probe beam, and of these epitaxially grown graphene has been tended to be used. As a result of this preference, results have mainly been performed on a number of graphene layers, rather than a monolayer.

Kampfath *et al.* studied a sample consisting of enough layers of graphene to be considered graphite ^[89]. The 17 nm thick graphite had the same linear dispersion relation around the Dirac point as graphene, and so the optical pump provided the same excitation as was shown in Fig 3.5. A 780 nm femtosecond Ti:sapphire laser oscillator was used both to excite the sample, and to generate THz pulses from frequency mixing in a GaSe crystal, yielding a spectral range of 8 to 30 THz.

In the experiment, the THz signal through the graphite film was sampled as a function of pump-probe delay time, τ , and the associated change in complex dielectric function, $\Delta\varepsilon_\tau$ determined. As a function of time, the THz signal decayed in a similar manner to the optical probe experiments discussed previously. In the frequency domain, it was found (Figure 3.6), that the imaginary part of ε_τ , and hence the transmittivity, increased below 15 THz (photo-induced bleaching), but decreased above that (photo-induced absorption). It was concluded that this effect can be explained by the interplay between direct optical transitions (DOTs) and indirect optical transitions involving a change in carrier momentum (IOTs). Specifically, exciting the sample with the pump pulse transfers electrons to the conduction band. After 0.5 ps, the hot electrons thermalise, and can be described by a Fermi-Dirac distribution with electronic temperature T_e . The newly created electron-hole pairs block some DOTs, limiting the absorption of photons of energy $\sim k_B T_e$. Simultaneously, however, the hot distribution enables additional IOTs, hence increasing the absorption in the THz range.

For further analysis, the IOT change in dielectric function was modelled using

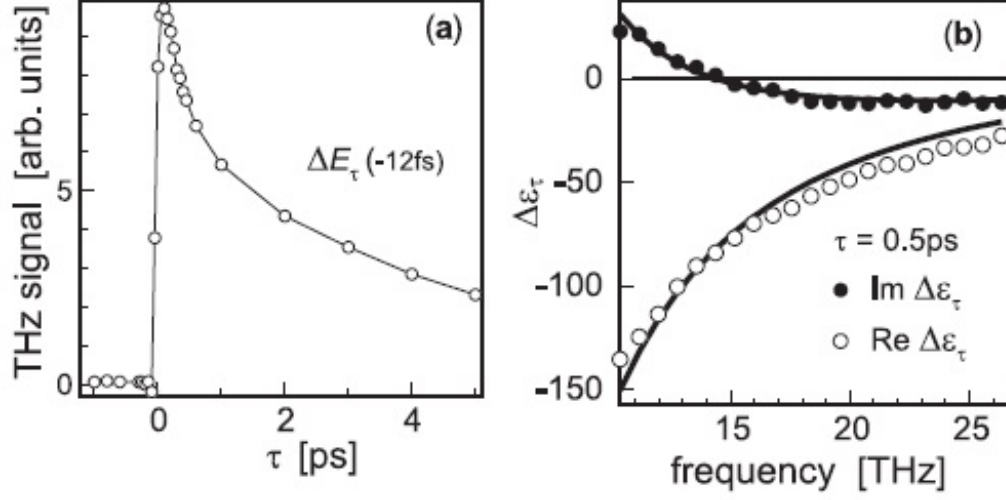


Figure 3.6: (a) Change in THz electric field as a function of pump probe delay, τ . (b) Pump induced changes in complex dielectric function at $\tau=0.5\text{ps}$ after photoexcitation. Taken from Reference 89.

Drude formalism: $\epsilon^{\text{TOT}} = -\omega_p^2/(\omega^2 + i\gamma\omega)$, where γ is the Drude relaxation rate. By comparing the electronic temperature T_e to the equivalent temperature of the pump photons (1200 K), it was observed that within the pump-probe delay time of 500 fs, the electron distribution cools rapidly, losing more than 90% of its initial energy. This was considered to be due to strong coupling of the electrons to hot phonons. This conclusion mirrors the hot phonon bottleneck explanation of Hale *et al.* and Wang *et al.* discussed previously [83,86]. The subsequent slower cooling of 7 ps is determined by the time for heat transfer from hot phonons to cold lattice modes. Kampfrath concluded that an increased relaxation rate from the SCOPs may limit the performance of graphene in electric circuits.

The first time resolved THz study on true graphene was performed by George *et al.* [46]. Two epitaxially grown graphene samples were investigated: sample B consisting of ~ 12 carbon atom layers, and sample C of ~ 20 layers [46]. Raman spectroscopy, an important tool in the analysis of the quality of graphene [34], showed that sample C contained significantly more disorder than sample B. The layers adjacent to the SiC substrate had a much larger carrier density than the further out, intrinsic layers.

It was found that the intrinsic layers dominated the change in terahertz intraband conductivity, so that the adjacent layers could be safely ignored in the analysis.

George *et al.* used a photo-conductive switch ^[90], and electro-optic sampling ^[91], to produce and detect pulses with bandwidth 0.3-3 THz. The graphene was excited by 90 fs pulses from a 780 nm Ti:sapphire laser, delivering 1–16 nJ of energy to a 350 μm spot size. It was found that the photoexcitation of graphene increased the absorption of the THz field, but did not cause a time delay in the transmission of the pulse. In frequency space, this corresponds to a flat, dispersionless real photo-induced conductivity with a negligible imaginary part. This is a result of the ultrafast momentum relaxation time in graphene, and is common to all the THz-TDS studies working in this low frequency range. Therefore, all such works have tracked only the peak of the THz pulse as a function of pump-probe delay time, rather than investigating the full photo-induced conductivity spectrum.

George *et al.* found that transmittivity through the graphene as a function of probe delay showed an initial rapid decrease, caused by an increase in conductivity due to the cooling of the thermalised carrier distribution, followed by a slower, few picosecond, non-exponential increase resulting from first intraband phonon scattering, then electron-hole recombination (Fig. 3.7). Thus the optically pumped electrons are once again behaving as in the schematic in Fig. 3.5.

Possible recombination mechanisms could include a combination of plasmon emission, phonon emission and Auger scattering. The recombination processes were modelled using simple coupled rate equations, expressing the recombination rate as a quadratic function of electron density n , $R(n) = B(n^2 - n_{\text{eq}}^2)$, where n_{eq} is the carrier density at thermal equilibrium, and B is a fitting function. For sample B, a constant value of $1.8 \text{ cm}^2 \text{ s}^{-1}$ for B was found to provide a good theoretical model for the observed reflectivity (see black line in Fig. 3.7). Thus recombination rates depend on carrier density. For sample C, the value was 3.1. The recombination rate for sample

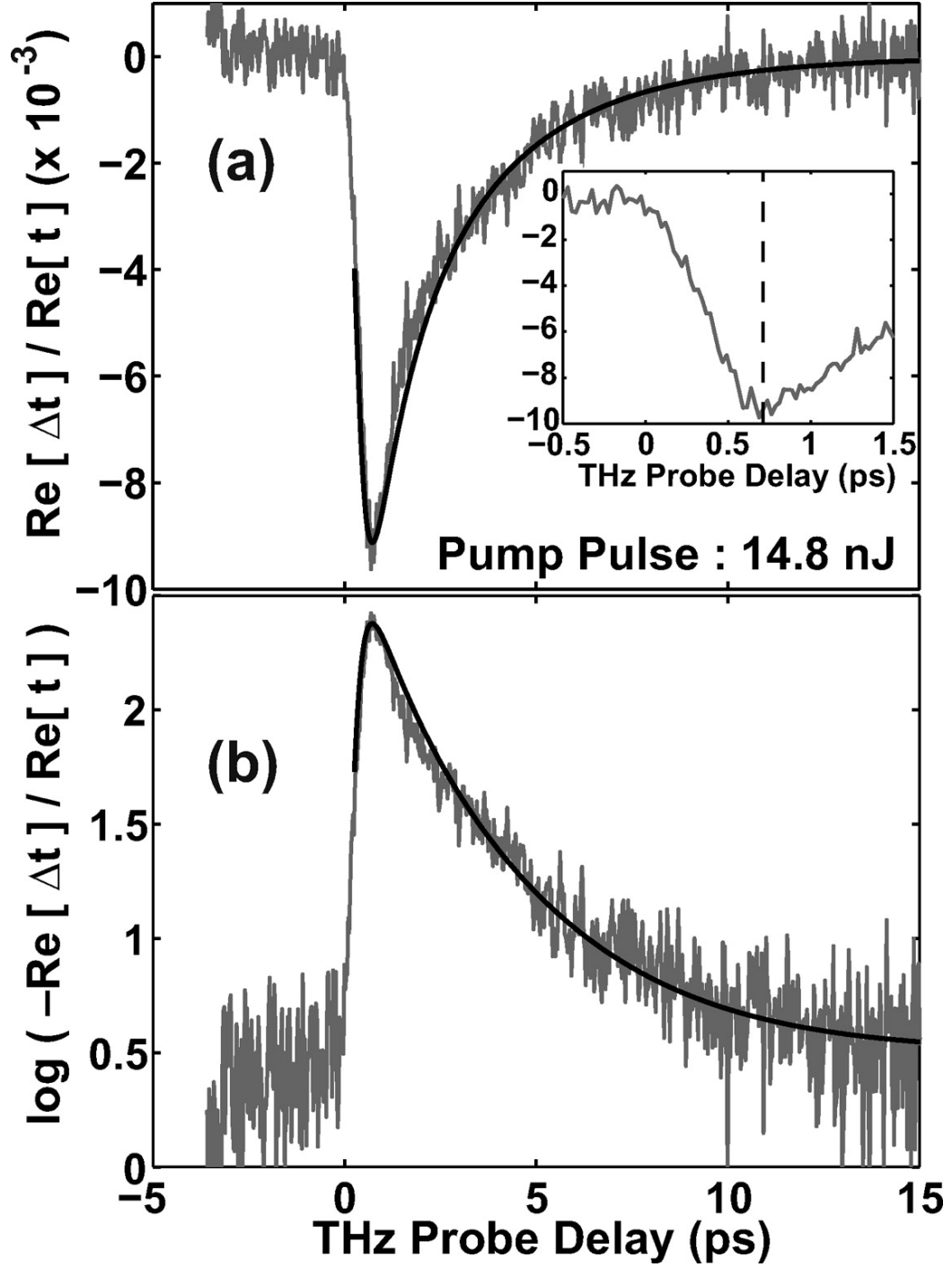


Figure 3.7: **a**, The measured change in the real part of the complex amplitude transmission (grey), and theoretical model (black). Inset: Closer view of initial rapid fall. **b**, The same data on a logarithmic scale, showing that the slow decay is not exponential. Taken from Reference 46.

C was twice that of sample B, showing that increased disorder increases recombination rates. The calculated recombination rates were ~ 2 times higher than that predicted for Auger scattering alone ^[92], suggesting multiple recombination mechanisms are involved. The model was also well able to take into account the increased initial transmission drop when higher pump pulses were used to excite the samples.

In a similar work, Choi *et al.* used THz TDS to investigate fewer layers of epitaxial graphene than George *et al.*, comparing nominally monolayer graphene and multilayer (~ 5 layers) ^[82]. Low-energy electron microscopy (LEEM), angle-resolved photoemission spectroscopy (ARPES), and scanning tunnelling microscopy (STM) ^[93,94] showed the monolayer sample to consist of single-crystalline nanoribbon-like terraces of monolayer graphene, with widths from 60 to 250 nm. These comparatively small widths are characteristic of early epitaxially grown graphenes (see Section 3.3.2).

Choi *et al.* employed 500 μm thick ZnTe crystals for both optical rectification ^[95] and electro-optic sampling to produce and detect THz pulses with bandwidth 0.5-3 THz ^[96]. An 800 nm Ti:sapphire regenerative amplifier was used to pump both the THz generation and the graphene samples, resulting in a maximum incident fluence of 0.9 $\mu\text{J}/\text{cm}^2$ on the samples. Once again, only the transmission of the peak of the THz pulse through the graphene was tracked, due to the dispersionless nature of the material.

In contrast to George *et al.*, a monoexponential decay of the photo-induced absorption was observed for both mono and multilayer samples. In such few layer epitaxial samples, the graphene is highly n-doped by the substrate, unlike thicker samples where the THz response is dominated by the undoped layers away from the substrate. Thus the THz response can reflect changes in minority and majority carriers.

To model their monoexponential absorption decay, Choi *et al.* assumed a monoexponential decay of photoexcited carrier density $n = p = p_0 \exp(-t/\tau_R)$ where

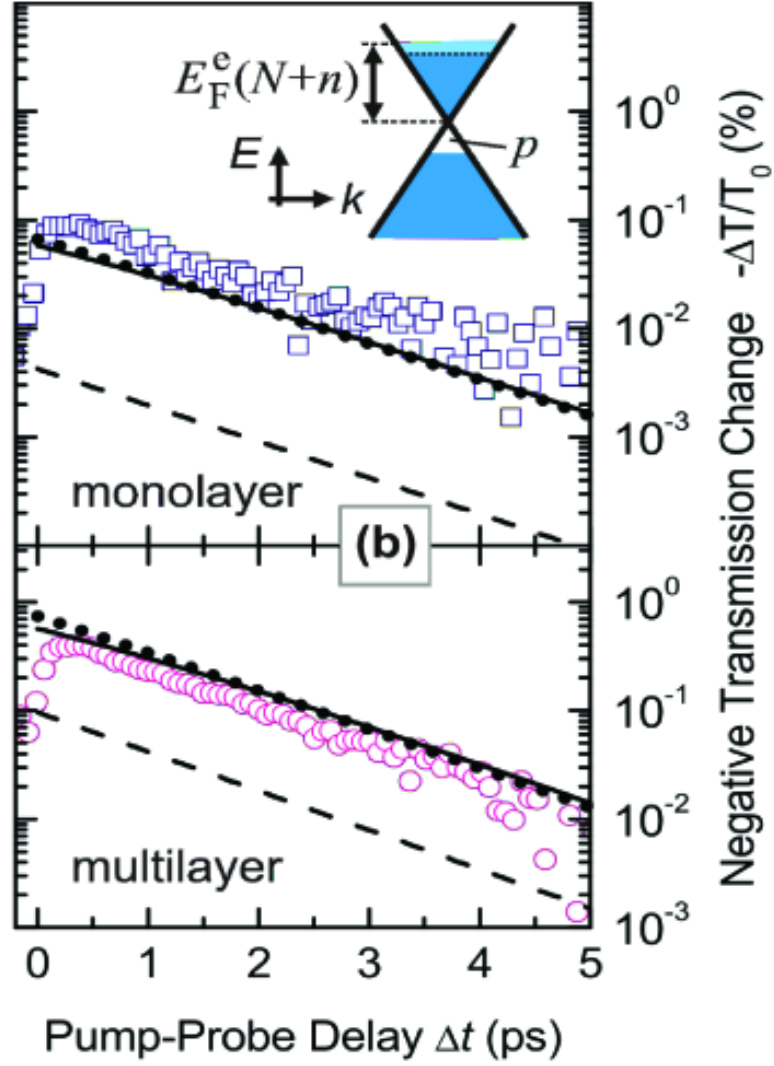


Figure 3.8: Monoexponential decay of photo-induced absorption in mono- and multilayer graphene observed by Choi *et al.* The dashed (dotted) lines represents the electron (hole) contribution from their conductivity model, showing the dominance of the hole response. Taken from Reference 82.

$p_0 = n_0 = 4.6 \times 10^{10} \text{ cm}^{-2}$ is the initial photoexcited carrier density corresponding to a pump fluence of $0.9 \mu\text{J}/\text{cm}^2$, and $\tau_R = 1.3 \text{ ps}$ and 1.2 ps for mono and multilayer graphene respectively. For a given carrier temperature, this allowed the photo-induced conductivity for electrons and holes to be calculated.

By comparison of the observed data to this model, it was found that the hole contribution to this conductivity far outweighed the electronic contribution. Furthermore, allowing for cooling of the carrier temperature had little effect on the calculated conductivity. Thus the THz response is dominated by the recombination of the minority hole carriers, with a largely fluence independent recombination time $\tau_R \simeq 1.2 \text{ ps}$. This time is consistent with that predicted for Auger and phonon-mediated recombination by some theoretical works [92].

More recent theoretical work on carrier recombination has suggested characteristic time scales shorter than one picosecond could be observed, particularly plasmon scattering [97–99]. To investigate the inconsistency of experimental results with theoretical behaviour, Strait *et al.* performed THz TDS on 14-layer epitaxially grown graphene at different substrate temperatures [100]. Terahertz pulses were produced and detected using photoconductive antennas, and the sample excited by 780 nm, 11.4 nJ pump pulses with spot size 1 mm^2 .

Upon excitation of the sample with the pump beam, the THz transmission fell sharply, similarly to previous investigations, with a system resolution limited time scale of $\sim 1 \text{ ps}$ (Figure 3.9). The transmission then recovered over a period of tens of picoseconds at room temperature, but hundreds of picoseconds at low substrate temperatures. At these low temperatures, two distinct time scales are clear, a first, ‘fast’ recovery lasting around 50 ps, then a much longer recovery lasting hundreds of picoseconds. Additionally, the magnitude of the peak pump induced transmission change ($|\Delta T|$) is of greater magnitude at lower substrate temperatures.

These observations were modelled using rate equations. Immediately after pho-

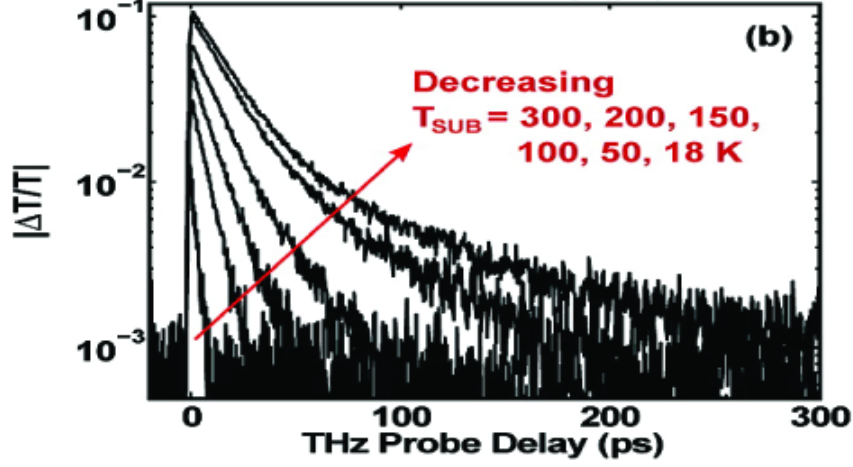


Figure 3.9: The differential THz probe transmission measured by Strait *et al.* as a function of pump probe delay time and substrate temperature, shown on logarithmic scale. Two time constants can clearly be seen at lower substrate temperatures. Taken from Reference 100.

to excitation, the hot carriers were assumed to thermalise by carrier-carrier scattering (as in Figure 3.5), leaving the carriers in Fermi-Dirac distributions with well defined Fermi Levels, E_{fe} and E_{fh} for electrons and holes respectively. The subsequent evolution of electron, hole and phonon distributions was then modelled, incorporating previously published models for optical phonon scattering^[83,98], Auger scattering^[92], acoustic phonon scattering^[101] and plasmon decay^[97]. This model accounted well for the observed data, and suggested the following mechanism for carrier cooling:

Immediately after thermalisation, optical phonon generation rapidly cools the initially large carrier temperature. For times < 1 ps, E_{fh} is greater than E_{fe} , and so the carrier generation rate exceeds the carrier recombination rate, increasing the electron and hole densities. This generation also assists in carrier cooling. This accounts for the increase of photo-induced absorption (and hence also photo-induced conductivity) up to 1 ps. After 1 ps, the situation is reversed, $E_{fe} > E_{fh}$, and so carrier population decreases and optical phonon scattering reduces the photo-induced absorption.

The generation of optical phonons in this initial period gradually raises the temperature of the phonon distribution, until the rising optical phonon temperatures

and the falling carrier temperatures match. As the carrier distributions cool further, inter- and intraband scattering by optical phonons becomes inefficient. As scattering by acoustic phonons is also inefficient in graphene ^[102,103], this causes a bottleneck in the cooling, and accounts for the slowing of the recovery of the THz transmission, an explanation similar to that of the more recent optical pump–optical probe measurements ^[83,86].

The experiment was re-run on a graphene sample consisting of 30 layers, yielding almost identical results, despite more than doubling the thickness of the sample. These results show the importance of optical phonons in graphene-based optical and electronic devices, with the relatively high energy of optical phonons in graphene (0.196 and 0.162 eV ^[34]) standing out in comparison to other semiconductors.

Terahertz spectroscopy has thus been put to good use investigating the cooling of photoexcited carriers in graphite and epitaxial graphene. The four papers discussed here have shown broadly similar results: photo-induced absorption of low photon energy probes (as opposed to the photo-induced bleaching observed in optical pump-optical probe experiments), a rapid change upon photoexcitation, and a room temperature relaxation over a few picoseconds. However there are still some differences in the interpretation of cooling mechanisms, perhaps related to the different samples investigated, which range from nanoribbon-like monolayers to many layered graphite, and the production method chosen to grow the samples.

Chapter 4 describes the use of THz TDS to investigate the photodynamics of CVD-grown graphene, revealing an unexpected sensitivity to gaseous adsorbates, not seen in the above studies. Subsequent to this work, several other THz TDS investigations of CVD-grown graphene were reported ^[104–106]. These studies are discussed at the end of Chapter 4.

3.5.3 Theoretical results and THz lasing

In addition to the experimental results described above, some authors have published theoretical works on the intraband conductivity of graphene. In particular, Ryzhii *et al.* used a model incorporating both the inter- and intra- band conductivities to calculate the frequency response of optically excited graphene ^[107]. Treating the photoexcited carriers as quickly thermalising to a Fermi distribution, as observed in the previous sections, and using a Drude mechanism, they calculated the real part of the conductivity, which is proportional to the absorption coefficient of the graphene. Their results are shown for weak pumping in Figure 3.10, for various values of optical pump intensity, at a temperature of 77 K. This is therefore the form of conductivity that a THz TDS investigation of graphene could expect to see. They further showed that under strong pumping, population inversion can be achieved, resulting in a negative net conductivity in the THz range, and hence negative absorption coefficient. Experimental observations of this behaviour have recently been reported ^[108]. Thus it may be possible to use graphene as a coherent source of THz radiation utilising stimulated photon emission - it could be possible to use graphene as a THz laser.

Following this work, Rana has shown the potential application of graphene for plasmon amplification ^[109]. Plasmons, charge density waves, have been shown to be in the THz range in graphene ^[110]. Utilising the population inversion of Ryzhii *et al.*, Rana has provided a model for potential plasmon oscillation. A step towards the realisation of this model was accomplished by the frequency tuning of plasmons in graphene micro-ribbons by Ju *et al.* ^[111].

