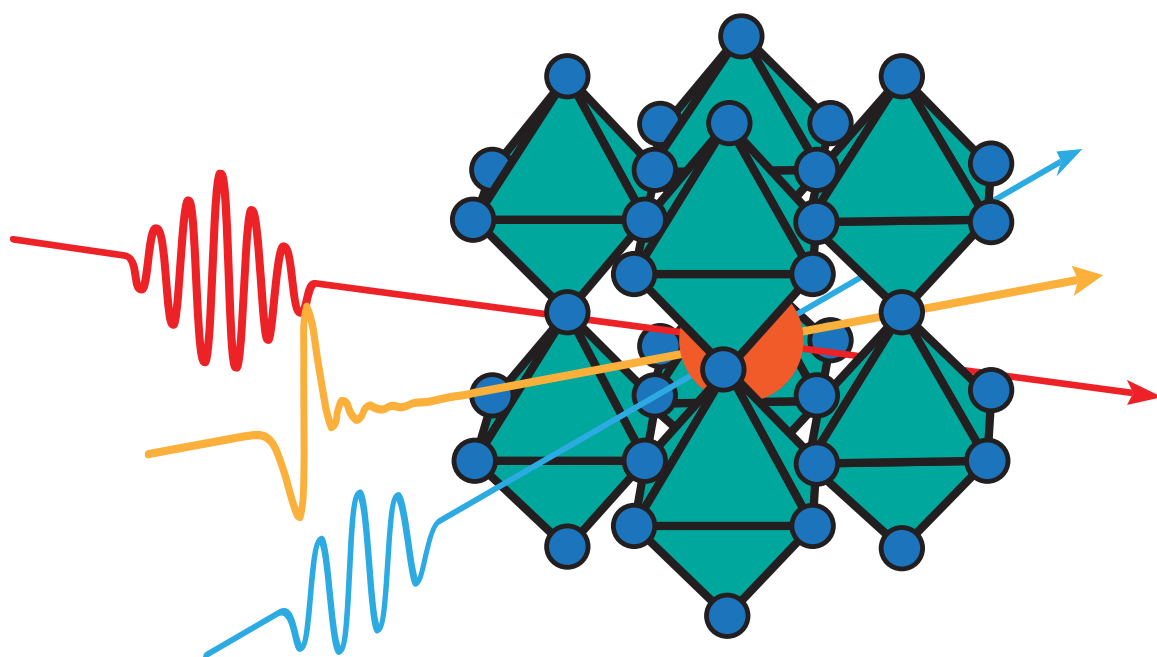


Dissertation for the degree of Doctor of Philosophy

Multi-Pulse Time-Resolved Terahertz Spectroscopy of Metal Halide Perovskite

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Nikolis, V. C.; Dong, Y.; Kublitski, J.; Benduhn, J.; Zheng, X.; Huang, C.; Yüzer, A. C.; Ince, M.; Spoltore, D.; Durrant, J. R.; et al. Field Effect versus Driving Force: Charge Generation in Small-Molecule Organic Solar Cells. *Advanced Energy Materials* 2020, 10 (47), 2002124. DOI: <https://doi.org/10.1002/aenm.202002124>

* Zheng, X.; Hopper, T. R.; Gorodetsky, A.; Maimaris, M.; Xu, W.; Martin, B. A. A.; Frost, J. M.; Bakulin, A. A. Multipulse Terahertz Spectroscopy Unveils Hot Polaron Photoconductivity Dynamics in Metal-Halide Perovskites. *The Journal of Physical Chemistry Letters* 2021, 12 (36), 8732-8739. DOI: 10.1021/acs.jpcclett.1c02102

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** Contents from these publications are referenced in this thesis.*

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List of abbreviations

2DES	Two-Dimensional Electron Spectroscopy
ABCD	Air-Biased Coherent Detection
ARPES	Angle-Resolved Photoelectron Spectroscopy
BBO	β -Barium Borate
DAQ	Data Acquisition
DIO	Digital Input/Output
DSP	Digital Signal Processing
EFA	Evolving Factor Analysis
EOS	Electro-Optical Sampling
EQE	External Quantum Efficiency
FIFO	First-In-First-Out Buffer
FPGA	Field Programmable Gate Array
GA	Genetic Algorithm
GUI	Graphical User Interface
HAC	Hierarchical Agglomerative Clustering
ICA	Independent Component Analysis
IQE	Internal Quantum Efficiency
MCU	Microcontroller
MPA	Multi-Photon Absorption
MHP	Metal-Halide Perovskite
NFA	Non-Fullerene Acceptor
NIR	Near-Infrared
NMF	Non-Negative Matrix Factorisation
OPA	Optical Parametric Amplifier
OPTP	Optical-Pump-Terahertz-Probe
OPV	Organic Photovoltaics
PCA	Photoconductive Antenna
PFO	Polydioctylfluorene
PIA	Photo-Induced Absorption
PPP	Pump-Push-Probe
PPP-THz	Optical-Pump-Infrared-Push-Terahertz-Probe
PSC	Perovskite Solar Cell
QDEC	Quadrature Decoder
RC	Reconstructed Component
RF	Radio Frequency
SDT	Spectrum Decomposition Tool
SF	Singlet Fission
SLG	Single Layer Graphene
SNR	Signal to Noise Ratio
SSA	Singular Spectrum Analysis
SVD	Singular Vector Decomposition
TAS	Transient Absorption Spectroscopy
TDS	Time-Domain Spectroscopy
TFA	Thin-Film-Approximation
TRTS	Time-Resolved Terahertz Spectroscopy
XPS	X-Ray Photoelectron Spectroscopy

Abstract

Processability is becoming an increasingly attractive property for optoelectronics that require mass deployment such as solar cells and LEDs. Processible optoelectronics can be fabricated using solution-based processes, such as ink-jet printing and still achieve remarkable performances. For instance, among single-junction processible solar cells, halide perovskite solar cells (PSC) show the highest efficiency. However, the photophysical properties of processible optoelectronics, including PSCs, are significantly more complex than those of traditional semiconductors.

Photoexcitation upon PSC generates populations of electron quasiparticles, such as excitons and polarons. Their kinetics and interaction with each other govern the fundamental physical properties of the PSCs. When a PSC is excited with photon energy well above its bandgap, which is a realistic situation concerning the solar spectrum, “hot” excitons with large excess energy are generated, and evolve into hot carriers populated deep into the conduction band. If hot carriers are not extracted before they relax to band edge, all excess energy is lost to heat. Therefore, it is crucial to understand hot carrier dynamics to enable rational design of PSCs.

This thesis employs time-resolved terahertz spectroscopy (TRTS) to study the underlying hot carrier photophysics of PSCs. Studies of perovskites utilising TRTS in the past decade are reviewed in detail, and their limitations are identified. The commonly used optical-pump-terahertz-probe (OPTP) scheme is found to be insufficient for studying hot carrier dynamics, and an improved TRTS scheme is proposed. The new scheme adds an infrared excitation pulse (push) well below bandgap, forming a pump-push-probe scheme (PPP-THz), which allows manipulation of carrier temperature without altering the carrier population.

Finally, non-parametric, model-less data analysis methods for high-dimensional time-resolved spectroscopy data are proposed and implemented, including rank estimation, matrix factorisation, eigendecomposition-based time-series analysis, and dimensionality reduction. Those methods are bundled into a GUI software which also features automatic data post-processing, visualisation and navigation of high-dimension datasets.

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1 Introduction

In Chapter 1, processible optoelectronic nanomaterials including organic heterojunctions, 2D materials, and halide perovskites are introduced with emphasis on halide perovskites, which is the primary system under study for the experimental sections in this thesis.

The basic principles of light-matter interactions at different wavelengths and their corresponding light sources and spectroscopies are introduced. Time-resolved spectroscopy is introduced as a tool to study ultrafast excited states dynamics of optoelectronics. Various time-resolved spectroscopic techniques are introduced to study the fundamental physics of those materials with emphasis on hot carrier dynamics of halide perovskites. In particular, TRTS is a powerful tool to investigate hot carrier dynamics in perovskites, as it directly retrieves intrinsic time-and-frequency-resolved photoconductivity from materials in a contactless manner without the need of a functional device.