3.6 Other 2D materials

The isolation and success of graphene renewed interest in other 2D materials. Initially focus was placed on hexagonal boron nitride (h-BN), a III–V compound with a similar hexagonal structure to graphite, and sometimes referred to as white graphite. Its

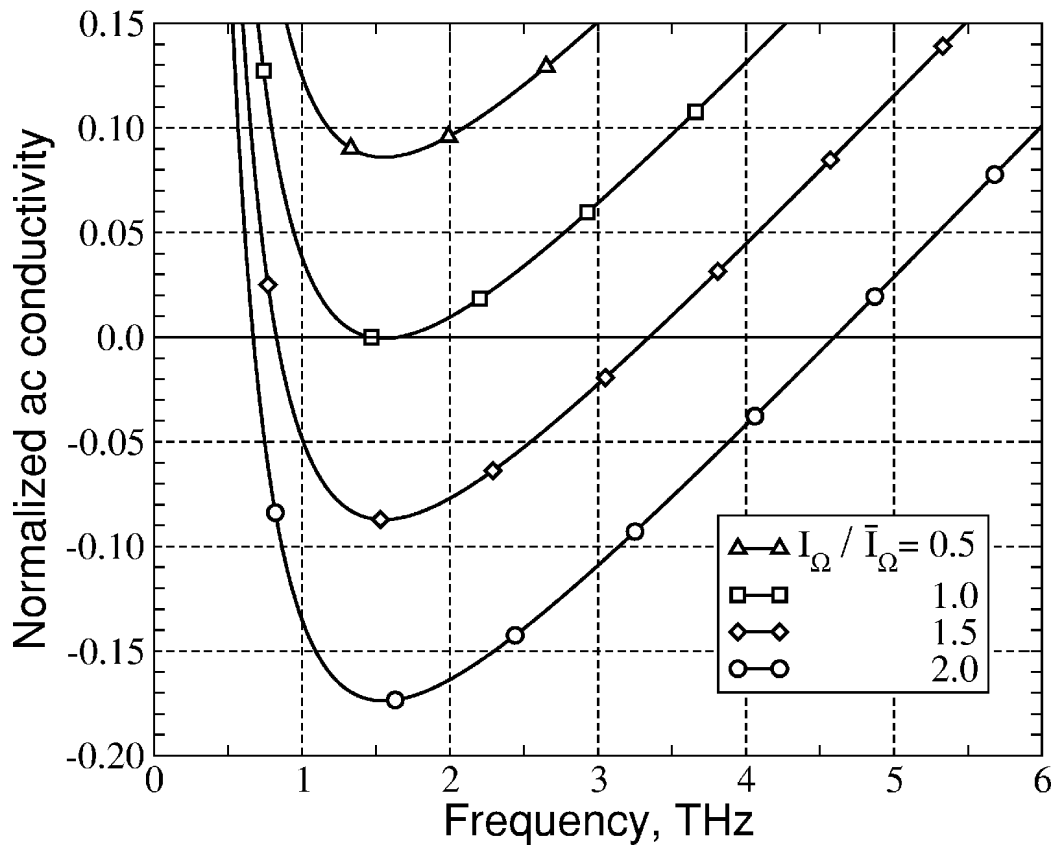


Figure 3.10: Frequency dependence of normalised real part of the ac conductivity of graphene as a function of frequency, for different intensities of optical pump radiation. Taken from Reference ^[107].

structural similarities to carbon were supported by the experimental realisation of BN nanotubes ^[112]. Synthesis of very thin (a few to ten layers) of h-BN was achieved using the same mechanical exfoliation technique used for graphene ^[113]. These sheets can be thinned down to monolayers in the high-energy beam used in TEM ^[114].

In the case of BN, the lateral, in plane symmetry is broken, rather than the symmetry in the direction of the c-axis, as for bilayer graphene. The inequivalence between the boron and nitrogen atoms induces a band gap. Single- and few-layer h-BN show promise as a wide band gap material with excellent mechanical, electrical and optical properties. It possesses an almost identical lattice constant to graphene, suggesting a joint use of the materials in composite devices ^[114], and could even be used to induce a band gap in graphene ^[113]. Indeed, the highest mobilities in CVD-grown graphene have been achieved by using a h-BN monolayer to isolate the graphene layer from the mobility limiting effects of other substrates ^[115].

However, the large bandgap of h-BN limits its use as a semiconductor. For semiconducting 2-dimensional applications, attention has now turned to transition metal dichalcogenides.

3.6.1 Transition metal dichalcogenides

Transition metal dichalcogenides are a family of materials of the form MX_2 , where M is a transition metal of groups 4-10, and X is a chalcogen (S, Se or Te). These materials show a broad range of properties, ranging from insulators and semiconductors to semi-metals, metals and superconductors ^[7]. These properties are summarised in Table 3.1.

Many TMDs crystallise into graphite-like layered structures. Each layer is composed of a layer of metal atoms surrounded on each side by a layer of chalcogens, as shown in Fig 3.11. This triple layer of material is referred to as the monolayer of the TMD. In the bulk structure, the monolayers are held together by weak van der Waals

Table 3.1: Electronic characteristics of TMD materials. ^[116]

Group	M	X ₂	Properties
4	Ti, Hf, Zr	S, Se, Te	Semiconducting
5	V, Nb, Ta	S, Se, Te	Narrow band metals or semimetals
6	Mo, W	S, Se Te	Semiconducting Semimetals
7	Tc, Re	S, Se, Te	Small-gap semiconductors
10	Pd, Pt	S, Se Te	Semiconducting Metallic

forces, and so layers can be easily exfoliated in the same way as graphite.

Although TMDs have been studied in their bulk form for decades ^[7,117,118], it is only since the advent of graphene that their 2-dimensional forms have been purposefully sought. The first of these materials to be exfoliated was molybdenum disulphide (MoS_2), hailed as a ‘semiconducting analogue to graphene’ ^[6,119].

Monolayers of MoS_2 have been prepared by mechanical exfoliation ^[119], liquid exfoliation ^[73], and more recently chemical vapour deposition ^[120–122]. As for graphene, the best quality material has so far been produced by mechanical exfoliation, but ultimately CVD growth is required for commercially viable MoS_2 applications ^[1]. More recently, other semiconducting TMDs have been produced, including tungsten diselenide (WSe_2) ^[123] and molybdenum diselenide (MoSe_2) ^[73].

Electronically, MoS_2 shows much lower mobilities than graphene, with values that largely depend upon the environment around the material. However, its natural bandgap is a great advantage for many applications, such as transistors ^[6,19,124,125], where high on-off current ratios have been achieved. In the semi-metal graphene, the lack of bandgap effectively prevents the switch to an ‘off’ state, limiting its potential for transistor type applications ^[1].

Arguably more excitingly is the opto-electronic application of monolayer MoS_2 .

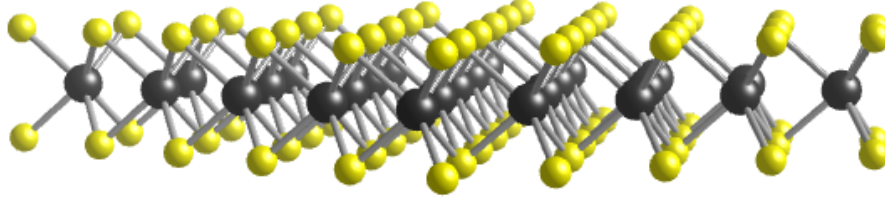


Figure 3.11: The structure of a graphite-like TMD monolayer. A layer of metal atoms is surrounded both above and below by a layer of chalcogen atoms.

In its bulk form, MoS_2 is an indirect gap semiconductor. As MoS_2 is reduced towards the monolayer form, the indirect transition increases in energy due to extra vertical confinement. By monolayer MoS_2 , the indirect transition energy is greater than a direct transition at 1.8 eV, thus monolayer MoS_2 is a direct gap semiconductor^[119]. This change is associated with a factor of 10^4 increase in photoluminescence (PL) quantum yield. Thus the optoelectronic properties of MoS_2 can be easily tuned by changing the number of MoS_2 layers present. This effect is also observed in other semiconducting TMDs, such as WSe_2 ^[126].

Photoluminescence measurements have also identified the presence of trions in MoS_2 and WSe_2 ^[127–129]. The optical absorption spectra of these materials show two prominent peaks, long identified as the ‘A’ and ‘B’ excitons at the direct gap transition. The higher energy ‘B’ exciton arises from a splitting of the valence band due to spin-orbit coupling. Studying the photoluminescence associated with these excitons in heavily doped MoS_2 , Mak *et al.* observed an additional peak at a slightly lower energy than the ‘A’ exciton peak, that was dependent upon the electron concentration^[127]. This peak showed the presence of negative trions, bound quasi-particles consisting of two electrons and a hole. The trion binding energy, the energy required to remove the extra electron and leave a normal exciton, was found to be 18 meV, in the terahertz range.

Additionally, MoS_2 has demonstrated ultrafast behaviour, showing potential for use in high-speed electronic and opto-electronics. Korn *et al.* measured the PL

from monolayer MoS₂ as a function of time after photoexcitation by a 400 nm pump pulse ^[130]. They found that PL intensity decreased rapidly within 5 ps, followed by a temperature dependent longer decay period, ranging from 50-100 ps for temperatures above 180 K. Wang *et al.* used optical-pump optical-probe spectroscopy to investigate few-layer MoS₂ ^[131]. Photoexcitation of the sample reduced the absorption of the optical probe, due to phase-filling effects. This absorption decrease decayed on a timescale of 100 ps. Transient absorption spectroscopy on mono-layer MoS₂ by Shi *et al.* found three timescales, an ultrafast 2 ps component, followed by longer decays of ~ 70 ps and ~ 800 ps ^[132].

However, these measurements were not able to observe the conductive species of interest for opto-electronic applications directly. Furthermore, of the various monolayer TMDs now available, only MoS₂ has been studied using time-resolved techniques. In Chapters 5 and 6, THz time domain spectroscopy is used to investigate the ultrafast nature of monolayer MoS₂, WSe₂ and MoSe₂.

3.7 Carbon nanotubes

Although not a 2-dimensional material, carbon nanotubes (CNTs) are also considered in this thesis as a material for ultrafast THz applications. Carbon nanotubes can be thought of as rolled up sheets of graphene. Depending on its chirality, a nanotube can be either metallic or semiconducting, i.e. the band gap is controlled by the direction of rolling of the graphene sheet ^[133]. Combined with very high mobilities ^[134], this makes nanotubes a good alternative to graphene, although the enhanced electronic properties of graphene ^[36] may make graphene a more attractive option for future devices.

Carbon nanotubes pre-date graphene by over a decade ^[135], and have been the subject of a huge research effort. A review of carbon nanotubes, and their opto-electronic properties can be found in Reference 136.

The intrinsic anisotropy of 1-dimensional nanotubes makes them useful for the polarisation of electromagnetic waves ^[137,138]. Single-walled carbon nanotubes (SWCNTs) have been shown to have a particularly strong optical anisotropy ^[136]. By embedding SWCNTs in a polymer film, and stretching the film to align all the nanotubes in one direction, Shojii *et al.* demonstrated polarisation of broadband optical radiation ^[137].

SWCNTs are particularly promising for THz frequency radiation. To realise the potential of THz waves in a range of applications, from communications to security, devices are required to modulate and polarise the THz radiation, and encode information on the wave. Few devices, however, currently exist ^[13,139].

Using the anisotropic THz absorption of metallic SWCNTs, Ren *et al.* have demonstrated THz polarisation by aligned SWCNTs, achieving 80% absorption when the nanotubes were aligned with the THz radiation, and almost no attenuation when the nanotubes were perpendicular to the polarisation of the THz waves ^[140]. The performance of such a polariser can be improved by stacking layers of the aligned nanotubes, producing a device capable of competing with expensive metallic wire-grid polarisers, the current standard THz polarisers ^[141].

Semiconducting SWCNTs also show promise for THz devices. Photoexcitation of semiconducting nanotubes generates excitons aligned along the length of the nanotube, retaining the highly anisotropic nature of the nanotube ^[142–144]. These excitons strongly absorb THz radiation, thus for the lifetime of the excitons THz radiation aligned with the nanotubes can be absorbed, allowing *dynamic* THz polarisation.

Such a THz polariser was demonstrated by Xu *et al.* ^[145]. Semiconducting SWCNTs were embedded in a gelatine matrix. The SWCNT-gelatine matrix was stretched to align the nanotubes along one direction. The absorption of THz probe in the matrix was examined as a function of time after photoexcitation by a 800 nm probe beam. When the nanotubes were aligned parallel to the polarisation of the THz wave, pho-

to excitation induced a strong absorption of the THz probe, which decayed on two timescales - a first fast decay of several picoseconds followed by a longer decay over hundreds of picoseconds. In contrast, if the nanotubes were aligned perpendicular to the THz wave, no additional absorption was found after photoexcitation. Thus ultrafast transient THz polarisation was achieved.

In Chapter 7, this idea is further developed to demonstrate tunable dynamic THz polarisation.

Chapter 4

Sensitivity of graphene photoconductivity to environmental gases

Before the unique properties of graphene can be used in terahertz-frequency electronics, the THz response of graphene must be studied. In this Chapter it is shown that the photoconductivity of graphene at terahertz frequencies is dramatically altered by the adsorption of atmospheric gases, such as nitrogen and oxygen. Furthermore, the signature of terahertz stimulated emission from gas-adsorbed graphene is observed. These findings highlight the importance of environmental conditions on the design and fabrication of high-speed graphene-based devices.

4.1 Introduction

The experimental realisation of graphene, a single layer of graphite, in 2004 ^[3] rapidly led to the observation of massless Dirac fermions and the half-integer quantum Hall effect^[37]. Since then many potential applications have been suggested that make use of graphene's unique properties ^[146]. Recently graphene-based touch-screen displays^[63], transistors^[18,147], and integrated circuits^[148] have been demonstrated. The combination of high mobility and transparency make graphene especially suited to use in opto-electronic devices ^[146,149]. The high mobility of charge carriers in graphene makes it an ideal material for extremely high-speed devices^[18,147], indeed terahertz frequency switching has been predicted^[146]. The potential for the realisation of such devices was greatly enhanced by the emergence of large area graphene sheets grown by chemical vapour deposition (CVD) ^[150]. However, the design and production of these high-frequency devices requires a fuller understanding of both nonequilibrium carrier dynamics in graphene ^[83], and its susceptibility to environmental conditions ^[151].

Ultrafast spectroscopic techniques provide an excellent probe of non-equilibrium carrier dynamics in graphene^[152]. Ultrafast cooling and relaxation of photoexcited charge carriers in graphene have been observed using optical pump–optical probe spectroscopy. As was discussed in Chapter 3, several studies ^[83,84,86] have shown that graphene becomes more transparent at optical frequencies after intense photoexcitation (photoinduced bleaching), owing to state blocking of interband absorption. Furthermore these studies showed that thermalisation of photoexcited carriers occurs within tens of femtoseconds, and a subsequent cooling by carrier–phonon interactions occurs on a picosecond timescale.

While optical photons probe interband charge dynamics, terahertz frequency photons are excellent probes of intraband dynamics. Studies of intraband relaxation in epitaxially-grown graphene have been performed using optical pump–terahertz probe

spectroscopy (OPTPS) [46,82,100]. Generally these studies revealed that the absorption of the terahertz photons in epitaxially grown graphene increases after intense (inter-band) optical excitation due to an increase in the density of mobile charge carriers after photoexcitation.

In this study, we used terahertz time domain spectroscopy to measure the photoconductivity of CVD grown graphene in four different environment types: air, oxygen, nitrogen and vacuum. We demonstrate that CVD grown graphene can display either photoinduced bleaching or photoinduced absorption depending on the type and density of gas adsorbed on its surface. Our results highlight the dramatic effects environmental conditions have on the high-frequency electrical properties of graphene. These results have important implications for the design of future graphene electronic devices. In particular, the order-of-magnitude changes in photoconductivity we observe could provide a basis for precise graphene based gas monitors. Conversely, the sensitivity of the optoelectronic properties of graphene to environmental conditions will need to be addressed during the design and fabrication of future devices.

4.2 Sample preparation

Large-area graphene films were prepared by chemical vapour deposition (CVD) on 25 μm copper foil (Alfa Aesar). Prior to the growth, the copper foil was heated in hydrogen from room temperature to 1000 $^{\circ}\text{C}$ for 60 minutes for removal of surface oxides. As temperature reached 1000 $^{\circ}\text{C}$, a mixed flow of H_2 (15 sccm) and CH_4 (60 sccm) was introduced for graphene growth. After CVD, the graphene film was separated from copper foil and then attached to the z-cut quartz substrate by the polymer transfer process: Poly(methyl methacrylate) (MicroChem Co., NANO PMMA 950K A4) was spin-coated on graphene/copper foil to form a protective layer. The copper foil was etched at 25 $^{\circ}\text{C}$ in ferric nitrate solution (50 g/L, J.T.Baker ACS reagent, 98%), leaving a transparent PMMA/graphene film floating on the solution. After rinsing,

the film was transferred onto the quartz substrate, and the PMMA capping layer was dissolved in acetone at 60 °C overnight. In order to remove the residual PMMA, graphene films were annealed at 450 °C at 500 Torr in the mixed gases of H₂ (20 sccm) and Ar (80 sccm) for decomposition of the polymer. It should be noted that sample growth, and Raman and AFM characterisation of the samples were provided by the group of Lance Li at the Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan.

4.3 Sample characterisation

Primary characterisation of the sample was performed by Raman spectroscopy using the Raman system described in Section 2.6. Monolayer graphene has a well-known Raman signature that distinguishes it from bi- or multi-layer graphene, consisting of a ‘G’ peak at 1580 cm⁻¹, a ‘D’ peak at 1350 cm⁻¹, and a ‘2D’ peak at 2700 cm⁻¹. The ratio of intensities of the G and 2D peaks can be used with the shape of the 2D peak to determine the number of layers, whilst the intensity of the D peak provides a measure of the quality of the sample [34].

A typical Raman spectrum of the CVD graphene samples is shown in Figure 4.1, exhibiting a Lorentzian-shape 2D Raman peak, and a ratio of intensities of the 2D and G peaks $I_{2D}/I_G \approx 2$, which is indicative of monolayer growth. Additionally, the relative weakness of the D peak demonstrates the small number of defects and low disorder in the samples, confirming their high quality.

UV-visible absorption measurements, shown in Figure 4.2 revealed an absorption of $\sim \pi\alpha$, where α is the fine structure constant, also suggesting monolayer growth [75]. AFM images of nominally identical samples (Figure 4.1b) showed the graphene sheet thickness measured from the edge to be ~ 0.72 nm, further suggesting monolayer growth [153].

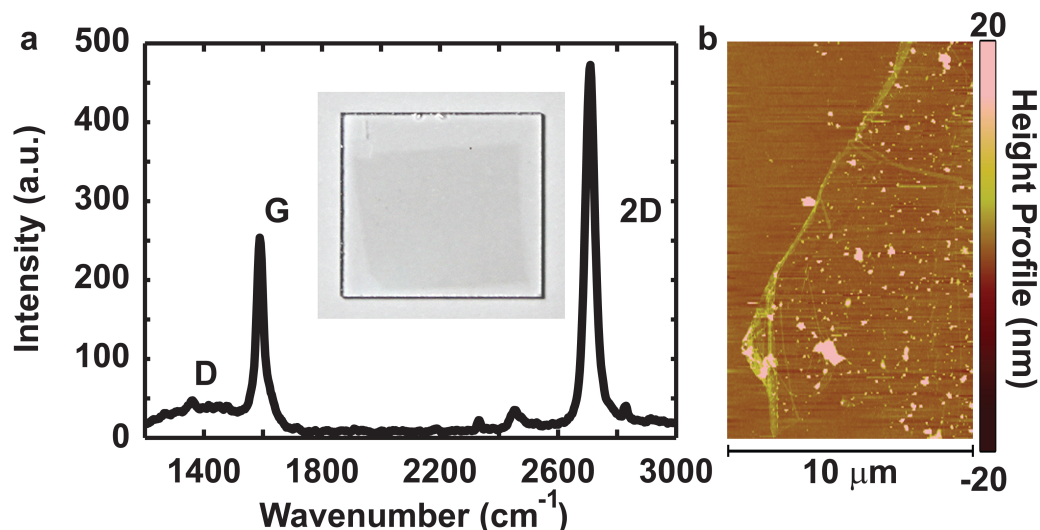


Figure 4.1: **a** Raman spectroscopy. The relative intensities of the 2D and G peaks suggest monolayer graphene [34]. **Inset** Photograph of graphene sheet with area of $1 \times 1 \text{ cm}^2$ on quartz. **b** Surface topography of CVD-grown graphene measured by AFM. The residuals remaining on graphene surface can be attributed to incomplete decomposition or carbonization of PMMA.

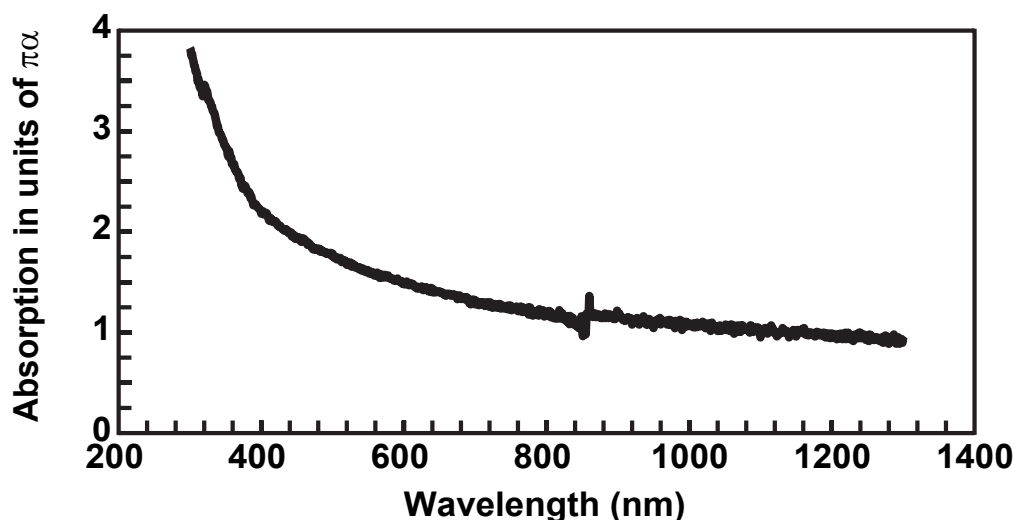


Figure 4.2: **UV-vis absorption spectra of sample.** The near constant absorption of $\pi\alpha$ at optical wavelengths suggests monolayer growth [75]. The deviation from $\pi\alpha$ beyond 500 nm occurs because of nonlinear effects in the band structure of graphene far away from the Dirac point. The feature at 860 nm is an artefact of the spectrometer.

4.3.1 Hall measurements

Samples were additionally characterised by room temperature Hall effect measurements based on the Van der Pauw method (3S Co., NI PXI-1033). From the Hall effect measurements averaged across 8 samples, the sheet resistance, carrier density and Hall mobility were found to be $1100 \pm 350 \Omega/\square$, $8 \pm 2 \times 10^{12} \text{ cm}^{-2}$ and $800 \pm 250 \text{ cm}^2/\text{Vs}$ respectively. The characterizations show that the quality of the graphene samples is fairly good.

Further Hall effect measurements were performed to examine the equilibrium electrical properties of the graphene samples under different gaseous environments. Two systems were used for the measurements, one based on a permanent magnet (0.68 T), and another using a swept electromagnet (0 – 0.91 T). Samples were held in a vacuum vessel, which could be purged with different gasses. The Fermi levels were deduced using the relation $\varepsilon_F = \hbar v_F \sqrt{\pi n}$, where $v_F \approx 10^6 \text{ ms}^{-1}$ [37, 111].

The equilibrium carrier density, and hence Fermi level, were found to be relatively insensitive to the gaseous environment, with variations in n and ε_F between samples being greater than changes induced by the gases. It was found that, compared with vacuum conditions (without laser annealing), exposure to pure nitrogen gas decreased the carrier density by $\sim 5\%$, exposure to oxygen increased the carrier density by $\sim 7\%$ and exposure to air increased it by $\sim 3\%$, corresponding to Fermi level changes of $\sim 2\%$, $\sim 3\%$ and $\sim 1\%$ respectively. These changes are consistent with previous observation of oxygen and nitrogen exposure doping CVD graphene p-type and n-type respectively [154, 155].

It has been shown that photoexcitation by near-infrared laser pulses can cause additional doping of graphene in the presence of oxygen. However, for the fluences used in the THz measurements, this effect is expected to be negligible compared to the equilibrium carrier density [156].

4.4 Terahertz time domain spectroscopy

In order to assess the influence of atmospheric gas adsorption on graphene we used terahertz spectroscopy. This technique allowed us to observe intraband charge dynamics and investigate the high-frequency electrical properties of graphene. Terahertz spectroscopy is ideal for electrically characterising surface sensitive materials such as graphene as it is a non-contact technique, and covers an important frequency range ($\sim 100 \text{ GHz} - >3 \text{ THz}$) for high speed device operation^[10]. OPTPS measurements were performed with CVD-grown graphene samples in an atmosphere of air, N_2 or O_2 , or in a vacuum. Before each set of measurements, the sample was left under a vacuum of 10^{-5} mbar for two hours, to remove existing adsorbants (see Section 4.5 for Langmuir coverage calculations). For the vacuum measurements, the graphene was left for a further two hours with 800 nm (1.55 eV) “pump” photons incident upon the sample before measurement. For the gaseous measurements, 1 bar of air, N_2 or O_2 was introduced after two hours under vacuum, and measurements were taken after a further two hours, again with the “pump” beam incident upon the sample. Measurements were found to be reproducible on different samples and were independent of sample history. That is, the effect of exposure to any of the gases could be “reset” by placing the sample in vacuum for 2 hours.