The TRTS studies of perovskites in the past decade were reviewed. While the experimental results are fairly consistent across the decade, the understanding of charge carrier dynamics has been evolving from complete denial of excitonic and polaronic coupling to quantum treatment of photoconductivity frequency-dependence.

1.1 Processible Optoelectronic Nanomaterials

Processible optoelectronic nanomaterials are a class of semiconductors whose primary function involve interreacting with light, e.g., photovoltaics, LEDs, photodetectors, photo-gate transistors and lasers. These materials distinguish from traditional semiconductors such as silicon and III-V materials because they often exhibit unusual electronic and photonic properties, and generally do not require expensive and sophisticated manufacture methods such as photolithography to fabricate semiconductor devices.

Research on novel processible optoelectronic materials with unconventional properties has been accelerating, and the performance gap between traditional and processible materials has been closing due to the efforts of ongoing research. The research landscape of processible materials is vast, encompassing a wide range of novel semiconducting systems such as organic single crystals, conjugated polymers, low-dimensional materials and perovskites.

One of the most prominent applications of processible optoelectronic nanomaterials is photovoltaics, as it is one of the most rapid-developing renewable energy sources, and solar cells require massive scalability in order to cover large surface area. Traditional semiconductor photovoltaics, such as single and polycrystalline silicon cells, while having better power conversion efficiency (PCE) and stability, are prohibitively expensive to up-scale, and their manufacture processes pose significant adverse environmental implications.

Material systems that can be processed in solution or gas phase enable higher throughput and less wasteful manufacture methods such as ink-jet printing. While processibility is very tempting, solution-based materials suffer an almost universal drawback, which is the lack of Columbic screening compared with traditional semiconductors as the relative permittivity of processible semiconductors are typically much smaller than that of traditional semiconductors. This is seen in terahertz spectroscopy that traditional semiconductors are typically opaquer than processible semiconductors. This leads to tightly bounded electron-hole pairs that tend to recombine instead of ionising.

1.1.1 Organic Semiconductors

Organic semiconductors have gained much attention recent years due to their solution processibility, massive scalability and potentially to be inkjet printable.¹⁻⁴ The downside is that charge carriers are strongly bounded by columbic attraction as the result of lack of screening due to low dielectric constants of organic materials compared with metals and traditional semiconductors.⁵ This is a problem for single-component organic photovoltaics (OPV) as the excited electrons have no reason to leave the vicinity of the vacancies (holes) and ultimately recombine.

One workaround of this problem is coupling the active material with electron acceptor material, which has lower energetic level than the donor material. This creates a donor-acceptor heterojunction with a driving force for electrons to travel to the cathode.^{6, 7}

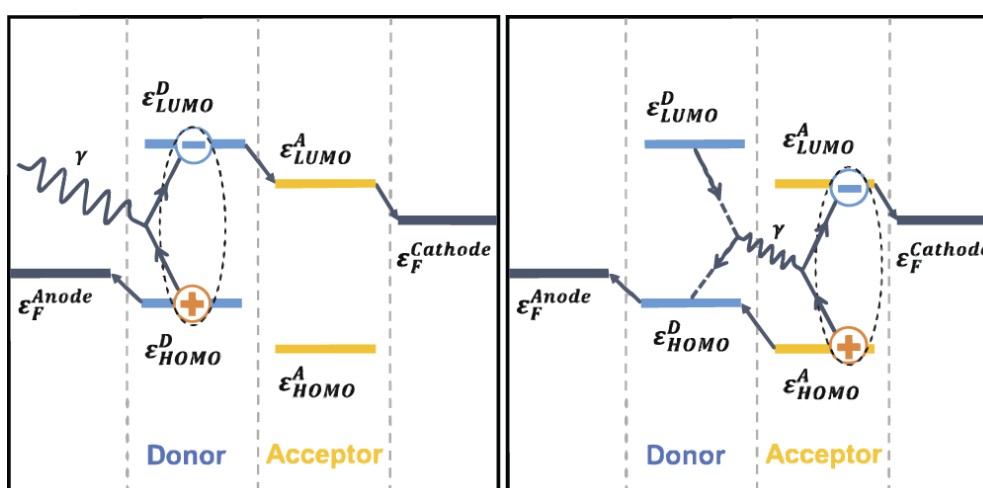


Fig. 1 Illustration of charge generation at donor-acceptor heterojunctions. (left) Excitation of donor by incident photon, followed by electron transfer to acceptor. (right) Excitation of acceptor by either incident photon or energy transfer, followed by hole back-transfer.