4.4.1 Terahertz Transmission

In the terahertz (THz) regime, the absorption of a graphene sheet is expected to be higher than at visible wavelengths, and to take a Drude free carrier form rather than a constant absorption^[77]. To investigate this for our samples, we used terahertz time domain spectroscopy without photoexciting the sample. The transmission of the graphene, T , can be found from the transmission through the graphene and its quartz substrate, E_{sample} , and the transmission through the quartz substrate alone, E_{quartz} . Fourier transforming these time domain measurements yields

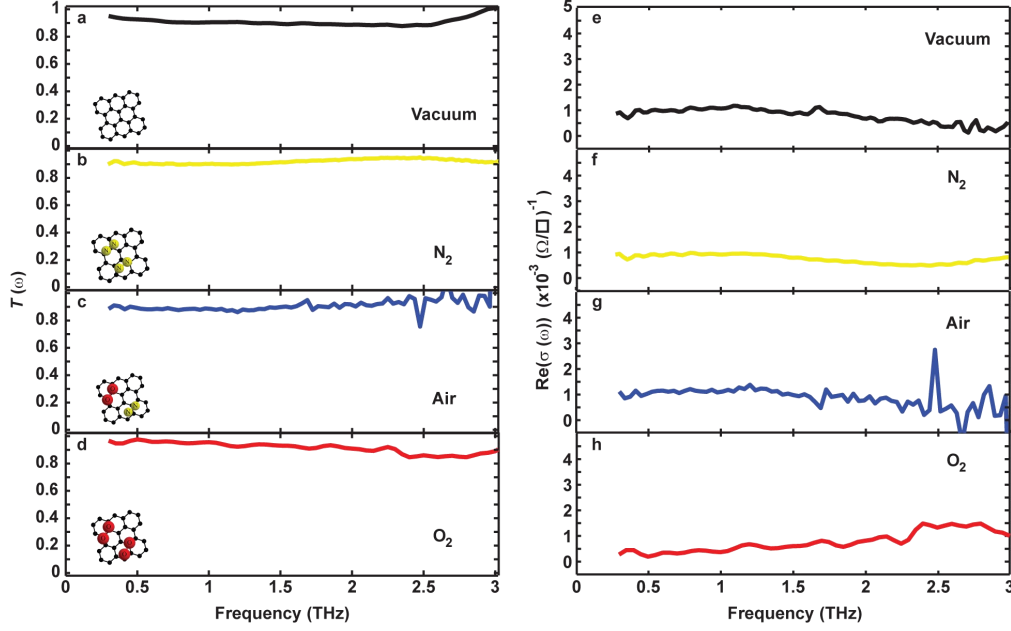


Figure 4.3: Measured equilibrium (non-photoexcited) THz transmission of graphene sheet in different environments. **a** In vacuum, **b** in N_2 , **c** in air, **d** in O_2 . **e-h** The corresponding real part of THz conductivity. Both transmission and conductivity are mainly constant, with no significant difference between the atmosphere types. The absorption lines in the air measurement are due to absorption of THz by water vapour [157].

$$T(\omega) = E_{\text{sample}}(\omega)/E_{\text{quartz}}(\omega).$$

We recorded the non-photoexcited transmission of the sample in all four atmosphere types used in the photoconductivity measurements: vacuum, N_2 , ambient air and O_2 . These data are presented in Figure 4.3a-d. From these data, the real part of the complex conductivity of graphene can be extracted using Equation 2.18, namely

$$\sigma(\omega) = \frac{1 + n_s}{Z_0} \left(\frac{1}{|T(\omega)|} - 1 \right), \quad (4.1)$$

where Z_0 is the impedance of free space, $Z_0 = 377 \Omega$, and n_s is the refractive index of the quartz substrate, $n_r = 2.1$ [158] at terahertz frequencies. The real part of this conductivity in each environment type is presented in Figure 4.3e-f. Due to small mismatches in thickness between the graphene on quartz sample and quartz reference, the imaginary part of the conductivity cannot be reliably calculated for these samples.

However, previous studies have shown $Im(\sigma)$ to be negligible for graphene in the THz region [79, 80].

Both transmission and conductivity in all environments are roughly uniform and featureless over 3 THz, suggesting that the Drude scattering rate is higher than the bandwidth of our measurements [79]. It should be noted that the sensitivity of these measurements is lower than the pump-probe measurements of the following section due to difference between the sample and reference substrate. There is no evidence of a bandgap opening due to adsorption of gas molecules, as is suggested could cause the observed photoconductivity in section 4.6. However, in heavily p-doped graphene, such a bandgap would not be expected to be observable in THz transmission measurements as there are no occupied electron states near the top of the valance band available to be excited by low energy THz photons.

4.4.2 Optical-pump–THz-probe measurements

For the photoexcited measurements, the electric field of a terahertz pulse transmitted through the graphene was sampled after photoexcitation by an 800 nm, $180 \mu\text{J}/\text{cm}^2$ fluence pump pulse, $E_{\text{THz}}^{\text{ON}}$, and without the photoexcitation, $E_{\text{THz}}^{\text{OFF}}$. The photoinduced change in terahertz transmission of the sample, $\Delta E = E_{\text{THz}}^{\text{ON}} - E_{\text{THz}}^{\text{OFF}}$ was recorded using lock-in detection. The principle of the measurements is illustrated in Figure 4.4a. The terahertz pulse probes the photoexcited graphene sample at a time t_2 after photoexcitation. The terahertz probe is then mapped out in time by varying the difference in time of arrival, t_1 , between the terahertz pulse and an 800 nm gate pulse at an electro-optic detection crystal (GaP).

In Figures 4.4b and c we present the measured terahertz electric field, E_{THz} , transmitted through graphene in an pure oxygen atmosphere, and the corresponding change in transmission due to photoexcitation, ΔE . The induced ΔE decreases as the delay between pump and probe, t_2 , is increased. The photoinduced change in

terahertz transmission is seen to decay within ~ 5 ps. Further information may be extracted from these data by performing a Fourier transform on the electric field data to give directly the frequency dependent complex photoconductivity, $\Delta\sigma(\omega)$, without resorting to the Kramers-Kronig relations, via Equation 2.23,

$$\Delta\sigma(\omega) = - \left(\frac{1 + n_s}{Z_0} \right) \frac{\Delta E(\omega)}{E_{\text{THz}}(\omega)}. \quad (4.2)$$

Figures 4.4d and e show the real and imaginary parts of the photoconductivity respectively as a function of pump-probe delay time.

To more easily compare the photoconductivity in different atmospheres, we take slices of the data from Figure 4.4, and the corresponding data for the other environment types. For instance, holding t_1 constant at the maximum terahertz electric field (e.g. $t_1=0$ in Figure 4.4c) and observing the resulting ΔE as pump-probe delay time t_2 is varied, yields an optical pump-terahertz probe measurement, which provides the average terahertz response of the sample. In Figure 4.5, we plot $-\Delta E/E_{\text{THz}}$, which is proportional to the photoconductivity of the graphene, as a function of the delay time between the pump and probe pulses in the four atmosphere types. It should be noted that due to the large number of holes already present near the Dirac point in this p doped sample, the transient response probed by the terahertz is dominated by electron dynamics.

Immediately after photoexcitation in vacuum, the terahertz conductivity increases (photoinduced absorption) within 1 ps, and subsequently relaxes with two distinct time scales. Initially fast cooling occurs within ~ 0.6 ps, and a longer, exponential cooling occurs with a time scale of ~ 2.5 ps. Such a relaxation is consistent with other studies, which associated the first rapid cooling with emission of optical phonons, followed by a bottleneck when the carrier temperature cools below the hot optical phonon temperature (~ 0.196 and 0.162 eV ^[100]), slowing further cooling ^[83, 86, 100].

However, when graphene is placed in a gaseous atmosphere, the photoinduced

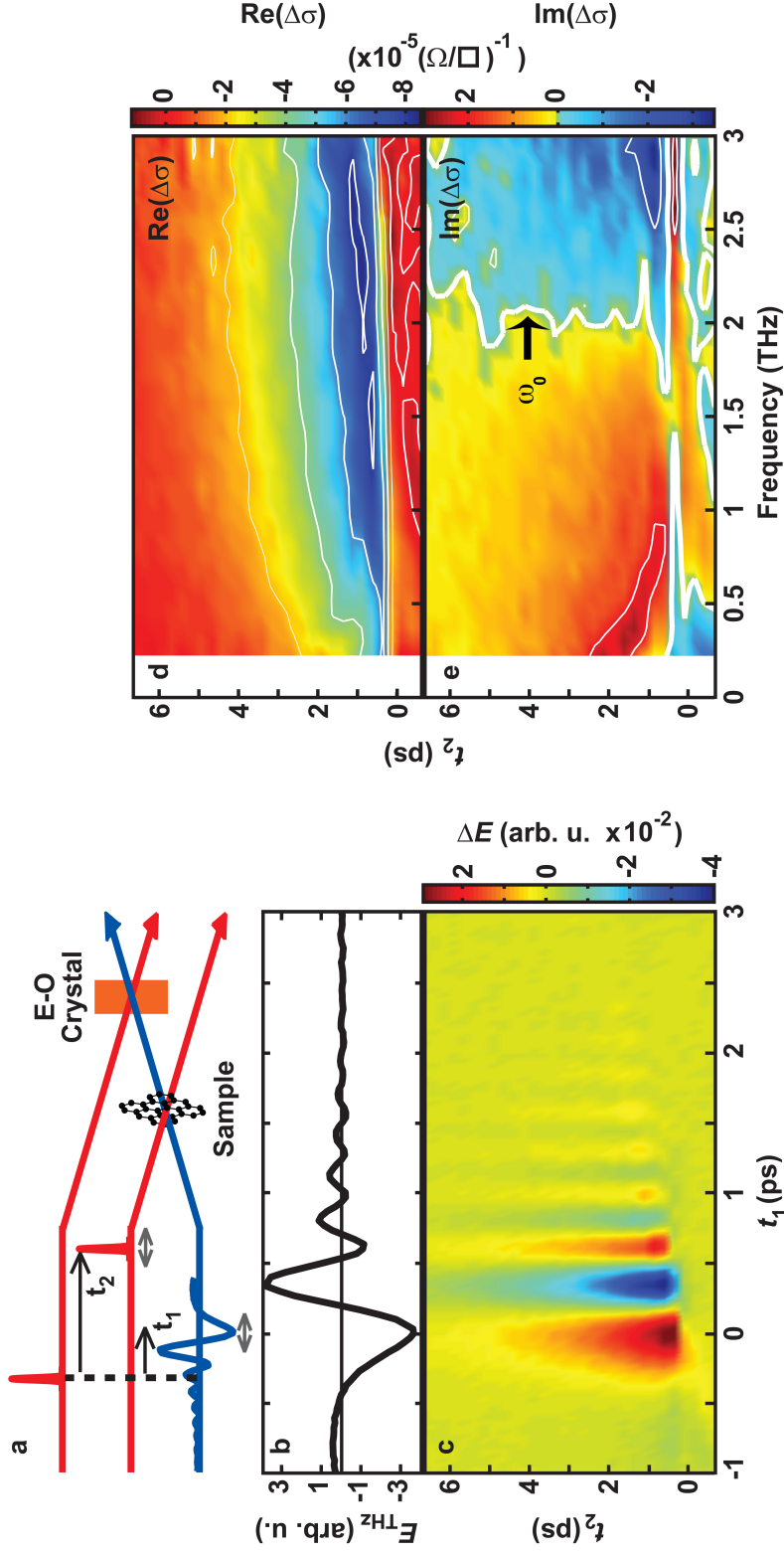


Figure 4.4: **a** Schematic representation of the measurement. Varying t_1 allows the electric field, E_{THz} , of the terahertz probe pulse to be sampled in the electro-optic (E-O) crystal. The sample can be probed at different times after photoexcitation by altering t_2 . **b,c** terahertz electric field, E_{THz} , transmitted through the sample (**b**), and the corresponding photoinduced change in transmission, ΔE (**c**), as a function of pump-probe delay time, t_2 . **d,e** Real (**d**) and imaginary (**e**) parts of the frequency dependent photoconductivity as a function of t_2 . The contours highlight increments of $2 \times 10^{-5} \text{ S}\square$. The thicker contour in **e** represents $\text{Im}(\Delta\sigma) = 0$, corresponding to the Lorentzian peak frequency, ω_0 .

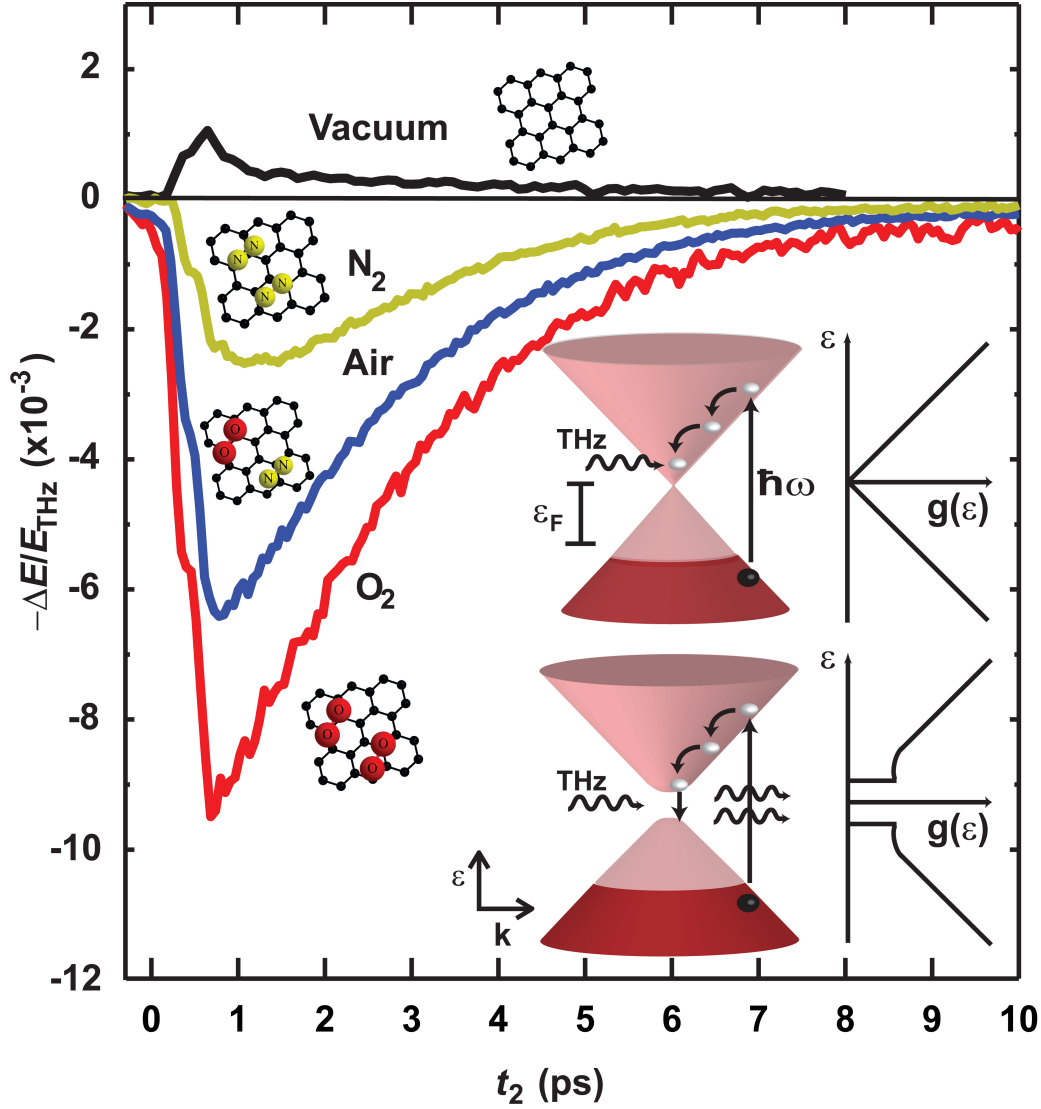


Figure 4.5: Here, $\Delta E = E_{\text{THz}}^{\text{ON}} - E_{\text{THz}}^{\text{OFF}}$. From top to bottom: graphene in vacuum, N_2 , air and O_2 . Photoinduced absorption is observed in vacuum, but photoinduced bleaching is observed in gaseous environments. Inset: Schematic representation of the pump-probe measurements of p-doped graphene ($\varepsilon_{\text{F}} \sim -0.3 \text{ eV}$) in vacuum (top), and in the presence of gases (bottom), with corresponding density of states ($g(\varepsilon)$). The high energy pump ($\hbar\omega$) excites carriers far above the Dirac point, which cool by phonon emission. In gapless graphene, terahertz photons can be absorbed by the photoexcited carriers. In the presence of gases, stimulated emission releases extra terahertz photons, yielding a bleaching pump-probe signal.

change is dramatically different. Surprisingly, the photoconductivity signal flips from being purely positive in vacuum to purely negative in all the gas environments. Following photoexcitation in air, N₂ or O₂, the terahertz conductivity decreases within 1 ps, and then relaxes with a common monoexponential time scale of 2.5 ps. The similarity between this time constant and that of cooling in vacuum suggests the continued importance of carrier–phonon interactions. Adsorbed O₂ was found to have the strongest influence on charge dynamics is graphene, with the negative photoconductivity almost an order of magnitude greater than the induced absorption under vacuum. A negative transient absorption, such as we observe, may be attributed to either stimulated emission in the samples or a bleaching effect. To understand more about the origin of the negative photoconductivity it is informative to consider the photoconductivity spectra at a fixed time after photoexcitation.

Figure 4.6 shows the photoconductivity in all four atmosphere types at 2 ps after photoexcitation ($t_2 = 2$ ps). The spectrum of graphene in vacuum reveals a relatively flat and positive real part of photoconductivity, in stark contrast to the strongly negative (real) photoconductivity seen for gas-absorbed graphene. Furthermore the spectral photoconductivity of graphene samples in the presence of N₂, air and O₂ can be seen to exhibit a Lorentzian form,

$$\sigma_{\text{Lorentz}} \propto \frac{i\omega}{\omega^2 - \omega_0^2 + i\omega\Gamma}, \quad (4.3)$$

where Γ is the linewidth, and ω_0 is the resonant frequency. The solid lines in Figure 4.6 represent a least square fit of Eq. 4.5 to the experimental data. The fitted resonant frequency for graphene in air and N₂ was found to be $\omega_0 \sim 1.8$ THz, compared with $\omega_0 \sim 2$ THz for graphene in an O₂ environment. The resonance in all gas types is spectrally very broad; the fitted linewidth was $\Gamma \approx 10$ THz, independent of the gas type. The Lorentzian fit begins to deviate from the measured photoconductivity at low frequencies. The deviation is most noticeable for O₂-exposed graphene (Figure 4.6d). The non-zero value of $\text{Re}(\Delta\sigma)$ evident in the data at low frequency suggests an

underlying Drude-like response, however inclusion of a Drude term does not enhance the fit within our observable bandwidth, so has been neglected. In contrast, the photoinduced absorption in vacuum leads to a small, positive, spectrally flat real conductivity, with a non-negligible imaginary part.

A negative transient absorption signal with a Lorentzian lineshape is characteristic of stimulated emission. Hence, our data provide evidence that stimulated emission of terahertz photons is occurring in photoexcited graphene in the presence of atmospheric gases. Theoretical studies have predicted amplified stimulated emission of terahertz radiation from sufficiently intensely photoexcited graphene^[107]. The proposed mechanism is that after photoexcitation, the charge carriers relax and populate states around the Dirac point, from where they can radiatively recombine. Thus terahertz emission over a large spectral range is expected to be possible^[107]. Whilst our measurements do not show amplification of the terahertz probe (losses are still greater than gain), stimulated terahertz emission, below the gain threshold is consistent with our observations.

4.4.3 Fluence dependence of photoconductivity

Using optically excited terahertz spectroscopy, we observed a Lorentzian type photoconductivity, in contrast to the Drude photoconductivity measured by previous authors. One explanation of a Lorentzian photoconductivity in other materials is the photoexcitation of plasmons^[159]. In order to investigate the possibility of a plasmon induced photoconductivity, we repeated the measurements at one tenth of the pump beam fluence, $18 \mu\text{J}/\text{cm}^2$ as opposed to $180 \mu\text{J}/\text{cm}^2$ used previously.

In plasmonic systems, the Lorentzian peak frequency, ω_0 , is dependent upon carrier density, n . In graphene, $\omega_0 \propto n^{1/4}$, due to the nature of the two-dimensional Dirac carriers^[111]. As the photoexcited carrier density is related to the pump fluence, a reduction in pump fluence would be expected to lower the frequency of the plasmon

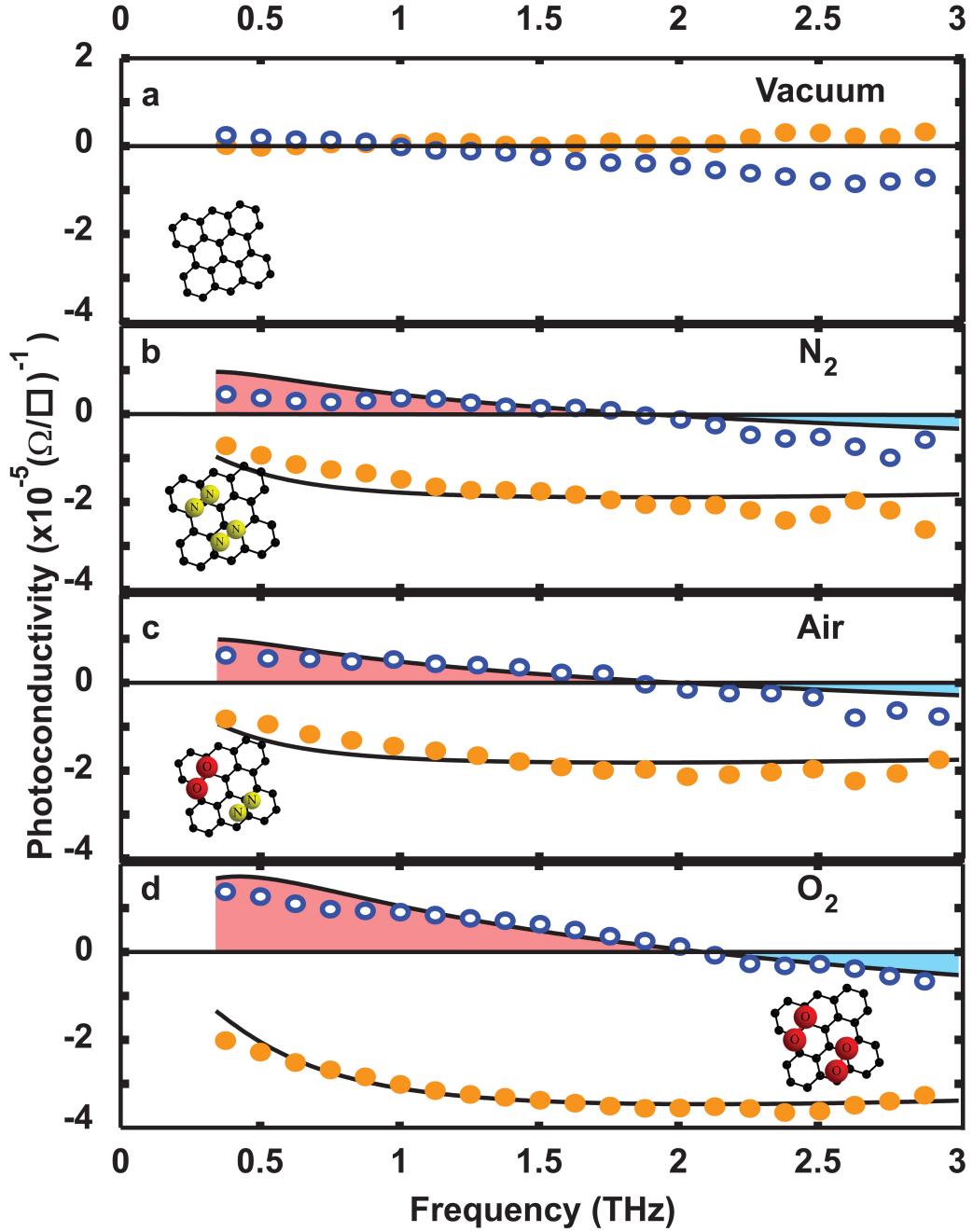


Figure 4.6: **a-d** Photoconductivity in vacuum (**a**), N_2 (**b**), air (**c**) and O_2 (**d**), taken at 2 ps after photoexcitation by the optical pump. Solid orange dots show the real part of the photoconductivity, hollow blue dots show the imaginary part. The solid black line in **b-d** is a Lorentzian model fit to the conductivity data, demonstrating the Lorentzian form of the photoconductivity in gaseous environments. Shading is used to emphasise the change from positive to negative $\text{Im}(\Delta\sigma)$. This point corresponds to the peak Lorentzian frequency, ω_0 .

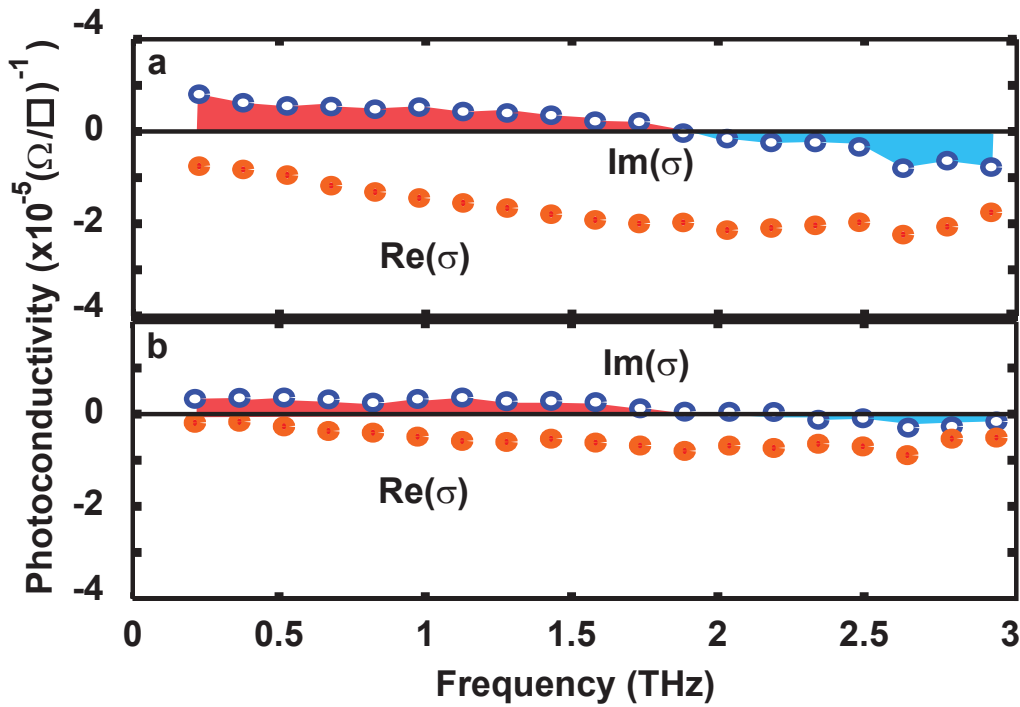


Figure 4.7: Pump fluence dependence of photoconductivity spectra in air. **a** Photoconductivity at 2 ps after photoexcitation by $180 \mu\text{J}/\text{cm}^2$ pump fluence. **b** Photoconductivity at 2 ps after photoexcitation by $18 \mu\text{J}/\text{cm}^2$ pump fluence. Solid orange dots show the real part of the photoconductivity, hollow blue dots show the imaginary part. Shading is used to highlight the change from positive to negative $\text{Im}(\Delta\sigma)$, corresponding to the Lorentzian peak frequency, ω_0 . ω_0 does not change with fluence, suggesting plasmons cannot explain the Lorentzian type photoconductivity.

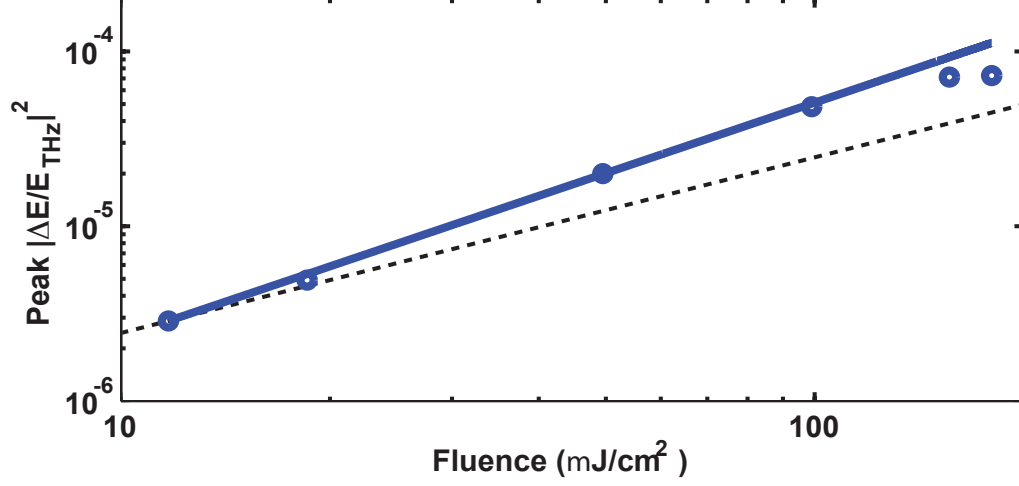


Figure 4.8: Fluence dependence of the maximum pump induced transmission intensity change, measured in air. The broken line represents linear behaviour. From this it is clear that the data are super-linear, suggesting stimulated emission of THz photons. The solid line shows a least squares fit to the data, $|\Delta T/T|^2 \propto (\text{fluence})^{1.34}$.

resonance.

Figure 4.7 shows a comparison of the photoconductivity of graphene in air at 2 ps after photoexcitation by the high and low fluence pump. The lower fluence pump yields a smaller magnitude of photoconductivity, as it photoexcites fewer carriers. However, the Lorentzian peak frequency, ω_0 , does not change with fluence, as would be expected for a plasmon dominated photoconductivity. Thus we conclude that the excitation of plasmons cannot explain our observations.

We further investigated the pump fluence dependence of the negative photoinduced change in conductivity using time domain pump-probe data (such as displayed in Figure 3 of the main paper). Figure 4.8 shows the $|\Delta E/E_{\text{THz}}|^2$, which is proportional to the intensity change in transmitted THz photons, as a function of the visible (800nm) photon fluence incident on a graphene sample in air.

The dashed line illustrates a linear relation while the solid line shows the result of

Species	E_B (kJ mol ⁻¹)	σ	ν (s ⁻¹)	m (g mol ⁻¹)
O ₂	12	1	8×10^{13}	32
N ₂	13	1	5×10^{10}	28
H ₂ O	46	1	9×10^{14}	18

Table 4.1: Parameters used for Langmuir isotherm calculations, taken from Ref. 161.

a power law fit, $|\Delta T/T|^2 = A(\text{fluence})^\alpha$. Best agreement with data was obtained for $\alpha = 1.34$, in accordance with slightly superlinear behaviour. This behaviour may for example arise from an enhanced density of states available for stimulated downward transitions in the spectral range of the THz pulse with increasing visible pump fluence.

4.5 Surface coverage calculations

For the discussion of the THz results in the following section, it is useful to know the coverage of the adsorbates on the graphene surface at the pressures used in the measurements. Simple Langmuir adsorption theory may be used to estimate the coverage of the surface of graphene with gas molecules. In Langmuir theory the fractional coverage of a surface with adsorbed gas molecules is

$$\Theta(p, T) = \frac{bp}{1 + bp}, \quad (4.4)$$

where

$$b = \frac{\sigma}{\nu N_0 \sqrt{2\pi m k_B T}} \exp\left(\frac{E_B}{k_B T}\right). \quad (4.5)$$

Here, E_B is the adsorption enthalpy, σ is the steric factor, ν is the Arrhenius factor for desorption, N_0 is the adsorption site density and m is the mass of the adsorbant [160].

The parameters used in the calculation are taken from literature values for graphite and are listed in Table 4.1. For room air at a pressure of 10^{-5} mbar the calculated coverage of graphene with adsorbed gases is negligible: $\Theta_{\text{N}_2} = 8 \times 10^{-9}$, $\Theta_{\text{O}_2} = 8 \times 10^{-13}$, $\Theta_{\text{H}_2\text{O}} = 4 \times 10^{-9}$.

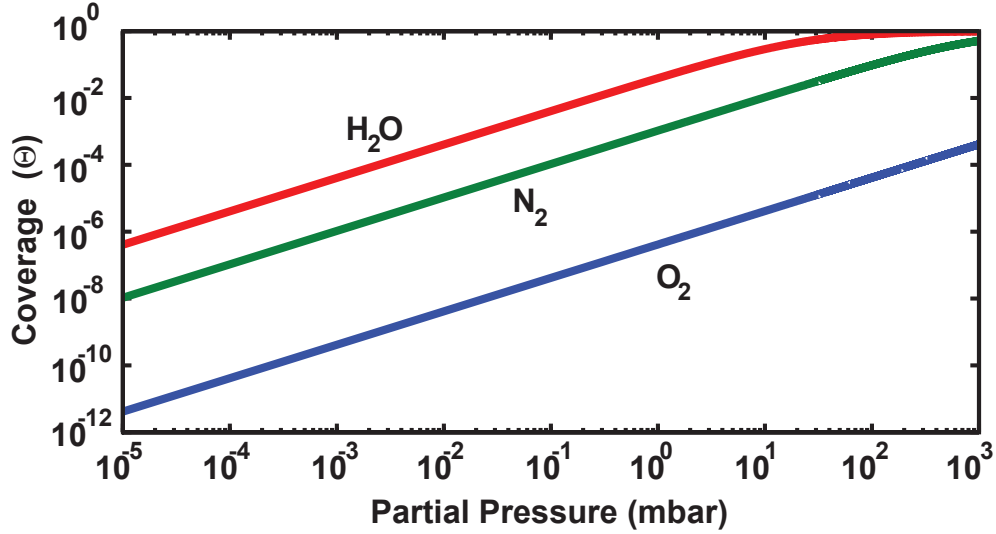


Figure 4.9: Surface coverage, Θ , of graphene with atmospheric gases. Calculated as a function of pressure using Langmuir theory. Temperature T was set to 300 K, and the other parameters were taken from Ref.161 and are summarised in Table 4.1.

Figure 4.9 shows the calculated fractional coverage Θ of the surface of graphene with N_2 , O_2 and H_2O molecules over the pressure range used in the experiments. At 1 atmosphere pressure of N_2 and O_2 the coverages are calculated to be $\Theta_{\text{N}_2} = 0.51$ and $\Theta_{\text{O}_2} = 4 \times 10^{-4}$ respectively.

4.6 Discussion

We now consider the mechanism for the dramatic changes of photoconductivity in graphene under the different gas environments. The ability to “reset” the effects of

gas exposure by placing the graphene samples in vacuum for two hours (at room temperature) suggests that the gas molecules are physisorbed rather than chemisorbed to the graphene surface. Physisorption of O_2 and N_2 on graphene could act as a dopant ^[154], lead to the opening of a small bandgap at the Dirac point ^[162,163], and/or lead to a modification of the density of states ^[164,165]. Hall measurements (see Section 4.3.1) showed only 3% changes in the Fermi level after gas adsorption, indicating that doping alone is unlikely to account for the huge change in photoconductivity we observe. The opening of a ~ 8 meV bandgap upon gas adsorption, and associated increase in the density of electron and hole states near the band extrema would be consistent with our observations. In this case, electrons injected into the conduction band by 800 nm (1.55 eV) photoexcitation would relax rapidly to near the band minimum via phonon mediated processes, as shown on the inset of Figure 4.5. Recombination for the photoinjected electrons across the bandgap with a sea of holes would lead to the observed stimulated emission signal. The spectral broadness ($\Gamma \approx 10$ THz) of the observed transition may then be explained by a combination of the following factors: a high interband transition rate (lifetime broadening), fast dephasing via electron-electron interactions and a cooling bottleneck below the optical phonon energies. However full *ab-initio* calculations would be required to confirm the exact mechanism. Note that since CVD graphene is heavily p-doped, the opening of a bandgap is not directly observable by terahertz transmission spectroscopy, as there are no electrons near the band gap to be excited by the low energy terahertz photons (see Section 4.4.1 and inset of Figure 4.5).

The adsorption of molecules on graphene would locally open a bandgap and hence alter the otherwise linear density of states ($g(\varepsilon)$) of the graphene, thereby increasing $g(\varepsilon)$ at the top of the valance band and bottom of the conduction band (see inset of Figure 4.5) ^[165]. However, a gap would only be opened in regions around adsorbed gas molecules, creating islands of semiconducting graphene amongst the unaltered, gap-

less graphene (see Section 4.5 for Langmuir coverage calculations). As the terahertz probe is much larger than these puddles, the observed photoconductivity behaviour is the result of an interaction with of both types of graphene. Increased stimulated emission will therefore be observed if gas molecules are more effectively adsorbed on the surface, thus creating a higher proportion of semiconducting material. Of the gases used in this study, O_2 is most likely to interact with graphene ^[166,167], which is consistent with the increased negative photoconductivity signal observed in pure O_2 compared with air and N_2 .

There are a number of other possible explanations for a Lorentzian photoconductivity in graphene. A positive Lorentzian conductivity may originate from the excitation of plasmons ^[159]. Terahertz surface plasmons have been predicted theoretically ^[109,110], and recently observed in spatially confined graphene ^[111]. However, the peak frequency of a plasmon dependent conductivity varies with carrier concentration as $\omega_0 \propto n^{1/4}$ ^[111] and $\text{Re}(\Delta\sigma)$ is expected to be positive, in contrast to our experiments. Figure 4.4 demonstrates that our measured ω_0 does not decrease with time after photoexcitation, and hence is independent of photoexcited carrier concentration. Additional measurements showed ω_0 to be independent of pump fluence (see Section 4.4.3). Thus it is unlikely that excitation of plasmons explains the Lorentzian response. A negative photoconductivity may also be attributed to a photo-induced reduction in conductivity, for example by an increase in the carrier-carrier or carrier-phonon (intraband) scattering rates. However it is not clear why such mechanisms would produce a Lorentzian form, or occur only in gas adsorbed graphene. Finally, ground-state bleaching could lead to a negative photoconductivity with Lorentzian form, however the states associated with the absorption of (1.55 eV) optical photons in graphene are well separated from the states near the Dirac point that are associated with interband terahertz absorption and emission (see the inset of Figure 4.5). We therefore conclude that the opening of a small band gap in the presence of adsorbed

gas molecules is the most likely explanation for our measurements.

4.7 Conclusion

In summary, we have used terahertz time domain spectroscopy to noninvasively probe photoexcited carrier dynamics in CVD grown graphene. We have observed that gas adsorption can dramatically alter the high frequency electrical response of graphene sheets. We also provide experimental evidence for stimulated emission of terahertz photons in graphene. Furthermore our results demonstrate the huge influence environmental factors can exert on the behaviour of hot carriers in CVD graphene, and highlight the importance of consideration of such factors for future CVD graphene opto-electronic devices.

After the completion of this study, several other authors reported optical-pump THz-probe measurements of CVD-grown graphene ^[104–106,168]. Only photo-induced bleaching of THz conductivity was observed in these studies, rather than the gas induced change observed here, and in contrast to the pure photoinduced absorption increase observed in non-CVD graphene.

Frenzel *et al.* and Jnawali *et al.* both used THz spectrometers similar to that used in this Chapter, photoexciting CVD-grown graphene with an 800 nm pump and probing the change in conductivity with a THz probe ^[104,105]. Both authors observed a negative photoconductivity, similar to the case of graphene in this chapter when in a gaseous environment. However, they did not observe an environment dependent response. In contrast to the stimulated emission argument employed to explain the results in this Chapter, these authors argued the negative photoconductivity was by an increase in scattering rate of carriers. The enlarged phase space for scattering at the high temperatures electrons are excited to, combined with the high number of phonons, can result in increased electron-phonon scattering. If the effect of increased scattering outweighs the increased conductivity due to increased carrier number (the

Drude weight), the free carrier conductivity can be suppressed, resulting in a negative photoconductivity.

In an attempt to explain the difference between studies resulting in a positive photoconductivity, and those finding a negative photoconductivity, Shi *et al.* used a back gate to alter the doping level in graphene during THz measurements ^[168]. They found that the sign of the photoconductivity could be modulated by changing the Fermi level of the sample. When highly doped, the change in Drude weight due to photoexcitation is much less than the change in scattering rate, leading to a negative photoconductivity. Conversely, with minimal doping, the increased carrier density due to photoexcitation yields a positive photoconductivity.

To use this model to explain the data in this chapter, a large shift in carrier concentration between vacuum and gas measurements would be required. Such a change was not observed by the Hall measurements performed here, suggesting that the model does not explain the gas induced negative photoconductivity. Furthermore, where photoconductivity spectra are presented in these later works, they do not match the Lorentzian form presented in this Chapter, and fluence dependent measurements show sub-linear behaviour, in contrast to the super-linear behaviour observed in this Chapter. Therefore, these later works do not necessarily show the same process as was observed here.

Preliminary theoretical work has suggested that the presence of water vapour trapped between the graphene sheet and quartz substrate could enhance the effect of gaseous adsorbates. Future experimental work will focus on removing this trapped water vapour, to determine any effect it has on the THz photoconductivity, and to attempt to resolve the differences between the work in this Chapter and that of other authors.

Chapter 5

Ultrafast transient terahertz conductivity of CVD-grown MoS₂ and WSe₂

Ultrafast charge carrier dynamics in monolayers and trilayers of the transition metal dichalcogenides MoS₂ and WSe₂ were measured using a combination of time resolved photoluminescence and terahertz spectroscopy. A photoconductivity and photoluminescence response time of just 350 fs was recorded from CVD-grown monolayer MoS₂, and 1 ps from trilayer MoS₂ and monolayer WSe₂. The results indicate the potential of these materials as high-speed optoelectronic materials.

5.1 Introduction

For the last three decades, technological advances towards terahertz speed electronic and opto-electronic devices have relied on the staple materials of low-temperature grown gallium arsenide (LT-GaAs) and ion implanted semiconductors ^[169–173]. The emergence of new two-dimensional materials ^[174], however, offers the prospect of novel, cheap materials for high speed applications.

Transition metal dichalcogenides (TMDs) consist of transition metal atoms covalently bonded to chalcogens (S, Se or Te) to form atomic trilayers.^[1, 7, 117, 175] The trilayers stack via weak van der Waals interactions to form a 3-dimensional solid. TMDs have the potential to become the building blocks of a wide range of future electronic device as they act as semiconductors, semi-metal or metals depending on the choice of transition metal ^[7].

Molybdenum disulphide (MoS₂) and tungsten diselenide (WSe₂) are semiconducting TMDs that have been well studied^[7, 117, 118] in their *multilayer* (3D) form. MoS₂ is extensively used in industry as a dry lubricant^[176] and as a catalyst for the hydrodesulphurisation of petroleum ^[177]. Only recently has truly *monolayer* (2D) MoS₂ been experimentally realised, exposing a wealth of new photophysics.^[119, 174, 178–181] For instance, while MoS₂ is an indirect bandgap semiconductor in the bulk (multilayer) form, it has a direct bandgap as a monolayer and thus exhibits greatly enhanced photoluminescence yield. ^[119, 178] Furthermore negative trions, which are quasiparticles consisting of two electrons and a hole, have been discovered in monolayer MoS₂.^[127, 182]

As a result of these discoveries, MoS₂ is already showing promise for use in electronic and photonic devices ^[1], such as field effect transistors^[6, 19, 174, 183–185], photodiodes^[186] and memory applications ^[187], however future exploitation requires a better understanding of its optical and electrical properties. In particular the mechanisms responsible for a relatively low electron mobility in MoS₂ is currently a matter of debate^[188–190].

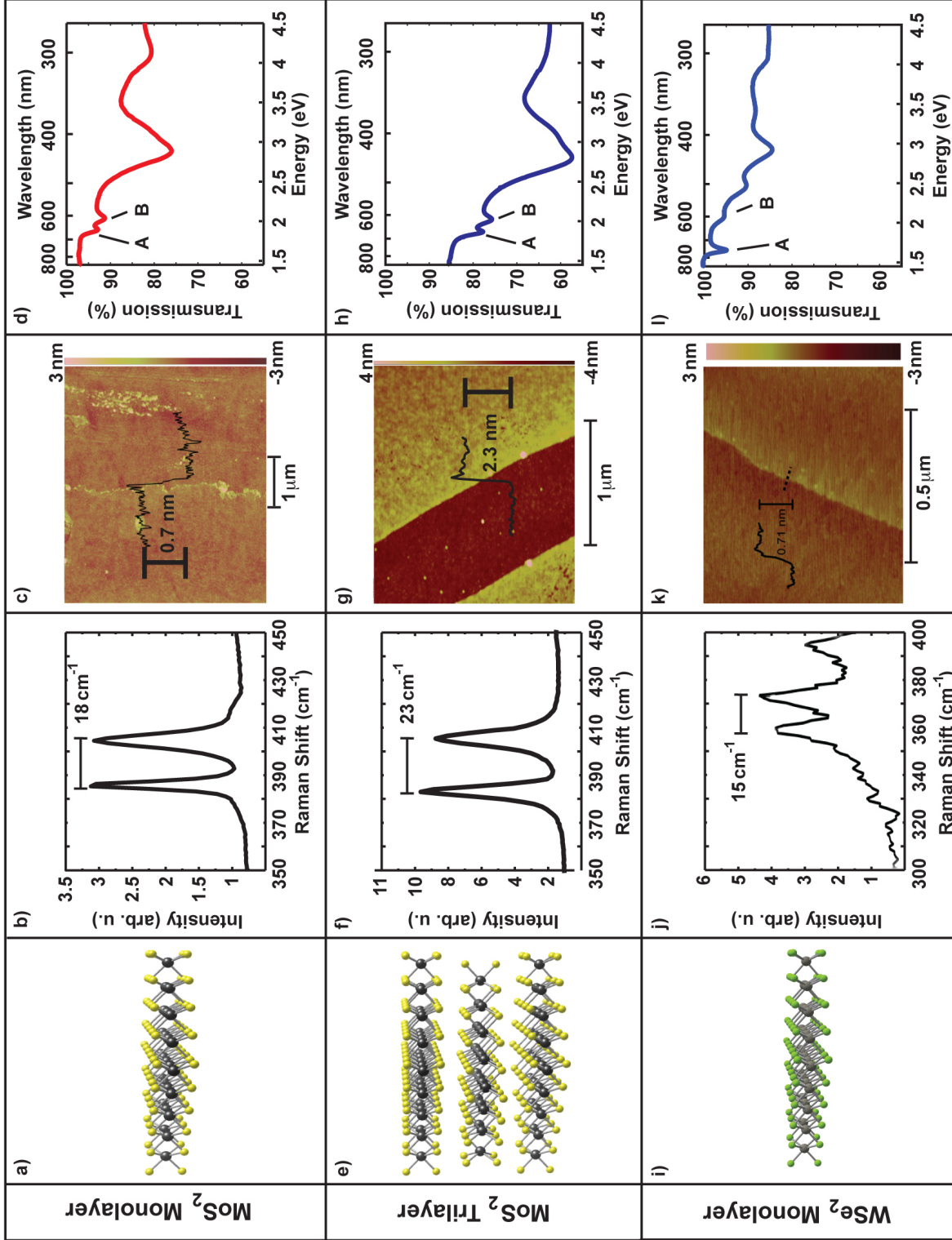


Figure 5.1: Characterisation of mono- (a-d) and trilayer (e-h) samples. (b), (f) Raman spectroscopy of the samples. (c), (g) AFM height profiles are overlaid at the position they were taken. The step heights again confirm the layer number of the samples. Height profiles are overlaid at the position they were taken. The step heights again confirm the layer number of the samples. Absorption features associated with the 'A' and 'B' excitons are labelled.