One popular acceptor material is functionalised fullerene derivatives,⁸ such as PC₆₁BM (6,6-phenyl-C61-butyric acid methyl ester) and PC₇₁BM (6,6-phenyl-C71-butyric acid methyl ester). They have relatively high charge carrier mobility and favourable charge transport properties,^{1-3, 8-10} but suffers from rigid energy levels, low absorption in the solar emission spectrum, few chemical modification options and environmental instabilities. This creates demand for alternative acceptor material (non-fullerene acceptors, NFA) that can be easily

chemically modified or even rationally designed. Donor-acceptor heterojunction research has shifted towards NFAs ^{2, 3, 11-20} including novel ternary blends¹⁹ and fullerene-NFA blends²¹.

The most favourable attribute of organic heterojunctions is perhaps the versatility of chemical modifications that freely alters the energetic landscape. Various organic building blocks can be used to construct donors or acceptors, typically fused-ring conjugated structures connected by conjugation-breaking sigma bond. One particular structure is “push-pull”, which incorporates electron donating and electron withdrawing groups to construct the donor-acceptor energetic levels.

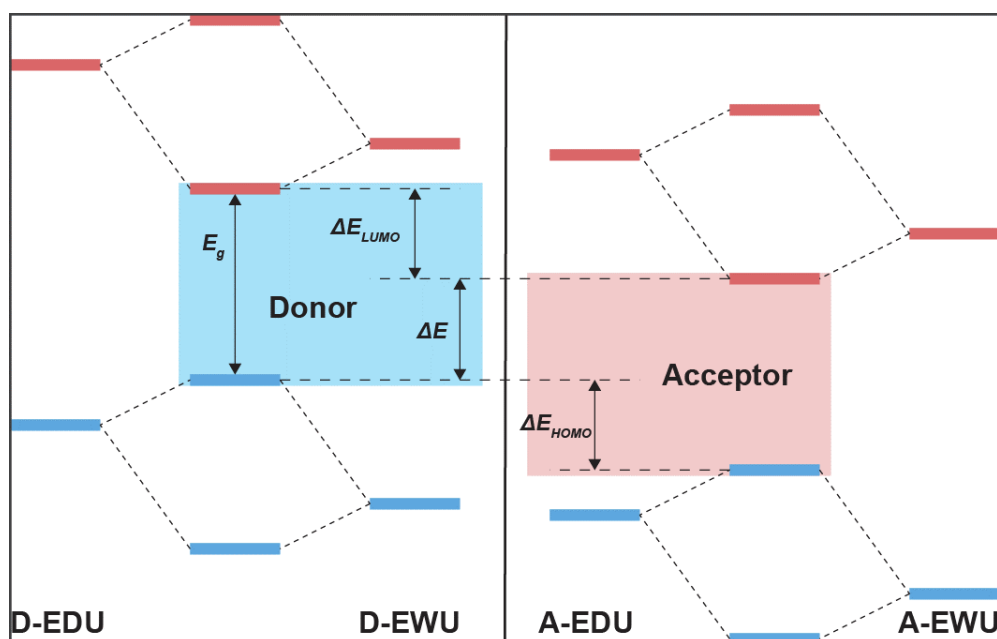


Fig. 2 Molecular orbital representation of the energetic landscape of the donor-acceptor heterojunctions with push-pull architecture on both donor and acceptor, where E_g is the bandgap, ΔE_{HOMO} / ΔE_{LUMO} is the energy offset required for charge transfer, and ΔE is the charge-transfer state energy.