More recently, a second monolayer TMD has been isolated. Tungsten diselenide (WSe₂) shows many similar properties to MoS₂, becoming a direct gap semiconductor in its monolayer form, and exhibiting trions^[128]. However, there have been few studies on the photophysics of WSe₂^[128, 191].

Most studies and devices reported to date have used mechanically exfoliated MoS₂ and WSe₂, using the “scotch tape” method pioneered in early graphene research^[3, 37, 126, 192]. Unfortunately this method of producing mono-layers of layered materials is not well suited to large-scale industrial production. Recently, MoS₂ and WSe₂ have been produced using chemical vapour deposition (CVD)^[120–123]. This bottom-up technique is compatible with current commercial production technologies and is also the method currently favoured for the production of graphene^[150].

Previous time-resolved photophysical studies of MoS₂ have used photoluminescence (PL) spectroscopy^[130], electroluminescence^[193], optical pump–probe spectroscopy^[131] and transient absorption^[132] to investigate exciton dynamics in mechanically exfoliated few- and mono-layer MoS₂. These studies generally observed a relaxation of photoexcited species on two distinct timescales: a fast, few picosecond decay followed by a slower component on the scale of several tens of picoseconds. However, these studies were not able to probe directly the conductive species that are of interest for opto-electronic devices. To our knowledge, no time resolved studies of monolayer WSe₂ have so far been published.

Here, we present studies of monolayer and trilayer CVD-grown MoS₂ and WSe₂ using terahertz time domain spectroscopy (THz TDS) and PL spectroscopy. Together, these techniques allowed us to observe the behaviour of free carriers and excitons in photoexcited MoS₂. We observed a photoconductivity response in CVD-grown MoS₂ of just 350 fs. Such an ultrafast response time is particularly promising for the future use of TMDs in high-speed (> 1 THz) photodetectors, emitters and transistors. The possibility of tuning the conductivity lifetime in MoS₂ via substrate interactions and

film thickness offers the option of producing cost-effective optoelectronic materials with tuneable charge carrier lifetimes. Further measurements suggest the observation of trions in monolayer MoS₂ and WSe₂.

5.2 Growth and characterisation

Predominantly Monolayer and trilayer MoS₂ films were grown directly onto sapphire substrates. Briefly, (0001)-oriented sapphire substrates (Tera Xtal technology Corp.) were cleaned with a H₂SO₄/H₂O₂ (70:30) solution at 100°C for 1 hour. For *monolayer* growth, the substrate was then placed at the centre of a 2-inch tubular furnace on a quartz holder. Precursors of 0.3 g MoO₃ (Sigma-Aldrich, 99.5%) in an Al₂O₃ crucible and S powder (Sigma-Aldrich, 99.5%) were placed at an upstream position in the reaction chamber. The furnace was first heated to 150°C and annealed for 30 minutes with 70 sccm of Ar at 10 torr, followed by heating at 650°C for 10 minutes. The furnace was subsequently cooled slowly to room temperature. *Trilayers* were grown by a two-step thermolysis of the precursor (NH₄)₂MoS₄ [122]. The sapphire substrate was immersed in a solution of the (NH₄)₂MoS₄ precursor dissolved in 20 mL of dimethylformamide. The substrate was slowly removed from the solution, leaving a thin (NH₄)₂MoS₄ film, and baked at 120°C for 30 minutes. A two-step annealing process was performed to transform the precursor film to trilayer MoS₂.

Monolayer WSe₂ was prepared similarly on sapphire substrates. WO₃ powders (0.3 g) were heated to 925°C at a ramping rate of 25°C/min with Se powder in the furnace. The sapphire substrates were put at the downstream side, where the Se and WO₃ vapours were delivered by an Ar/H₂ flowing gas (Ar = 80 sccm, H₂ = 20 sccm, chamber pressure = 1 Torr). After reaching 925°C, the heating zone was kept for 15 min and the furnace was then naturally cooled to room temperature. Additional details about the growth methodologies may be found in References 120–123.

The number of layers in each sample was determined by Raman spectroscopy and

atomic force microscopy (AFM). Figure 5.1 (b) and (f) show the Raman spectra of the monolayer and trilayer samples respectively. The splitting between the E_{2G}^1 and A_{1G} peaks in the Raman spectrum of the monolayer (trilayer) MoS₂ was 18 cm⁻¹ (23 cm⁻¹), which is indicative of predominantly single (tri) layer growth [194]. The AFM images of intentionally scratched samples are presented in Figure 5.1 (c),(g) and (j). They show step heights of 0.7 nm, 2.3 nm and 0.73 nm, which confirm that the samples consist of monolayer MoS₂, trilayer MoS₂, and monolayer WSe₂ respectively. Figures 5.1 (d) and (h) show the optical transmission spectra of monolayer and trilayer MoS₂. The two absorption features at 1.89 eV and 2.04 eV are characteristic of MoS₂ and are known as the ‘A’ and ‘B’ excitons. Similarly, the features at 1.65 eV and 2.06 eV of Figure 5.1 (l) correspond to the ‘A’ and ‘B’ excitons of WSe₂.

It should be noted that growth, Raman spectroscopy and AFM imaging were performed by the group of Lance Li, at the Institute of Atomic and Molecular Sciences, Academia Sinica, Taiwan.

5.3 Photoluminescence and THz photoconductivity measurements

We used a combination of photoluminescence (PL) and THz conductivity spectroscopy to observe the dynamics of photoexcited charge species in the samples. Here we use the term “charge species” to refer to free electrons and holes as well as correlation between charges such as excitons, charged excitons (trions) and plasmons. PL is sensitive only to the subset of photo-injected charge species that recombine radiatively. In contrast THz conductivity spectroscopy is sensitive to any conductive or polarisable charge species independent of whether the excitation relaxes radiatively or non-radiatively^[10]. Furthermore, THz spectra can be used to identify types of charge species and how they evolve on a picosecond time scales. For example excitons, plasmons and free charges have distinct spectral signatures at THz frequencies.^[8]

Therefore, together time-resolved PL and THz spectroscopy allow complicated charge dynamics involving more than one type of charge species to be interpreted.

The optical pump THz probe spectrometer (OPTPS) described in Chapter 2 was used to measure the photoconductivity $\Delta\sigma(t, \nu)$ of MoS₂ and WSe₂ as a function of frequency ν and time t after photoexcitation. Samples were photoexcited by 35 fs laser pulses (typical fluence 175 $\mu\text{J}/\text{cm}^2$) at selected wavelengths using an optical parametric amplifier, or by frequency doubling pulses in a 0.2 mm-thick Type I BBO crystal. Photoluminescence measurements were carried out using an 80 MHz 100 fs pulsed Ti:Sapphire excitation source. Time-resolved photoluminescence was measured using photoluminescence up-conversion spectroscopy as described in Reference 195. All measurements reported here were performed in vacuum ($< 10^{-3}$ mbar) at room temperature. Photoluminescence measurements were performed by Patrick Parkinson.

5.3.1 Monolayer MoS₂

Figure 5.2a shows the photoluminescence arising from monolayer MoS₂ as a function of time after photoexcitation with 3.0 eV photons. The energy of the absorbed photons are significantly above the MoS₂ bandgap and hence should photoinject electron-hole pairs with significant kinetic energy (i.e. “hot” carriers). Overlaid on this graph is the THz photoconductivity $\Delta\sigma(t)$ of the same sample as a function of time after photoexcitation with similar energy (3.1 eV) photons. The pump fluence dependence of this photoexcitation is linear, as shown in Figure 5.3.

Photoexcitation of the sample leads to a sharp (instrument response limited) rise in both THz photoconductivity and PL emission followed by an ultrashort 350 fs exponential decay of both signals. An exponential decay suggests carrier trapping, rather than bimolecular decay. Over the next 10 ps the PL signal disappears, in contrast to a significant persistent THz photoconductivity signal. The quenching of PL emission in combination with a persistent photoconductivity is indicative of

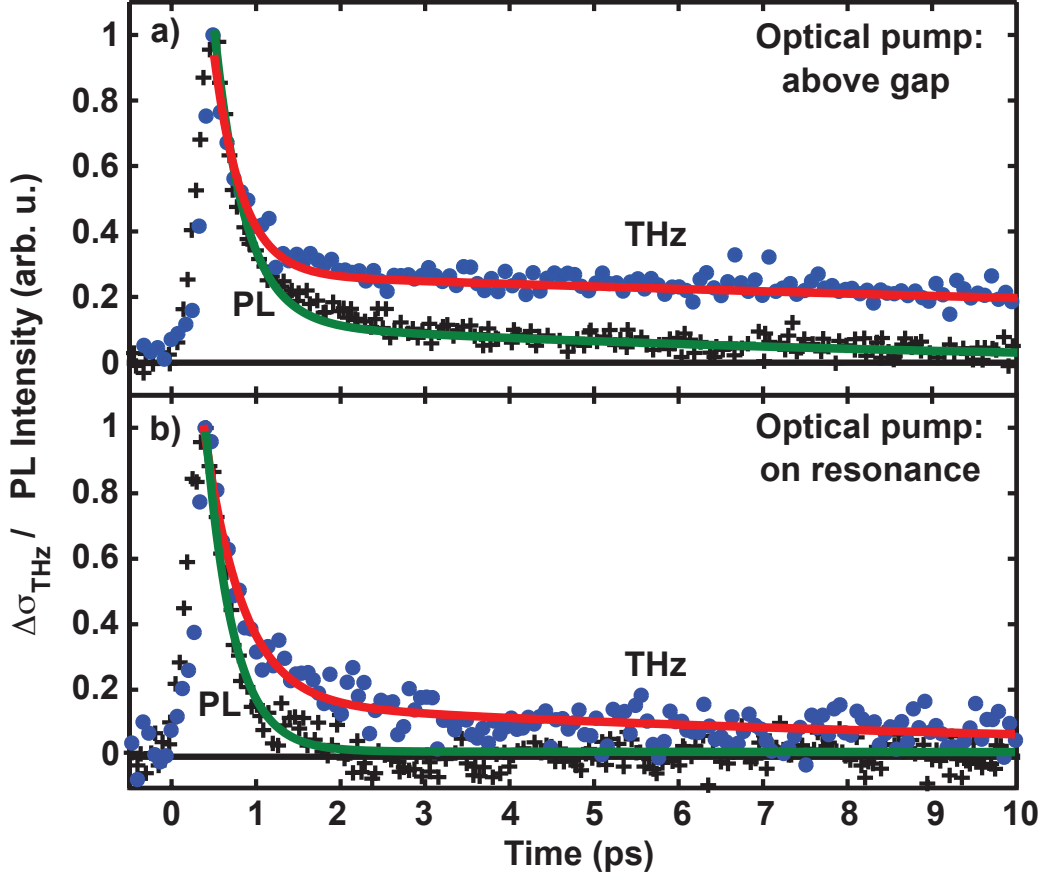


Figure 5.2: Photodynamics of monolayer MoS_2 measured by optical pump–THz probe spectroscopy and PL upconversion spectroscopy. **a)** Normalised THz photoconductivity, $\Delta\sigma$ as a function of time after photoexcitation by 3.1 eV photons, blue pump pulse (blue circles), and the normalised PL emission as a function of time after photoexcitation by 3 eV photons, measured at 1.86 eV (black full circles) of monolayer MoS_2 . Solid lines are biexponential fits to the data, parameters are given in Table 5.1. **b)** Similar THz (blue circles) and PL (black full circles) measurements following photoexcitation on resonance with the direct gap excitons (1.9 eV for THz and 2.1 eV for PL).

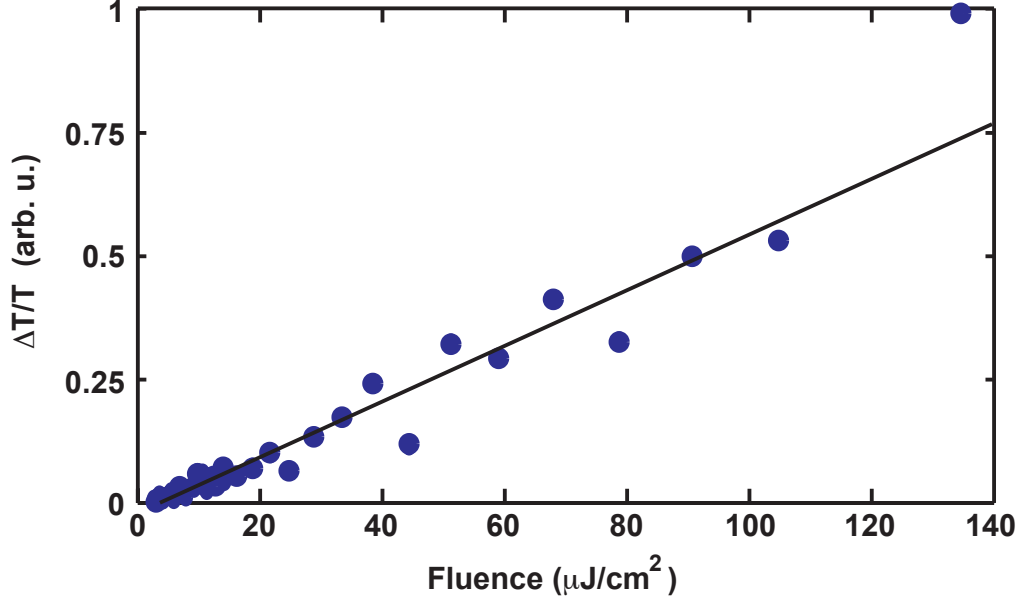


Figure 5.3: Fluence dependence of the peak pump induced THz transmission intensity change, $\Delta T/T$. Measured on monolayer MoS_2 using 3 eV (400 nm) photons. The solid black line is a least squares fit to the data, showing the linear relationship between fluence and transmission intensity change.

Table 5.1: Biexponential decay time constants and relative weightings for pump-probe and PL measurements.

	THz Photoconductivity			PL
	MoS_2 Tri	MoS_2 Mono	WSe_2 Mono	MoS_2 Mono
Above gap	1 ps [90%]	0.33 ps [91%]	1.31 [80%]	0.36 ps [96%]
	24 ps [10%]	33 ps [9%]	13.1 ps [20%]	8.6 ps [4%]
Resonant	0.63 ps [88%]	0.36 ps [95%]	0.861 ps [90%]	0.32 ps [100%]
	10 ps [12%]	35 ps [5%]	15 ps [10%]	—

trapping of one carrier type or the separation of electrons and holes either spatially or in k-space. Parameters for the biexponential fits to these decays, shown as solid lines in Figure 5.2, are given in Table 5.1.

To understand more about the origin of the persistent photoconductivity in monolayer MoS_2 we also resonantly photoexcited the ‘A’ and ‘B’ excitons and recorded the THz conductivity and PL dynamics. Figure 5.2b shows that upon resonant photoexcitation the early-time PL and $\sigma(t)$ dynamics are remarkably similar to the case of above-bandgap photoexcitation. At later times however the persistent photoconduc-

tivity signal is far less pronounced and the PL is quenched even more effectively. Therefore the persistent photoconductivity after excitation with high energy photons is likely to be caused by the photoinjected electrons having enough energy to populate indirect-gap side-valleys.

Together, these results indicate that there is a rapid quenching of both PL and photoconductivity in monolayer MoS₂ within 350 fs photoexcitation. This quenching is independent of whether excitons are created resonantly or a hot electron–hole population is photo-injected into the sample. The fast quenching is likely to be a result of fast surface trapping or surface–substrate interactions for monolayer MoS₂. This conclusion is supported by an observed invariance of exponential decay rates as the fluence was varied, as expected for trap dominated quenching [159]. This can be seen in Figure 5.4, where the normalised photoconductivity of monolayer MoS₂ photoexcited on resonance at two different fluences are compared, demonstrating fluence independent dynamics.

5.3.1.1 Pump energy dependence of THz measurements

For experimental reasons, slightly different pump energies were used for the THz and PL resonant photoexcitation measurements presented above - 1.9 eV for THz and 2.1 eV for PL. However, as Figure 5.5 shows, the THz photodynamics are identical for both 1.9 eV and 2.1 eV, justifying the comparison of the THz and PL data. Figure 5.5 additionally demonstrates that photoexcitation at 1.55 eV, below the band gap of monolayer MoS₂, yields no photoconductivity response. The spectra of all pump beams used in these measurements are shown in Figure 5.6

5.3.2 Monolayer WSe₂

Similar measurements were performed on monolayer WSe₂. The THz photoconductivity of WSe₂ is presented in Figure 5.7. Above gap photoexcitation was provided by a 3 eV pump beam, as for the MoS₂ measurements. For excitation resonant with

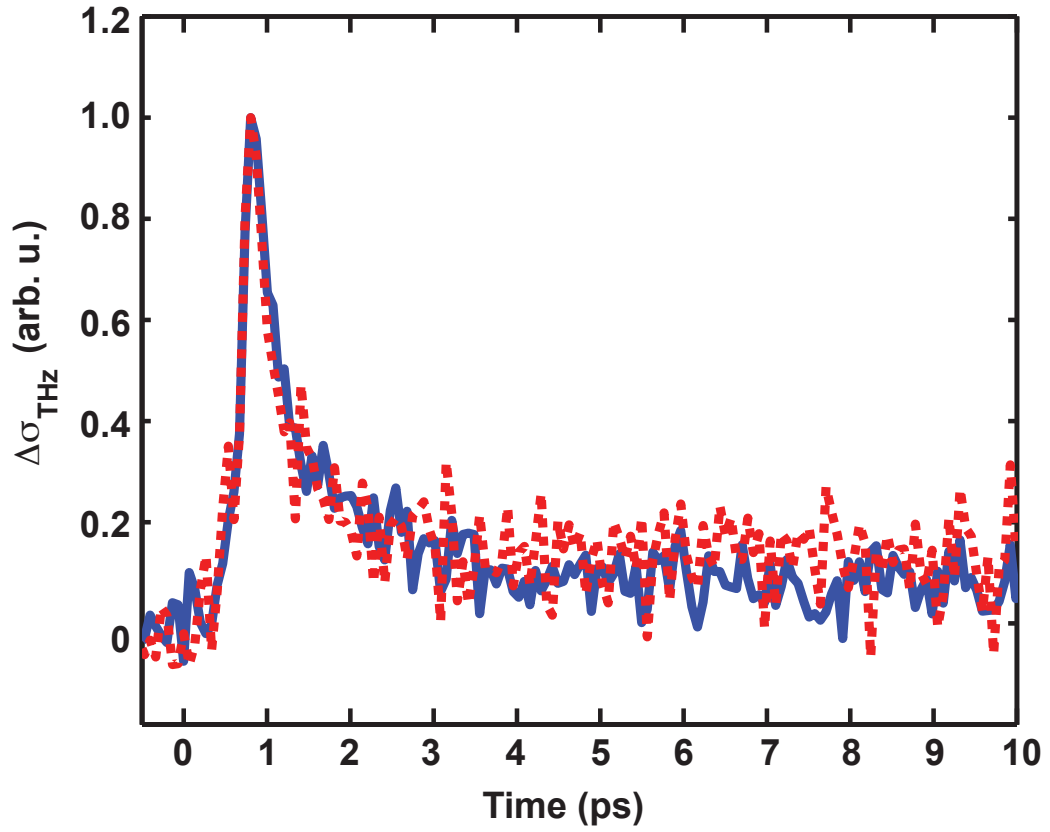


Figure 5.4: Normalised photoconductivity of monolayer MoS_2 photoexcited at 1.9 eV with two different fluences - $175 \mu\text{J}/\text{cm}^2$ (solid blue line) and $87.5 \mu\text{J}/\text{cm}^2$ (i.e. 100% and 50% of the full fluence). The photodynamics overlap exactly, showing the independence of decay dynamics to pump fluence.

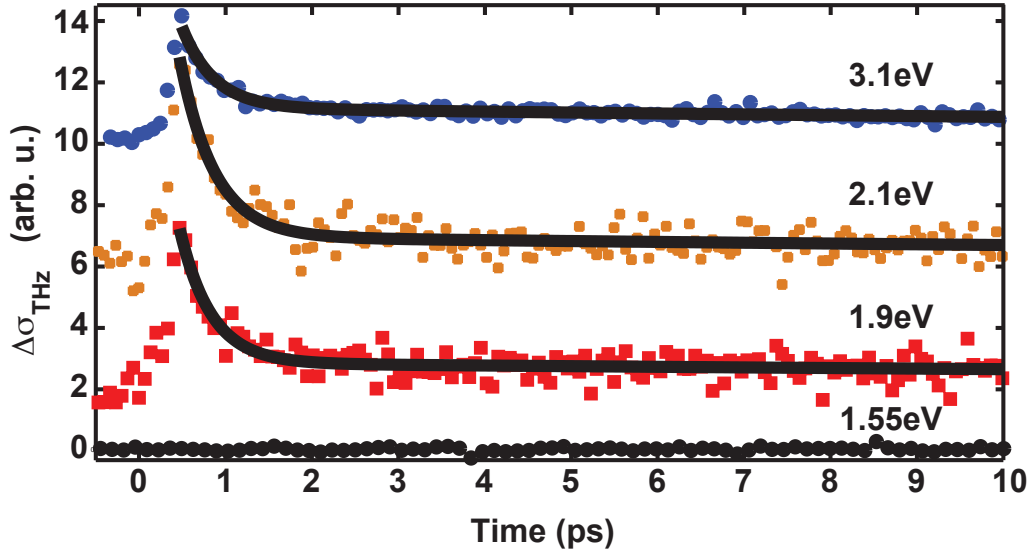


Figure 5.5: Photoinduced THz conductivity, $\Delta\sigma_{\text{THz}}$, of monolayer MoS₂ as a function of time after photoexcitation. Excited with pump beam energies of, from top to bottom, 3.1 eV (400 nm), 2.1 eV (600 nm), 1.9 eV (650 nm) and 1.55 eV (800 nm). The photoexcited dynamics are identical for 2.1 eV and 1.9 eV photoexcitation. The solid lines represent biexponential fits to the data.

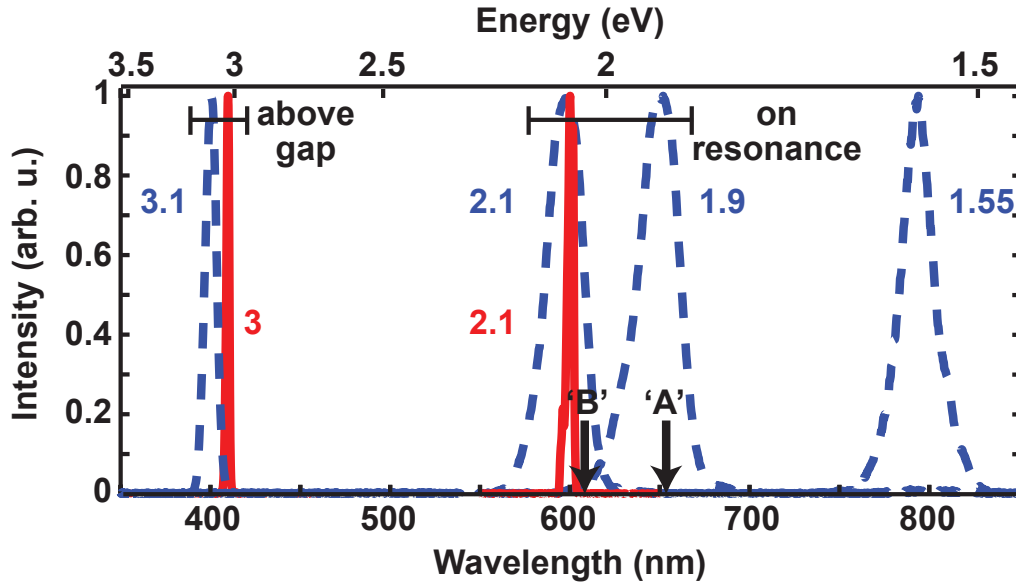


Figure 5.6: Spectra of the pump beams used for THz (blue dotted lines) and PL (red solid lines) measurements. 1.9 eV (650 nm) and 2.1 eV (600 nm) photons were used to photexcite the samples on resonance with the excitons. Above gap energies of 3.1 eV (400 nm) from THz and 3 eV (410 nm) for PL were used for higher energy photoexcitation. Arrows demonstrate the position of the 'A' and 'B' excitons in MoS₂.

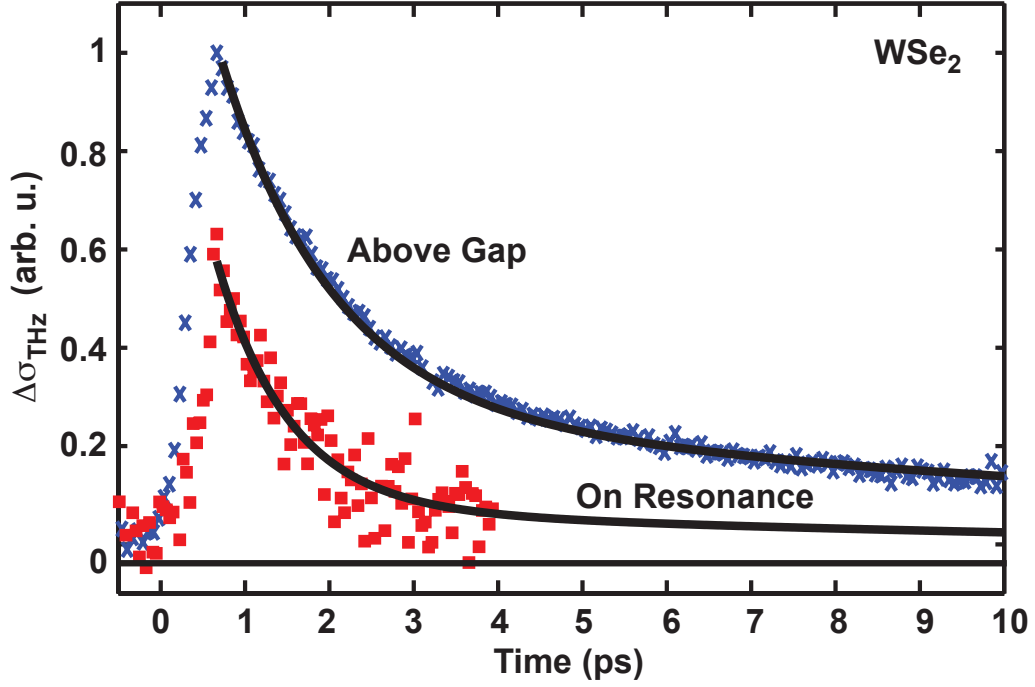


Figure 5.7: Normalised photodynamics of monolayer WSe_2 measured by optical pump–THz probe spectroscopy photoexcited at 1.65 eV, on resonance with the ‘A’ exciton in WSe_2 (squares) and at 3.1 eV (crosses). Solid lines are biexponential fits to the data. Fit parameters are detailed in Table 5.1

the excitons in WSe_2 , however, a lower energy pump of 1.65 eV was used, matching the lower energy of the ‘A’ exciton in WSe_2 compared to that in MoS_2 .

As was observed for MoS_2 , upon photoexcitation of WSe_2 by either pump energy, the THz photoconductivity rises sharply, but with a slower rise time than for MoS_2 (~ 700 fs compared to an instrument limited rise time of 350 fs in MoS_2). The photoconductivity then decays with a fast exponential lifetime of 1 ps followed by a slower fall over ~ 15 ps. For both photoexcitation energies the time constants in WSe_2 are noticeably longer than those in monolayer MoS_2 .

5.3.3 Trilayer MoS_2

In nano-scale materials the influence of surface trapping can be assessed by observing changes in transient photoconductivity as a function of the surface-area-to-volume ra-

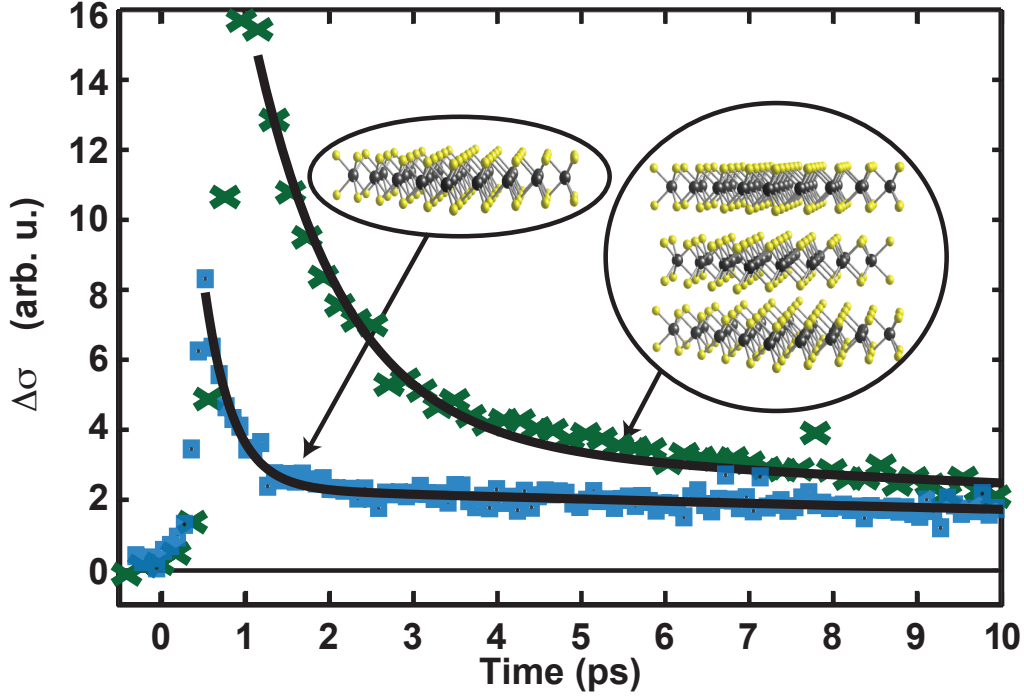


Figure 5.8: Comparison of THz photoconductivity, $\Delta\sigma$, in trilayer (green crosses) and monolayer (blue squares) MoS_2 as a function of time after photoexcitation by 3 eV photons, measured by optical pump–THz probe spectroscopy. Solid lines show biexponential fits to the data. Fit parameters are listed in Table 5.1. Additional reflections due to the thinness of the substrate have been removed from the trilayer data for clarity (see Section 5.3.3.1).

ratio of the sample^[196,197]. We compared the photoconductivity dynamics of *monolayer* MoS_2 with the *trilayer* sample to gauge the importance of the surface-area-to-volume ratio on conductivity dynamics. As can be seen in Figure 5.8 and the biexponential fit parameters displayed in Table 5.1, photoconductivity decays three times slower in the trilayer sample compared with the monolayer MoS_2 . It is notable that even in high-quality bulk crystals of MoS_2 , DC photoconductivity measurements are dominated by surface trapping effects^[198]. Thus for our CVD-grown monolayer sample we expect surface trapping to be the dominant mechanism of ultrafast PL and THz conductivity quenching.

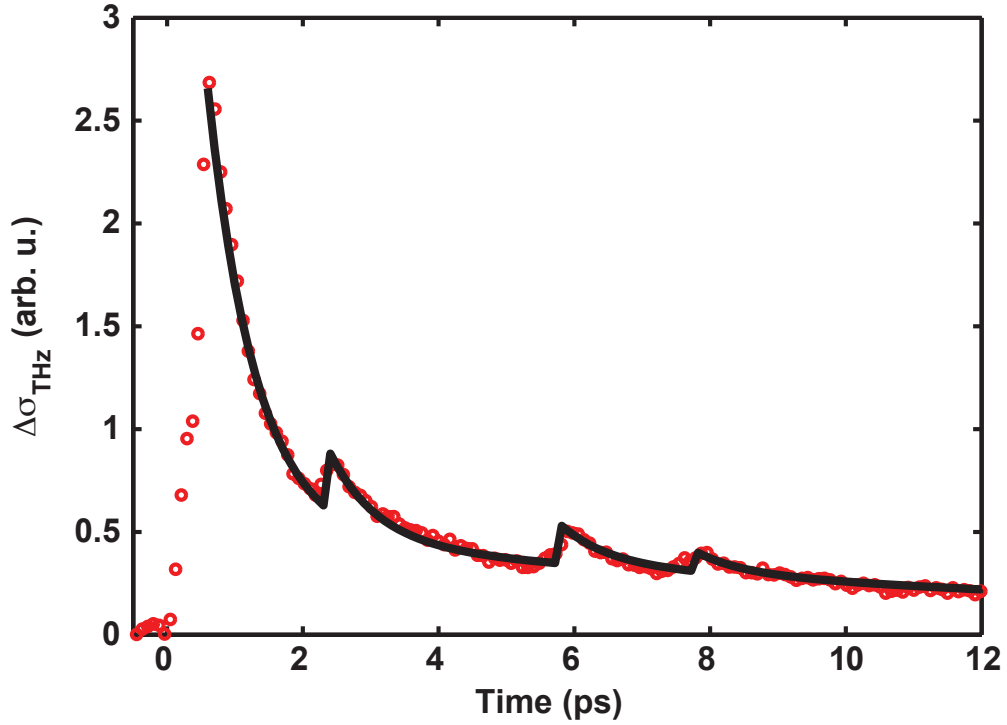


Figure 5.9: Original trilayer optical pump–THz probe data, shown here for 1.9 eV (650 nm) photoexcitation, before removal of reflections from the data. Red dots show the measured data, the solid line is a biexponential model to the data accounting for multiple substrate reflections.

5.3.3.1 Reflections in the trilayer data

Due to the thinness of the sapphire substrate, the optical pulse used in optical pump–THz probe measurements was able to reflect from the far edge of the substrate and re-photoexcite the sample before the signal from the initial excitation had decayed. This manifested itself as additional peaks within the pump–probe data, as can be seen in Figure 5.9. For clarity, these peaks were removed from the data presented in Figure 5.8 by adopting a biexponential decay model with additional terms for subsequent smaller excitations, and then subtracting the subsequent excitation terms from the data. This effect of reflections within the substrate was only observable in the trilayer data, as it is too small an effect to be visible in the smaller $\Delta E_{\text{THz}}/E_{\text{THz}}$ of the monolayer sample.

5.4 THz photoconductivity spectra

Further information can also be gained from the complex THz photoconductivity spectrum, $\Delta\sigma(\omega)$. In Figure 5.10 we present the photoinduced THz conductivity for mono and trilayer MoS₂ taken at 1.5 ps after photoexcitation, and for monolayer WSe₂ at 1 ps after photoexcitation. All three samples display a significant free carrier, Drude type response, suggesting the presence of charge carriers other than neutral excitons. Trilayer MoS₂, however, exhibits noticeably different behaviour to both monolayer MoS₂ and WSe₂. The photoconductivity of trilayer MoS₂ appears to show a resonance far beyond the bandwidth of the experiment, consistent with the behaviour expected from excitons of binding energy ~ 100 meV. In contrast, the monolayer samples show a resonance at ~ 15 meV. The solid lines in Figure 5.10 represent potential models of these data, assuming a sum of Lorentzian oscillators,

$$\sigma_L = \sum_m \frac{C_m i\nu}{\nu^2 - \nu_{0m}^2 + i\nu\gamma_m}, \quad (5.1)$$

where C_m is a spectral weight coefficient, ν_0 is the resonant frequency and γ_m is the linewidth of oscillator m , as discussed in Chapter 4 for fitting to CVD-grown graphene. In contrast to those fits, however, the monolayer samples here required three terms in the sum - one $\nu_0 = 0$ Drude term for free carriers, one high energy resonance outside of the bandwidth of the experiment consistent with the expected exciton binding energy, and one additional term to account for the resonance at ~ 15 meV. The parameters of these fits are displayed in Table 5.2.

Recently trions, quasiparticles consisting of two electrons and a hole or two holes and an electron, have been observed in PL spectra from MoS₂ and WSe₂ with binding energies of 18 meV and 24 meV respectively ^[127,128]. The similarity of these values to the monolayer resonance energies suggests the direct observation of trions in the monolayer samples. However, the signal to noise ratio in the spectrum is not high

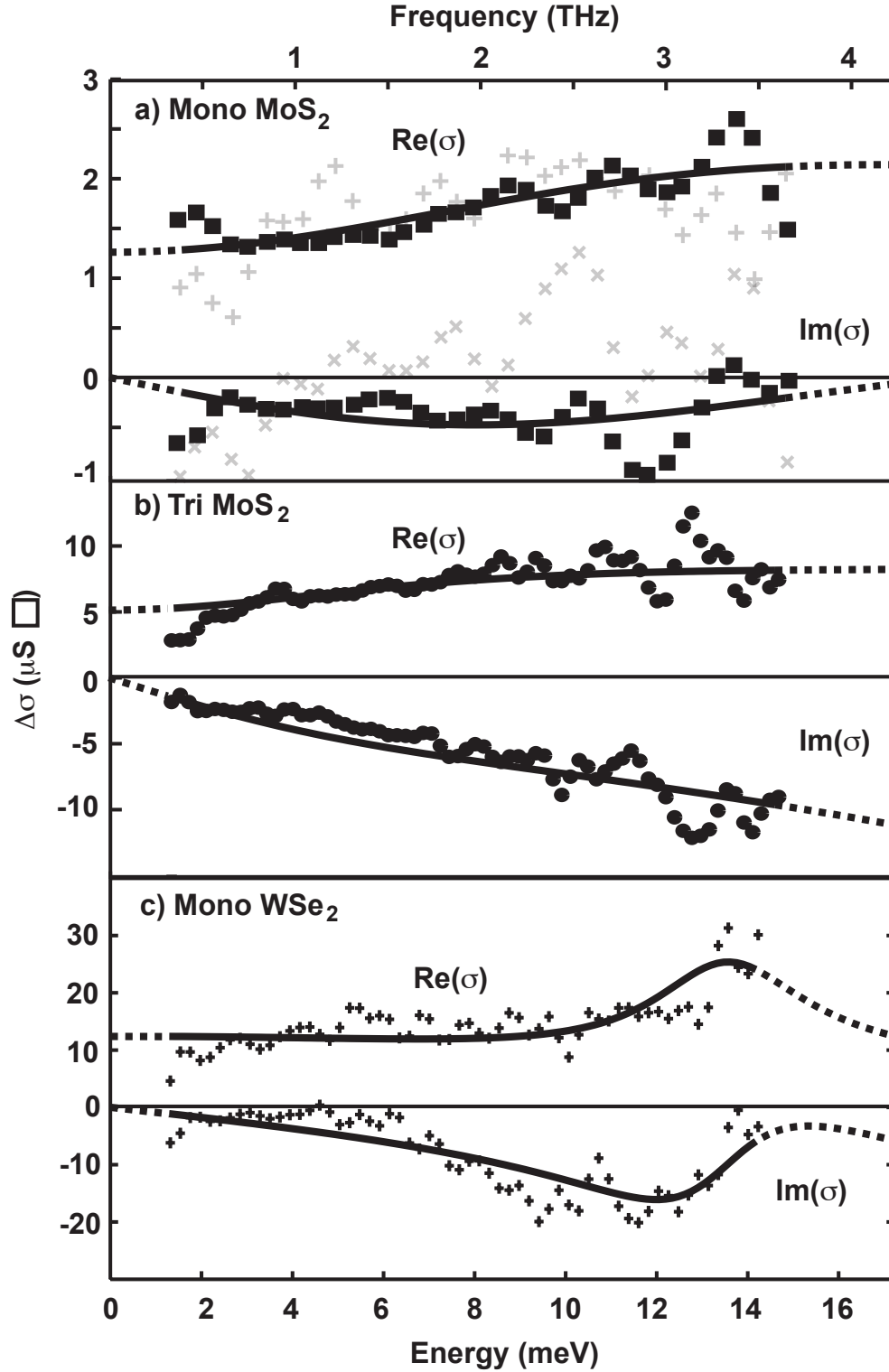


Figure 5.10: THz complex photoconductivity spectra, $\Delta\sigma(\nu)$. **a)** Monolayer MoS₂ 1.5 ps after photoexcitation with 3 eV (squares) and 1.9 eV (crosses) photons. A low energy resonance at ~ 18 meV (4.5 THz) is apparent. **b)** Trilayer MoS₂, 1.5 ps after photoexcitation by 1.9 eV photons. **c)** Monolayer WSe₂, 1 ps after photoexcitation on resonance with the WSe₂ ‘A’ exciton at 1.65 eV. Solid lines show possible fits to the data, detailed in Table 5.2

Table 5.2: THz photoconductivity fitting parameters.

	σ_D		σ_X			σ_T		
	$C_{\text{Drude}}(\%)$	γ (THz)	$C_X(\%)$	γ (THz)	ν_{0_X} (THz)	$C_T(\%)$	γ (THz)	ν_{0_T} (THz)
Mono	11.7	5	78	10	25	10.3	6	4.5
Tri	1	5	96.6	10	25	2.4	10	4.5
Mono	3	5.21	96.5	8	25	0.5	1	3.33

enough to draw firm conclusions.

In summary, we have observed ultrafast photoconductivity responses in monolayer MoS₂ and WSe₂, which we attribute to charge trapping at surface states. A monolayer semiconductor with such a fast response is likely to be a key component of future high-frequency opto-electronic devices including photoreceivers, emitters, modulators as well as microwave and THz switches. The low-cost and scalable CVD production of these monolayers, and their easy integration into devices, make them particularly attractive materials for such devices.

Chapter 6

Evaluating the photoconductive performance of semiconducting and semi-metal nanoflakes using terahertz time domain spectroscopy

Chemical vapour deposition offers a scalable method of producing high-quality novel two dimensional systems, such as graphene and transition metal dichalcogenides. However, for some proposed applications of these new materials, where lower material qualities are acceptable, a cheaper and easier production method is desirable. Liquid-phase exfoliation of layered materials is a cheap and versatile method of producing mono- and few-layer nanomaterials. In this Chapter we test optoelectronic potential of graphene and molybdenum diselenide nanoflakes produced by liquid-phase exfoliation, and find that the cheaper nanoflakes retain the ultrafast behaviour observed in their CVD-grown equivalents, showing promise for use of liquid-phase exfoliation in future opto-electronic devices.

6.1 The potential of liquid-phase nanoflake production

In the ten years since the first production of graphene, it has remained true that mechanical exfoliation can produce the highest quality two-dimensional materials [57]. An intense global effort to improve the quality of chemical vapour deposition (CVD) grown materials has borne fruit, particularly for graphene, where the mobilities achievable are now almost competitive with mechanically exfoliated graphene [115, 199]. Continued research should improve CVD-grown graphene and other two-dimensional materials, such as transition metal dichalcogenides (TMDs), producing large size, high quality materials for moderate to high-cost device applications.

However, not all potential uses of these novel materials require expensive, large mono-crystalline materials. For some applications, such as in batteries [200–202], cheap, easy production and integration into devices are the desired properties, rather than record breaking mobilities. An alternative production method to CVD for these applications is liquid exfoliation [73].

It has been shown that many layered materials can be exfoliated chemically, yielding advantages such as a greatly increased surface area. For liquid-phase exfoliation, a powder of the 3D bulk material is dissolved in a solvent whose surface energy is similar to that of the crystal layers. Application of ultrasonic waves to the solution generates the force to break the layers apart, leaving small mono and few-layer nanoflakes in the solution [64, 203].

This versatile method can be used with a wide range of materials, forming a straightforward, scalable and sustainable production route for cheap 2D materials. Furthermore, processing directly from the nanoflake suspensions allows techniques that would be difficult or impossible using mechanically exfoliated or CVD growth techniques. For example, free-standing films can be produced, the suspension can be used directly as a filler in a polymer matrix, or the suspension can be readily mixed

with other nanomaterials to form exotic heterostructures [73,200,204,205]. Alternatively, the nanoflakes can be deposited on a substrate, and the solvent evaporated, yielding devices on any desired surface, without the difficulties involved in transferring CVD-grown materials, such as the PMMA layer used for the graphene in Chapter 4.

Graphene and 2-dimensional TMDs produced this way [73,204,206] have already shown promise in a broad range of areas. Graphene nanoflakes have been used in liquid crystal displays [207], demonstrated good mobility ($100 \text{ cm}^2/\text{Vs}$) when integrated into printed circuits [208] and have been used for the reinforcement of polymers [209]. TMDs, such as MoS_2 , MoSe_2 and WSe_2 have been used in batteries [200–202], capacitor electrodes [210,211], and have been suggested for use in hydrogen extraction from water, a particularly important application in the search for clean fuels [212]. The edge molybdenum sites on Mo-based TMDs are highly active for hydrogen evolution reactions and thus are being considered as electrodes for water splitting using sunlight, an application that small cheap nanoflakes are better suited for than other forms of 2D TMDs.

Other desirable applications could include ultrafast flexible optoelectronics, or easily fabricated THz devices based on free standing nanoflake films. However, no studies have been performed to test the behaviour of hot carriers in these materials, and evaluate their potential for ultrafast optoelectronics.

Here, we use optical-pump THz-probe time domain spectroscopy to investigate the dynamics of carriers in photoexcited graphene, a semi-metal, and semiconducting MoSe_2 nanoflakes produced by liquid-phase exfoliation. We demonstrate that the nanoflake samples share the ultrafast response of the CVD-grown forms of the materials, suggesting promise for cheap, ultrafast optoelectronic devices. Furthermore, we observe strong, broad absorption resonances in the THz range, allowing for strong coupling to THz radiation in nanoflake based devices.

Samples of graphene and MoSe_2 were produced by liquid-phase exfoliation, and

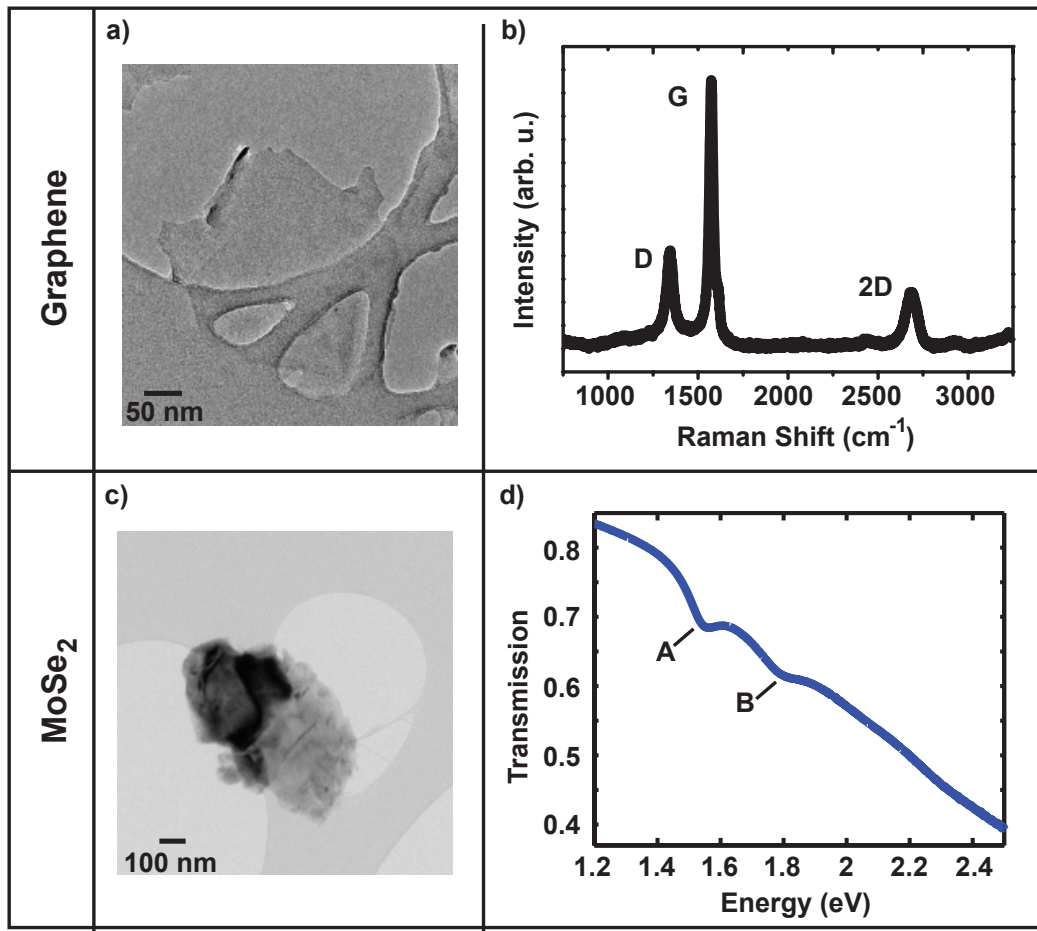


Figure 6.1: Characterisation of graphene (**a-b**) and MoSe₂ (**c-d**). **a, c** TEM images of graphene and MoSe₂ nanoflakes respectively. **b** Raman spectroscopy of graphene nanoflakes, showing few-layer characteristics. **d** Optical absorption spectrum of MoSe₂ nanoflakes showing the ‘A’ and ‘B’ exciton peaks. A peak related to the HeNe laser in the spectrometer has been removed from the data.

deposited on quartz substrates for terahertz spectroscopy. For the graphene samples, graphite powder (1.5 g) was added to NaC aqueous solution (0.1 mg ml^{-1} , 300 ml), and ultrasonicated at low power for 51 hours. The solution was then placed in a centrifuge at 3000 rpm for 90 minutes, and the supernatant containing graphene subsequently collected, and deposited on the quartz. Further details can be found in 211. As the TEM images displayed in Figure 6.1 show, the resulting sample contained monolayer flakes of graphene. Raman spectroscopy, the standard tool for judging the quality of graphene, was performed, and is displayed in Figure 6.1. In contrast to the Raman spectrum of CVD-grown graphene presented in Figure 4.1, three peaks are present in the nanoflake Raman data - the D peak at 1340 cm^{-1} , G at 1570 cm^{-1} , and 2D at 2683 cm^{-1} . The presence of a prominent D peak highlights the increased number of defects in the nanoflake samples compared to the CVD-grown sample, caused primarily by the increased number of edge defects in the nanoflake sample. The height and shape of the 2D peak demonstrates that few-layer graphene is present in the sample [34].