As indicated in Fig. 2 the HOMO of the donor is mostly affected by the electron-withdrawing unit, and the LUMO of the acceptor is mostly affected by the electron-donating unit.

Therefore, utilizing more electron-withdrawing unit in the donor material “push-down” the conduction band edge, and more electron-donating unit in the acceptor material “pull-up” the valance band edge. This “push-pull” effect closes the bandgap, allowing more overlap with the solar spectrum, but at the cost of smaller driving force.

High energy photons from the solar spectrum create “hot” excitons that tend to relax to band edge before separation, losing excess energy to heat. However, some energy can be recycled

by singlet fission, which is a spin-allowed process that converts a high energy singlet exciton into two triplets, thus enhancing quantum efficiency. OPVs can be engineered to enhance singlet fission that recycles excessive energy from high-energy photons.^{22, 23}

1.1.2 2D Materials

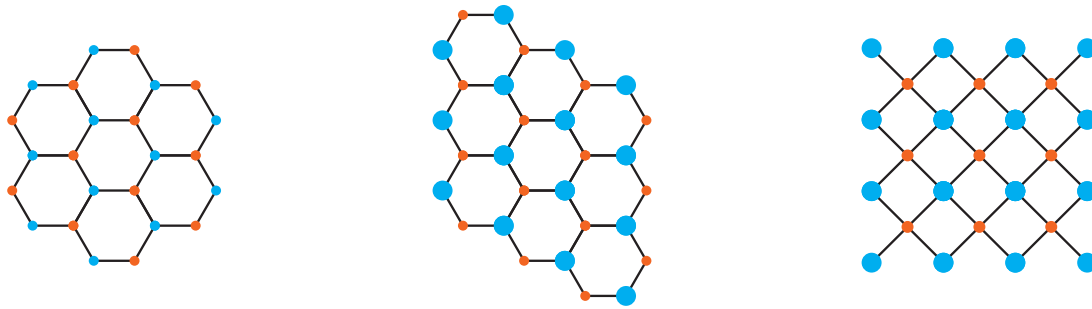


Fig. 3 Illustration of Graphene (left), TMD (middle), and MXene (right)

Quantum confinement can be achieved through reduced dimensionality. 2D materials²⁴ such as graphene²⁵⁻²⁷, transition metal dichalcogenides (TMDs)²⁸ and MXene^{29, 30} are single or few layers of stable and quantum-confined atoms, which exhibits exotic properties such as superconductivity³¹, spin-valley polarisation³² and abnormally high in-plane mobility^{24, 28}.

Graphene is single or few layers of carbon atoms arranged similar to that of graphite, and was discovered early this century²⁷ and soon became the most studied 2D material due to its gapless semimetal nature, and extremely high mobility with electrons drifting at relativistic velocity. In addition, the band structure can be tuned by doping and the graphene layers can be chemically modified. This leads to a wide range of electrical and electrochemical applications such as transistors³³, conductive composite polymers³⁴, lithium storage³⁵, supercapacitors³⁶, chemical sensors³⁷, and superconductors^{31, 38}.

MXene are atomic-thin transition metal carbides, nitrides and carbonitrides^{29, 30} synthesised by etching and exfoliating layered hexagonal ternary metal carbides and nitrides (MAX)³⁰, where etching removes “A” layers from MAX phase.

Low-dimension materials are not limited to those intrinsic to the dimension. Bulk materials can also be made into 2D (atomic thin), 1D (nano wire), and 0D (quantum dot).

1.1.3 Halide Perovskites

Halide perovskites are ternary metal halides (ABX_3 , where cation A can be either metallic or organic, B is a small set of bivalent metals³⁹ and X is halogen) with distinct orthorhombic octahedral cell structure that surrounds cation A within 8 adjacent BX_6 octahedra. They are semiconducting with direct bandgap ranging from roughly 1.2-2.5 eV depending on material composition and crystal structure³⁹.