The molybdenum diselenide flakes were obtained by sonicating a 5 mg ml^{-1} dispersion of MoSe_2 (American Elements- 99.9% metal basis) in 2-Propanol. After 5 hours of ultrasonic treatment at 37kHz and 100W power, the suspensions were centrifuged at 1500 rpm for one hour. The supernatant was collected and dropcast onto the quartz substrates. Again, the sample was characterised by TEM imaging, revealing 500 nm sized monolayer flakes. The quality of the sample was confirmed by X-ray diffraction, show in Figure 6.1.

The optical transmission of the MoSe_2 samples was measured using a FTIR spectrometer. Figure 6.1d shows the resulting transmission spectra, showing absorption features at 1.55 eV and 1.8 eV corresponding to the ‘A’ and ‘B’ excitons in MoSe_2 respectively, similar to those excitons observed in the absorption spectrum of CVD-grown MoS_2 in Figure 5.1.

Sample growth, and Raman, X-ray diffraction and TEM imaging were provided by the group of Valeria Nicolosi at CRANN, Trinity College, Dublin.

6.2 THz spectroscopy

To test the photodynamics of the nanoflake samples, we used optical-pump THz-probe spectroscopy. The system was identical to that used for the measurements on CVD graphene in Chapter 4. The samples were photoexcited with an 800 nm (1.55 eV) pump pulse, of $180 \mu\text{J}/\text{cm}^2$ fluence. Photoexcitation of the MoSe_2 samples with 1.55 eV resonantly excited the ‘A’ exciton in MoSe_2 . In contrast, photoexcitation in the semi-metal graphene generated free carriers in the conduction band - the exciton energy in graphene is at the much higher value of 3 eV above the Dirac point and so no excitons were excited in the graphene nanoflakes. It should be noted that all measurements were performed in a vacuum.

6.2.1 Pump-Probe Measurements

In Figure 6.2, the normalised change in THz transmission, related to THz photoconductivity $\Delta\sigma$, is shown as a function of time after photoexcitation for both graphene and MoSe_2 samples. Upon photoexcitation by the pump pulse, the THz absorption, and hence conductivity, of graphene increases rapidly, within an instrument limited rise time 300 fs. The photoconductivity then decays on two distinct timescales - a first, fast 0.3 ps fall followed by a slower 3.3 ps decay. The solid line in Figure 6.2 represents a biexponential fit to these data. Thus the graphene nanoflakes retain the ultrafast, two timescale nature common to CVD-grown, mechanically exfoliated and expitaxially grown graphene.

The MoSe_2 sample displays similar, although slower, behaviour. The photoconductivity rises after photoexcitation, to a maximum within 800 fs. The subsequent fall in photoconductivity can be characterised by two exponential timescales - 1.68 ps

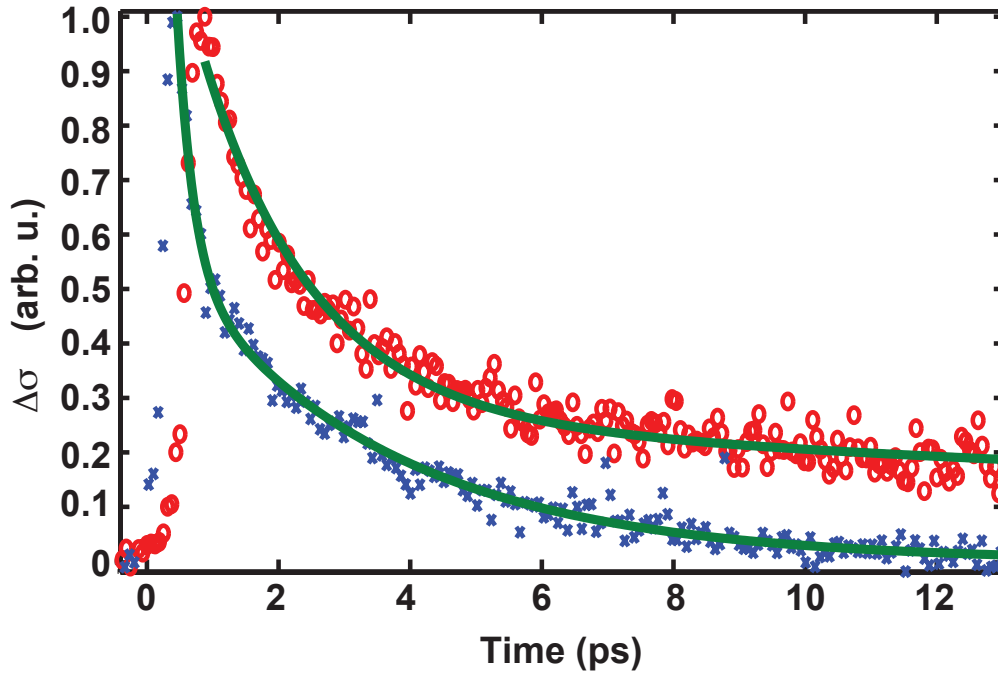


Figure 6.2: THz photoconductivity of graphene (blue crosses) and MoSe₂ nanoflakes (red circles) after photoexcitation by a 800 nm (1.55 eV) pump beam. Solid lines represent biexponential fits to the data.

followed by 35 ps. This decay is very similar to that observed in the related material MoS₂ in Chapter 5.

The similarity of photodynamics in nanoflakes and CVD-grown material can be seen explicitly for the case of graphene. In Figure 6.3 we compare the normalised THz photoconductivity of these graphene nanoflakes with the CVD-grown graphene as measured in vacuum in Chapter 4. There is a remarkable overlap between the photoconductivity in the two very different graphene samples, highlighting that the nanoflakes retain the ultrafast photodynamics of better quality graphene (with quality determined by the intensity of the D peak in Raman spectra of the samples). It should be noted, however, that the nanoflakes do not display any change of behaviour in the presence of gases, unlike the CVD-grown sample's extreme sensitivity to environmental adsorbates, discussed in Chapter 4. That the smaller flakes are not sensitive to adsorbates suggests the gap opening behaviour in the CVD-grown sample

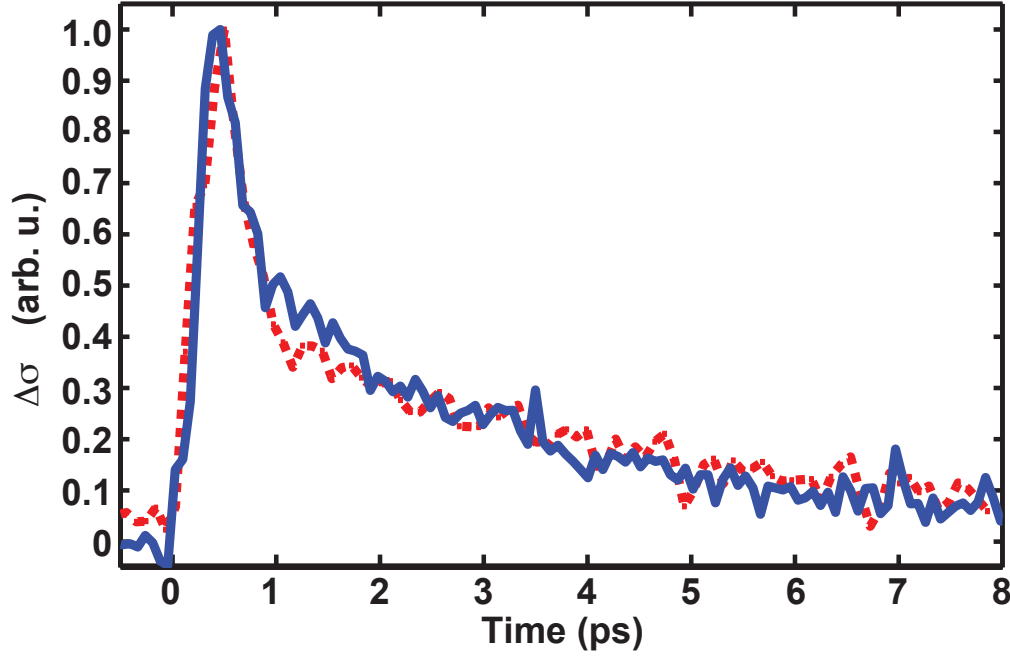


Figure 6.3: Comparison of the normalised THz photoconductivity of graphene nanoflakes prepared by liquid-phase exfoliation (solid blue line), and the CVD-grown graphene film measured in Chapter 4 (broken red line). For both cases the measurement was performed in vacuum, removing the gap-opening effect of adsorbates on the CVD sample (see Chapter 4). The near perfect overlap of the two sets of data demonstrates that the graphene nanoflakes retain the ultrafast photodynamics of CVD-grown graphene.

was related to the nature of the transfer of the film to the graphene substrate, or was caused by molecules, for example water, trapped between the large graphene film and the substrate.

As the decays of both graphene and MoSe₂ photoconductivities were so similar to their CVD grown counterparts, it is likely that the same mechanisms are responsible for hot carrier cooling discussed in Chapters 4 and 5 for graphene and TMDs respectively - i.e. rapid cooling by optical phonons in graphene, until a bottleneck when carriers cool below the optical phonon energy, creating two distinct timescales, and rapid recombination of excitons in MoSe₂, until inter-valley scattering spatially separates the electron-hole pairs and slows recombination, again creating two distinct

timescales. The similarity of the ultrafast timescales in the nanoflake samples to those in the CVD-samples suggests that hot carrier cooling is not dependent upon the number of defects, which is greater in the nanoflakes. More importantly, the similarity suggests that liquid-exfoliation can produce materials with equal potential for ultrafast opto-electronic applications as chemical vapour deposition.

6.2.2 Photoconductivity spectra

Fourier transforming the THz time domain data, and utilising Equation 2.23 yields the complex THz photoconductivity spectra displayed in Figure 6.4. Spectra are shown for MoSe₂ nanoflakes at 1.2 ps and 1.5 ps after photoexcitation by the 1.55 eV pump pulse, and for graphene nanoflakes at 1.5 ps after photoexcitation. A resonance, i.e. a peak in the real part of photoconductivity and a change of sign in the imaginary part, is apparent in the two MoSe₂ spectra. Following the method used in Chapter 5, the data were fit by a sum of Lorentzian oscillators. Unlike the monolayer MoS₂ spectrum in Chapter 5, here we find only a single Lorentzian and a small Drude (free carrier) term are necessary to fit the data, i.e.

$$\begin{aligned}\Delta\sigma(\nu) &= \Delta\sigma_{\text{Lorentz}} + \Delta\sigma_{\text{Drude}} \\ &= \frac{C_L i\nu}{\nu^2 - \nu_0^2 + i\nu\gamma_L} + \frac{C_D i\nu}{\nu^2 + i\nu\gamma_D},\end{aligned}\tag{6.1}$$

where C_L and C_D are the spectral coefficients of the Lorentzian and Drude components respectively, γ_L and γ_D the corresponding linewidths, and ν_0 is the resonant frequency of the Lorentzian oscillator. Fitting parameters are given in Table 6.1.

In MoSe₂ at 1.2 ps after photoexcitation, the data are well fit by a resonance at 2.6 THz, with an order of magnitude smaller Drude component accounting for the non-zero conductivity at $\nu = 0$ THz. By 1.5 ps after photoexcitation, however, the resonance has blue-shifted to 3.63 THz. This blue shifting spectral signature may have several different causes.

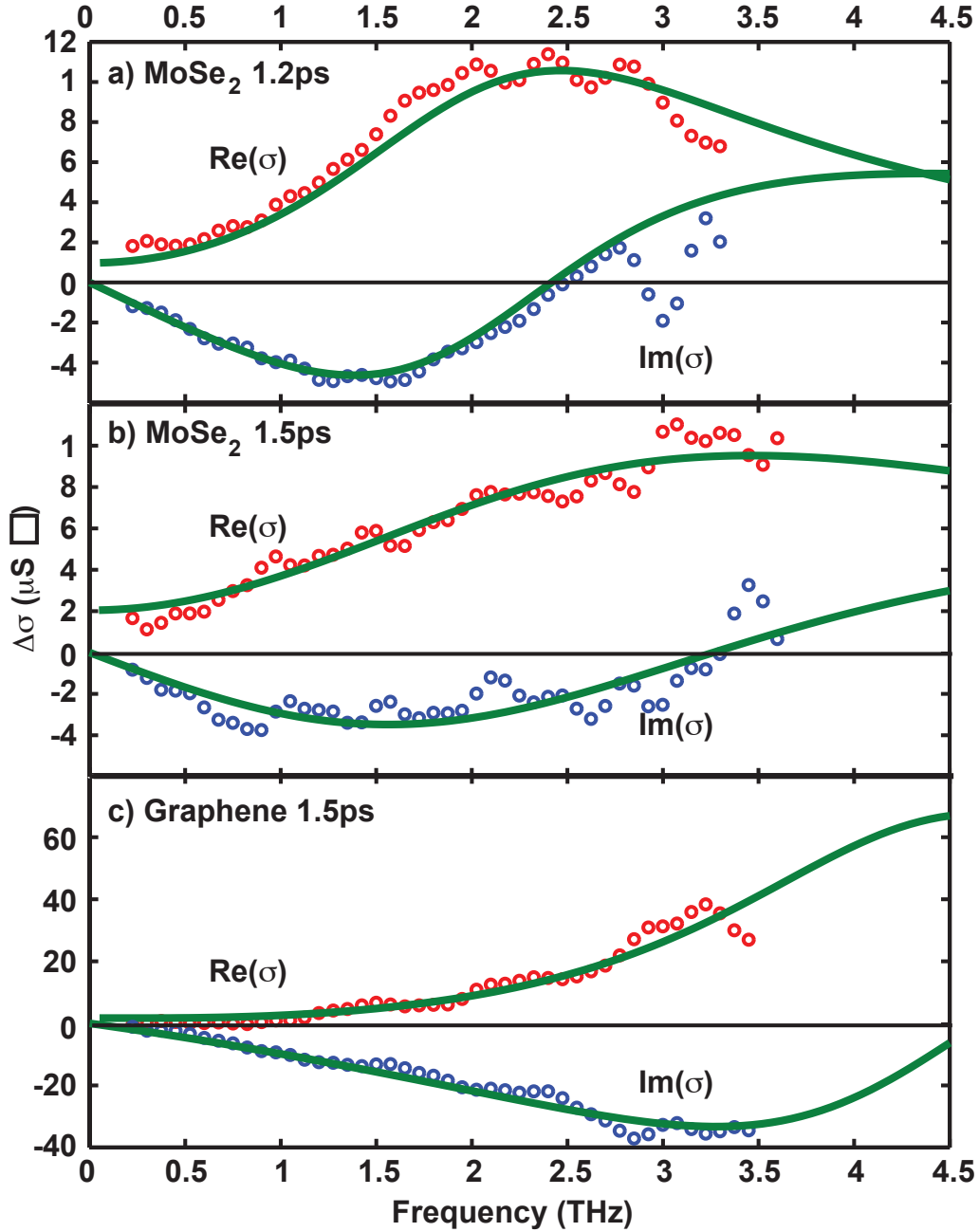


Figure 6.4: Photoconductivity spectra of MoSe₂ and graphene nanoflakes. **a)** Real (red circles) and imaginary (blue circles) parts of the complex THz photoconductivity, $\Delta\sigma$ of MoSe₂ at 1.2ps after photoexcitation by the 1.55eV pump beam. The solid lines represent fits to the data assuming a sum of a Lorentzian oscillator and a Drude conductivity. Fit parameters are given in Table 6.1. **b)** $\Delta\sigma$ at 1.5ps after photoexcitation in MoSe₂. **c)** $\Delta\sigma$ at 1.5ps after photoexcitation in the graphene nanoflakes.

Table 6.1: THz photoconductivity spectra fit parameters

		σ_{Lorentz}			σ_{Drude}	
		C_L (THz)	γ_L (THz)	ν_{0x} (THz)	C_D (THz)	γ_D (THz)
MoSe ₂	1.2 ps	3.95×10^{-5}	5	2.62	7.86×10^{-6}	5
	1.5 ps	5.31×10^{-5}	5	3.63	9.94×10^{-6}	10
Graphene	1.5 ps	2.28×10^{-4}	3.38	4.66	1.69×10^{-6}	5

Due to the confinement of carriers in the small nanoflakes, a likely source of the resonance at THz frequencies in the samples is the excitation of surface plasmons, collective carrier oscillations, across the flakes ^[111,213,214]. In this case, the plasmon resonant frequency would depend upon the flake size and the carrier density (N) dependent plasma frequency, given by ^[196],

$$\omega_0 = \sqrt{\frac{Ne^2}{m^* \epsilon_r \epsilon_0}}, \quad (6.2)$$

where m^* is the effective carrier mass, and ϵ_r the relative dielectric response in MoSe₂.

It would be expected that as time after photoexcitation increases, the carrier density would decrease, leading to a redshift in resonant frequency. In MoSe₂, however, we observe the opposite. This could be explained by an increase in free carrier density at later times because of exciton disassociation, by inter-valley scattering for example.

Alternatively, there could be a much higher energy resonance, outside of the bandwidth available here, associated with transitions within the exciton. If the excitons form slowly, this high energy resonance would increase in strength at later times, dragging the apparent plasmon frequency in the THz spectrum to higher frequencies.

Further information could be acquired about the origin of the resonance by repeating the measurements with a lower pump fluence, exciting a lower carrier density. However, the signal-to-noise ratio of these low fluence measurements proved to be too small to draw any conclusions about the resonance.

In contrast to the MoSe₂ spectra, in the graphene nanoflakes there is no resonance peak within the bandwidth of these measurements. However, fitting Equation 6.1

to the data suggests the presence of a resonance just outside of the bandwidth, at 4.7 THz.

It is notable that in all three spectra there is only a very small photoconductivity as $\nu \rightarrow 0$, particularly for graphene. The THz photoconductivity as $\nu \rightarrow 0$ is equivalent to the DC conductivity that would be measured from the sample after photoexcitation. That there is such a low DC photoconductivity here suggests that no conductive channel exists between the nanoflakes. Thus at the density present in these samples, the nanoflakes are not suitable for applications such as optical photodiodes, where a large induced current is desired to signify detection of photons. However, the large resonant response across a broad band of the THz region in both MoSe₂ and graphene samples suggests promise for THz optoelectronic devices, where strong coupling to THz radiation is required.

In summary, we have measured the photoconductive response of liquid-exfoliated graphene and MoSe₂ samples. Both samples displayed ultrafast responses to photoexcitation, maintaining the photodynamics observed in CVD-grown materials, and coupled strongly to broadband THz radiation. These properties, found in materials grown by a cheap, easy and versatile method, suggest great promise for use of nanoflakes in THz optoelectronic devices.

Chapter 7

An ultrafast carbon nanotube terahertz polarisation modulator

In this Chapter, ultrafast modulation of terahertz radiation by unaligned optically-pumped single-walled carbon nanotubes is demonstrated. Photoexcitation by an ultrafast optical pump pulse induces transient terahertz absorption in nanowires aligned parallel to the optical pump. The terahertz polarisation and modulation can be tuned by controlling the polarisation of the optical pump, allowing sub-picosecond modulation of terahertz radiation. Such speeds suggest potential for semiconductor nanowire devices in terahertz communication technologies.

7.1 Introduction

Whereas microwaves and near-infrared light have been widely used in communication technologies, the terahertz region of the electromagnetic spectrum, lying between microwaves and IR, has been notably underused. Historically, intense sources of THz waves, with a frequency from 50 GHz to 10 THz, have been difficult to find ^[10,215]. A range of sources, from optical rectification to quantum cascade lasers are now available ^[10,216], but high speed THz communications have yet to be realised. A lack of satisfactory practical THz modulators, required to encode information in the THz wave, is a chief reason for the lack of progress ^[13,139].

Terahertz intensity modulators have already been demonstrated using a range of approaches^[139,217], including optically pumped silicon wafers ^[218–220] and electrically modulated metamaterials ^[221,222]. Liquid crystals have been suggested for use as terahertz polarisation modulators ^[223,224]. However these methods do not provide fast enough switching speeds to exploit the full potential of THz communication applications, where picosecond scale switching is desirable. On the other hand, static THz polarisers have also been developed, for example by arranging fine wires in a grid ^[225,226], but again cannot provide fast switching speeds.

Carbon nanotubes may offer a solution to the problem of fast switching. It has been shown that highly aligned single-walled carbon nanotubes (SWNTs) can act as optical ^[137,138] and THz polarisers ^[140,141], utilising the intrinsic anisotropy of these one-dimensional materials. Previously, we have shown that photoexcitation of highly aligned semiconducting nanotubes can provide *dynamic* THz polarisation ^[145]. Photoexcitation of these nanotubes creates an exciton along the length of the nanotube, which can absorb THz radiation aligned with it during the lifetime of the exciton (10-100 ps ^[142–144]). Rotation of such a nanotube structure allows selective

transient polarisation of incident THz waves.

However, our previously reported device required the nanotubes to be highly aligned, and only allowed modulation of THz intensity by rotation of the nanotube grid. Here, we present ultrafast dynamic THz modulation by an unaligned nanotube device. Selective photoexcitation of the nanotubes by a polarisation-controlled optical pump creates a transient and tunable THz polariser which can modulate THz waves on a sub-picosecond timescale.

7.2 Sample growth and characterisation

The SWNT sample was produced using a fast, simple and cheap method described previously [227–229]. Briefly, a narrow chirality distribution of semiconducting single-walled carbon nanotubes was produced by selectively dispersing the nanotubes with the polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO). The polymer and SWNT mixture was agitated using an ultrasonic probe, leading to a selective wrapping of semiconducting species. Unwrapped and bundled SWNTs precipitate out of solution and were removed via centrifugation. High yields of polymer-wrapped SWNTs were obtained by optimizing the polymer:nanotube ratio and the sonication time. The polymer-nanotube blends were then simply drop-cast from the o-xylene dispersions on to z-cut quartz discs while gently heating the substrates at 60°C to create an unaligned SWNT sample. Z-cut quartz was selected for its high transmission of THz radiation, and unresponsiveness to photoexcitation.

Figure 7.1 shows the characterisation of this SWNT film. Photoluminescence emission (PLE) spectroscopy was used to determine the chirality of nanotubes present in the sample. As corroborated by the absorption spectrum in Figure 7.1b, photoexcitation by a 650 nm pump, as used in the THz measurements, selectively photoexcites the (7,5) semiconducting nanotubes.