Perovskites have been highly investigated for optoelectronic applications particularly in photovoltaics and light emission.⁴⁰⁻⁴⁷ For photovoltaics, perovskite solar cells (PSC) can achieve over 25% energy conversion efficiency.⁴⁸ The evolution of PSC from metallic cations to organic cations (hybrid perovskites) such as methylammonium (MA) and Formamidinium (FA), to mixed PSC (mixed elements for A, B, X), then double perovskites ($A_2B_2X_6$) has resulted in the jump of efficiency of PSCs more than 15% in the past decade,⁴⁸ and now comparable to the efficiency of Si solar cells.

One important challenge that PSC faces is energy loss due to non-radiative hot carrier cooling. Excitons created by excitation above bandgap are considered “hot” and readily give up excess energy by phonon emission, which eventually lost in heat. Unlike OPV, PSC cannot utilise singlet fission to recycle the excess energy, but other processes such as carrier multiplication and hot carrier extraction can be exploited to harvest the excess energy.

The time scale and mechanism of hot carrier cooling is important for devising strategies to mitigate thermalisation losses, and has been highly debated⁴⁹⁻⁵⁵. Recently, more sophisticated experiments have determined that the cooling is mostly modulated by carrier-carrier scattering and carrier-phonon scattering.⁵⁶⁻⁵⁸ In event of high carrier density, phonon density become rate-limiting, which is known as “hot phonon bottleneck”⁵⁴. Therefore, the fundamental physics of PSCs, namely the charge carrier transport properties warrant deeper investigations in order to facilitate rational design and material discovery.

1.2 Time-Resolved Spectroscopy

1.2.1 Light-Matter Interaction and Spectroscopies

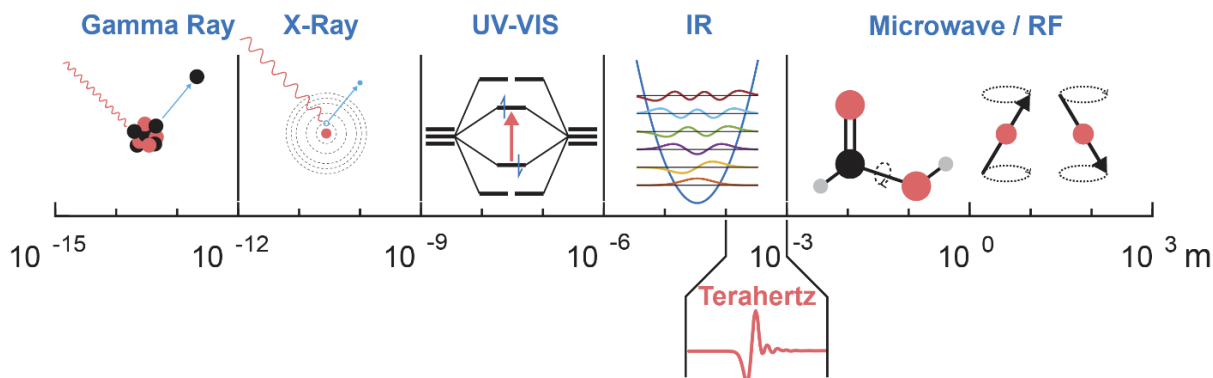


Fig. 4 Illustration of simple light-matter interactions. From left to right: (1) Neutron scattering by gamma-ray; (2) Core electron scattering and ionisation by x-ray (3) valance electron scattering and ionisation by ultraviolet and visible light; (4) vibrational excitation by infrared light; (5) rotational excitation by microwave; (5) Nuclear magnetic resonance RF.

The properties of optoelectronics are fundamentally governed by light-matter interactions, which can be directly investigated by spectroscopies. The spectra useful for optoelectronics spans from X-ray to radio frequency (RF). In this sub-chapter, the commonly used light sources and spectroscopies at each band of electromagnetic radiation are introduced.