Sample growth at PLE spectroscopy were provided by the group of Robin Nicholas

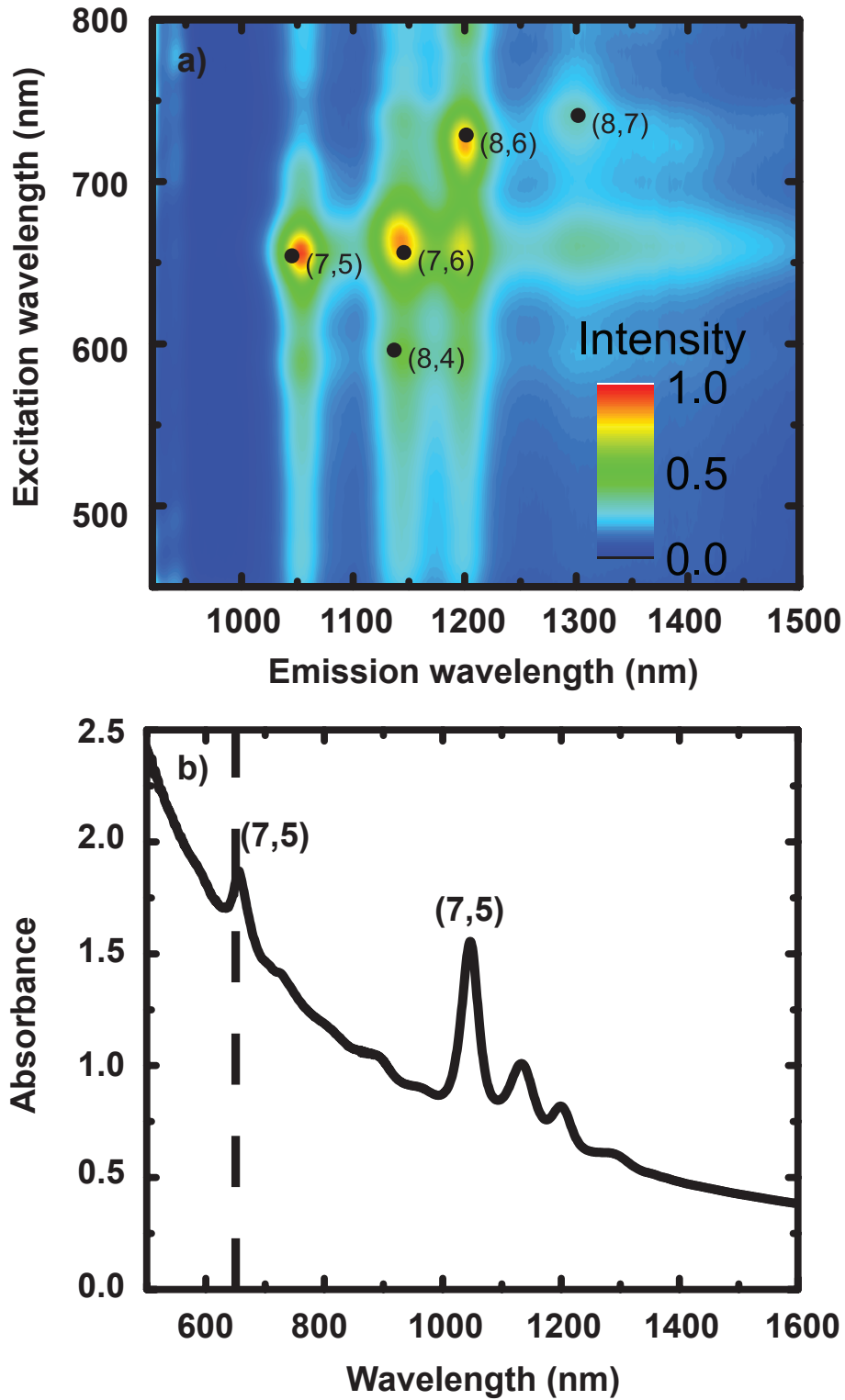


Figure 7.1: Characterisation of the SWNT dispersion. **a)** Photoluminescence emission spectroscopy of the nanotube sample. A very narrow distribution of semiconducting chiralities is apparent. **b)** Absorption spectrum of the nanotubes. Photoexcitation by the 650 nm pump used in the optical-pump THz-probe measurements (represented by the dashed line) selectively excites only the (7,5) nanotubes.

at the Department of Physics, Oxford.

7.3 Using THz TDS to demonstrate optically activated polarisation

The transient THz modulation provided by the SWNT sample was determined using the time domain THz spectrometer described in Chapter 2. THz radiation was generated by optical rectification in a 2 mm thick GaP crystal, photoexcited by 800 nm femtosecond pulses^[10]. The electric field of the THz radiation was detected by electro-optic sampling in a second GaP crystal, and the difference in THz transmission through the photoexcited SWNT sample and the sample without photoexcitation determined by lock-in detection referenced to a chopper in the pump beam. The 650 nm pump pulses used to photoexcite the nanotube modulator were generated with a fluence of $175\mu\text{J}/\text{cm}^2$ by a TOPAS optical parametric amplifier, pumped from an 800 nm Ti:Sapphire regenerative amplifier.

The nanotube sample was photoexcited by femtosecond pulses of the 650 nm polarised pump beam. Due to the inherent anisotropy of the nanotubes, nanotubes aligned in the same direction as the pump pulse polarisation are preferentially photoexcited. The resulting exciton population resides predominantly on nanotubes aligned in the direction of the pump polarisation, and hence incident THz radiation also polarised in this direction will be preferentially absorbed by these carriers. Thus, by selecting the polarisation of the pump beam, we were able to control the THz modulation capability of the nanotube sample.

The polarisation of the pump beam was controlled by a half waveplate placed in the beam before the nanotube sample. Rotating the waveplate by an angle θ rotated the pump beam polarisation by an angle 2θ - i.e. the pump beam was rotated from vertical polarisation to horizontal polarisation by rotating the waveplate by 45° . This measurement is schematically demonstrated in Figure 7.2b.

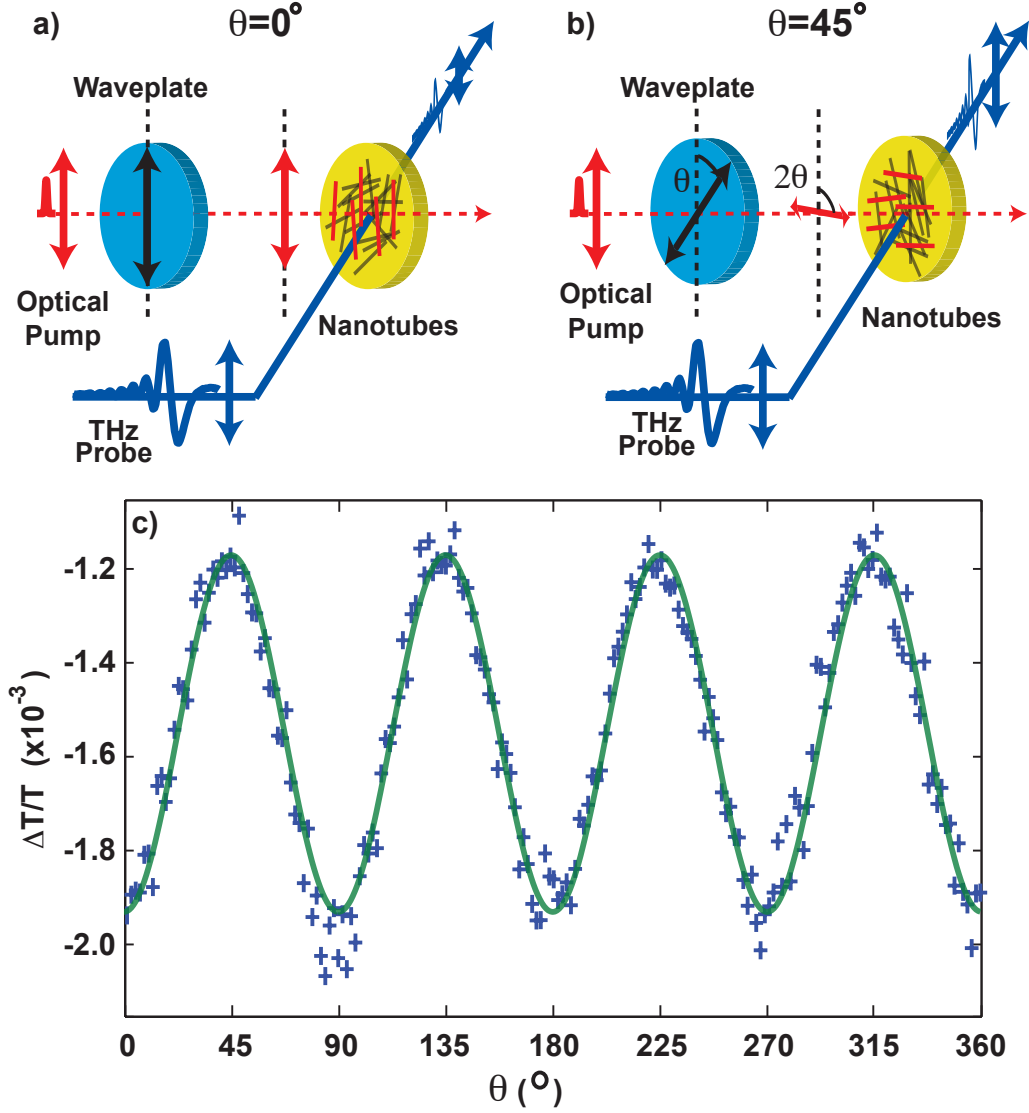


Figure 7.2: Selective modulation of THz radiation. **a, b** Schematic representation of the measurements. A half-wave plate rotates the polarisation of a 650 nm pump beam by 2θ , where θ is the angle between the vertical and the waveplate axis. This rotated pump beam selectively excites nanotubes aligned with the pump polarisation. THz waves are only absorbed by those photoexcited nanotubes that are aligned with the THz polarisation. **a** $\theta = 0$, and so excited nanotubes are aligned with the THz wave, yielding maximum absorption. **b** $\theta = 45^\circ$, so excited nanotubes are perpendicular to the THz polarisation, and so there is minimum absorption of the THz wave. **c** Photoinduced change in THz transmission, $\Delta T/T_{\text{OFF}}$, equivalent to modulation depth of the device, as a function of half-wave plate angle θ . The induced THz transmission change follows a cosine-squared relationship with waveplate angle, as expected from Malus' law, represented by the solid line.

In Figure 7.2c, we present the effect of rotating the waveplate on the THz modulation through the nanotube sample. The ratio of change in THz transmission intensity due to photoexcitation to the transmission through the non-photoexcited sample, $\Delta T/T_{\text{OFF}}$, is plotted as a function of waveplate angle. Here, $\Delta T = T_{\text{ON}} - T_{\text{OFF}}$, where T_{ON} and T_{OFF} represent the THz transmission of the sample with and without photoexcitation respectively. As such, $\Delta T/T_{\text{OFF}}$ is equivalent to the modulation depth of the nanotube THz modulator.

As expected from Malus' law for transmission through a polariser, the data display a cosine-squared relationship. At 0° , the pump pulse is polarised parallel to the THz probe, and nanotubes photoexcited by this pump pulse can absorb the THz probe, leading to maximum absorption. When the waveplate is rotated by 45° , the pump pulse is polarised perpendicular to the THz probe pulse, and so nanotubes photoexcited in this case absorb much less of the THz radiation.

7.3.1 Transient polarisation

To analyse the transient nature of this polarisation, the time between photoexcitation by the pump and probing by THz pulses can be varied. Figures 7.3a-d display the modulation depth of the nanotubes at the peak of the THz pulse as a function of time after photoexcitation, for waveplate angles of $\theta = 0^\circ, 15^\circ, 30^\circ$ and 45° . As can be seen from these figures, upon photoexcitation the modulation depth increases sharply, with a rise time of 500 fs. This is followed by a fall in modulation depth characterised by two exponential timescales - a first, rapid decay ~ 400 fs, followed by the decay of a small residual signal over several picoseconds. Thus ultrafast transient modulation of THz transmission can be achieved with the carbon nanotube polariser, at speeds suitable for communication technologies.

These dynamics can be understood by the creation and decay of excitons in the nanotubes. As discussed previously ^[144], photoexcitation preferentially generates exci-

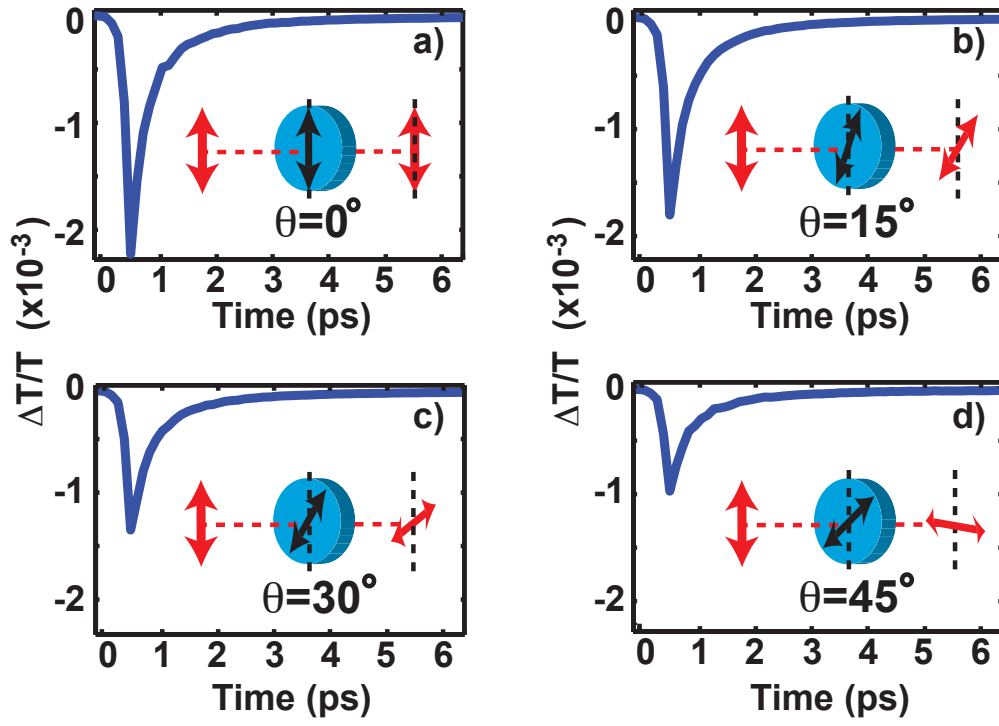


Figure 7.3: Time dynamics of $\Delta T/T_{\text{OFF}}$ as a function of time between optical pump and THz probe pulses, at waveplate angles of a) 0° , b) 15° , c) 30° d) 45° .

tons in those nanotubes parallel to the polarisation of the pump beam. Internal transitions within these excitons are in the THz range, and thus THz radiation incident upon the photoexcited nanotubes can be absorbed. The change in THz absorption decreases on two distinct timescales, corresponding to the decay of the generated excitons. At the high fluences used in these experiments, multiple excitons per nanotube are likely to be formed initially, leading to many-body interactions. These rapidly decay by Auger processes ^[143, 230, 231], leading to the first fast decay of photoinduced THz absorption. The longer timescale is then associated with single excitons.

7.3.2 Switch on speed

The switch-on speed of the polariser can be determined by measurement of the electric field of the THz probe pulse passing through the nanotube device. The THz electric field, E_{THz} , transmitted through the unexcited nanotube sample is shown in Figure 7.4a. Photoexcitating the sample long before the arrival of the THz pulse, as shown in Figure 7.4b, yields a change in electric field, ΔE_{THz} due to additional absorption in the nanotubes. In Figure 7.4c, however, the photoexcitation happens during the passing of the THz pulse through the nanotube sample. A modulation signal appears less than a picosecond after the ‘switch on’, indicating the speed of the device.

Our study demonstrates that ultrafast, dynamic control over the polarisation of THz radiation is possible with unaligned carbon nanotube films. With a modulation depth (related to $\Delta T/T$) of -27 dB, this technique has clear scope for improvement, e.g. through an increase in the density of nanotubes present in the sample, or alternatively by stacking of layers of the CNT samples yielding a thicker device. These techniques will be explored and developed in future work.

In summary, we have demonstrated the potential of unaligned, semiconducting carbon nanotubes for use in ultrafast THz modulators with sub-picosecond switch-on speeds. Photoexcitation by a polarised pump beam creates a tunable and transient

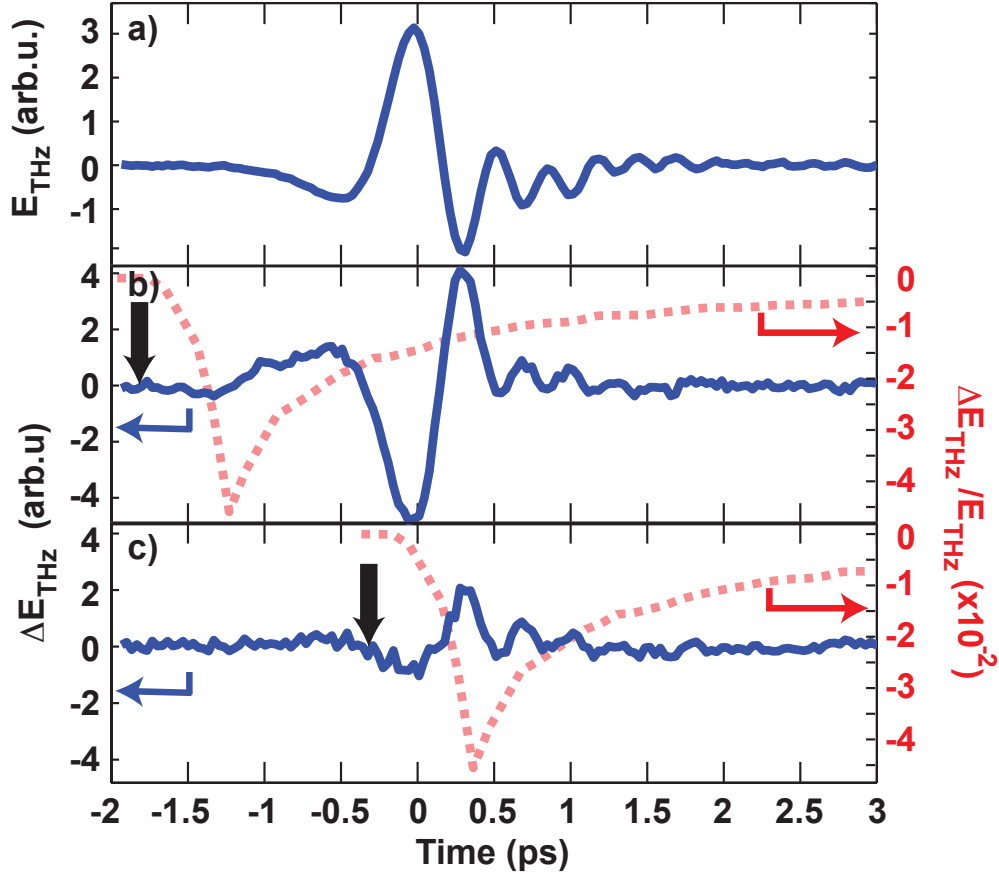


Figure 7.4: The THz electric field, E_{THz} , passing through the polariser. a) E_{THz} through the un-photoexcited sample. b) Change in THz electric field, ΔE_{THz} , when the sample was photoexcited before the arrival of the THz pulse. The solid black arrow represents the time at which the sample was photoexcited with the waveplate set to $\theta = 0^\circ$. c) ΔE_{THz} when the sample was photoexcited during the THz pulse. The dotted red lines are the electric field (rather than intensity) equivalent of the pump-probe data from Figure 7.3a, giving an indication of relative signal strength expected at that time after photoexcitation.

polarisation of THz radiation through the nanotube device, which decays within a picosecond of the photoexcitation allowing for ultrafast modulation switching speeds. These properties, combined with the ease and cost effectiveness of production of the nanotube device, suggest promise for SWNT devices in THz communication technologies.

Chapter 8

Conclusion

A vast array of applications for novel two-dimensional systems have been suggested in the excitement following from graphene's discovery ^[232]. The primary motivation of this work was to assess these new materials for use in high-speed applications, and investigate any novel physics arising in the THz region.

In graphene grown by chemical vapour deposition (CVD), optical-pump THz-probe spectroscopy revealed an unexpected sensitivity to the presence of atmospheric gases adsorbed on its surface (Chapter 4). The presence of oxygen or nitrogen molecules on the graphene surface induced the opening of a small bandgap, allowing emission of THz radiation by stimulated emission. Whilst this sensitivity is promising for applications using graphene as a gas sensor, and for advances towards using graphene as a THz laser medium, it highlights the need to carefully control the environment around 2-dimensional materials.

MoS₂, the semiconducting analogue to graphene, was investigated in Chapter 5, along with WSe₂. These materials demonstrated sub-picosecond responses to photoexcitation, showing promise for high-speed device applications. The spectrum of the THz photoconductivity hinted at the presence of trions, excitons bound with an extra electron, not previously observed using THz spectroscopy.

An alternative growth route for 2-dimensional materials was investigated in Chapter 6. Liquid-phase exfoliation is both cheaper and easier than CVD growth. The

graphene and MoSe₂ samples measured here, however, demonstrated ultrafast responses that matched those found in their CVD-grown counterparts, highlighting their potential for use in ultrafast opto-electronics for applications where high mobilities are not required.

Finally, in Chapter 7, the application of carbon nanotubes for THz polarisation was studied. Photoexcitation of an unaligned film of semiconducting carbon nanotubes allowed ultrafast, dynamic and tunable modulation of THz radiation.

This work has therefore shown the potential for novel 2-dimensional (and carbon nanotubes) in ultrafast device applications. Their picosecond scale responses to photoexcitation should allow the development of THz speed devices. Equally, their ability to couple strongly to THz radiation suggests potential for use in fast devices within THz technologies, such as communications.

However, this work, and its comparison to the literature, highlight the sensitivity of these materials to their production method and environment. This is perhaps unsurprising for systems composed mainly of surfaces, but means that their implementation in viable devices requires careful control of growth techniques and substrates to maintain consistent performance.

8.1 Future work

A number of studies could extend and enhance the work reported in this thesis. Most notably, the THz photoconductivity of the transition metal dichalcogenides studied here showed resonances at the edge or just outside of the experimental bandwidth. These resonances were tentatively assigned to the presence of trions in the samples, as expected from PL measurements. However, to confirm the nature of these resonances, the bandwidth of the system must be extended (for example by using plasma based THz generation and detection techniques ^[233,234]), and studying materials with varying degrees of carrier concentration.

Additional work could also demonstrate more practically the potential of these materials for THz device applications. The ultrafast lifetime of photoexcited carriers in MoS₂, for example, suggests this material could be used to form a photoconductive switch for THz generation. The small modulation depth of the carbon nanotube device in Chapter 7 must be improved to form a viable device. Stacking layers of the nanotubes together may form one route to improving the modulation depth.

The difference between the results presented in Chapter 4 and other studies reported in the literature ^[104–106] should be investigated. Other authors have not observed the environmental dependence of the THz photoconductivity in CVD-grown graphene that was demonstrated in Chapter 4, therefore the origin of this environmental dependence must be found. Preliminary theoretical work has suggested that water vapour trapped between the graphene sheet and the substrate could be responsible for enhancing graphene’s sensitivity to environmental adsorbates. In future studies, graphene will be grown by chemical vapour deposition on a heated substrate in a glovebox, to prevent water vapour becoming trapped during the growth process, and the THz photoconductivity of this graphene measured. In an alternative study, in-situ annealing could be performed during the THz measurements in varying atmospheres, to observe the effect of annealing in real time. In this way, the impact of water vapour and adsorbates can be more accurately determined.

Further information could be provided by attaching contacts to the graphene sample in the THz spectrometer, to determine the carrier concentration during measurements, or, with the addition of a suitably transparent back gate, to tune the Fermi level during THz spectroscopy. Such measurements would allow the sample to be precisely compared to the materials measured in the literature, and so the reasons for differences in results elucidated.

More generally, THz spectroscopy can be used to continue to assess these materials as their quality improves. The rapid nature of THz measurements, not requiring

contacts to be attached to materials, can be used to feed results quickly back into the growth process, and so further improve the quality of CVD-grown materials.

Finally there are many potential 2-dimensional crystals that have not yet been isolated ^[235]. The transition metal dichalcogenide family, in particular, possesses a wealth of electronic properties that may prove useful for future technology. Terahertz spectroscopy remains well placed to investigate these materials when they become available.

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