1.2.1.1 Core Level Spectroscopies

X-ray radiation ionises core electrons leaving behind vacancies, which valence electrons are very eager to fill. X-ray photoemission spectroscopy (XPS) capture and measure the energy of emitted electron and thus determining the local molecular states.⁵⁹ The more sophisticated version of XPS, angle-resolved photoemission spectroscopy (ARPES) is capable of mapping the entire band structures. X-ray absorption spectroscopy captures emissions from the radiative process that valance electrons filling the core vacancy, which revels local symmetry and core-level potentials.⁶⁰

1.2.1.2 Electronic Spectroscopies

Ultraviolet and visible light do not have enough energy to ionise core electrons but they are able to manipulate energetic states of valance electrons, where chemical and most

optoelectronic processes occur. UV and visible light are the most abundant light sources and readily available from lasers, LEDs, arc lamps and incandescence sources. In semiconductors, visible light can promote charge separation by exciting electrons from valance band to conduction band, leaving behind vacancies (holes), which can be treated as particles just like the electrons in the conduction band. The UV-Vis spectroscopy measures absorption of light by the sample and is commonly used for determining energetic level transitions. Photoluminescence and electroluminescence spectroscopies promote carrier population by photoexcitation and electron injection respectively and the resultant emission is measured. In semiconductors, they are useful for determining band edge energies and calculating quantum yield of electron-photon conversion.

1.2.1.3 Vibrational Spectroscopies

Infrared light is available from lasers in near IR (NIR) range ($\lambda < 2\mu m$) and broadband infrared light can be generated from incandescence sources. IR light lacks the energy to excite ground states electron to anti-bonding states or conduction band, while their energy level falls within molecular vibrations and thus useful for vibrational spectroscopies such as IR and Raman spectroscopy. Steady-states IR directly probe the ground state vibrational structure often interpreted with local symmetry, and has the selection rule of $\Delta V = \pm 1$ where V is the vibrational quantum number, and requires non-zero polarity. This allows assignment vibrational signatures to particular ground states vibrational mode, which is very useful for chemical identification. Raman spectroscopy utilises inelastic scattering and works on non-polar molecules with non-zero polarizability. IR and Raman spectroscopy can be coupled with electronic transitions (resonant Raman spectroscopy) and/or rotational transitions (rotational-vibrational spectroscopy).

1.2.1.4 Rotational and Spin Spectroscopies

The light sources for microwave and RF drastically change from optical sources to electronic sources such as magnetrons and RF oscillators. At this region, light only have enough energy to excite ground rotational states and useful for pure rotational spectroscopy. Spin spectroscopies such nuclear magnetic resonance (NMR), nuclear quadrupole resonance (NQR) and electron paramagnetic resonance (EPR) also operate in microwave and RF region. They are useful for material identification by resolving spin-orbital couplings.

1.2.1.5 The Terahertz Gap

Light borderlines far IR (FIR) and microwave regions are notoriously difficult to generate and is sometimes called “the terahertz gap”. Terahertz radiation shares the properties of FIR and microwave, and thus it can be used for rotational spectroscopy and non-contact conductivity measurement.

Imagining with terahertz radiation is also a recent hot research topic.⁶¹⁻⁶⁴ Terahertz radiation is generally absorbed by conductors and can pass through insulating materials. Such contrast provides the basis of the imagining application. Like optical spectroscopy, near-field imagining can be applied to achieve sub-wavelength resolution.⁶⁵

In addition, due to the slow cycle of terahertz radiation, it is possible to collect discrete reflected wavelets (time-of-flight) that enables depth perception, and can be used to reconstruct interior structure of samples. This makes true tomography and holography possible with terahertz radiation.⁶⁴ With coherent terahertz radiation source, even ptychography, which produces super-resolution image with depth perception by deconvolution of coherent diffraction patterns, can be achieved, and has been gaining research attention in recent years.⁶⁶

1.2.2 Ultrafast Spectroscopies of Excited States Dynamics

While spectroscopies at most wavelengths are well-established for steady-states, excited states dynamics are much harder to access. Semiconductors exhibit their optoelectronic properties after carrier creation by either optical excitation or electrical injection. Their non-equilibrium states immediately after excitation decay rapidly. Insights into the behaviour of materials immediately after photoexcitation could give us fundamental understanding of the underlying physical processes, and thus not only deepen our understanding the fundamentals of condensed matter physics, but also enabling rational design of optoelectronic materials.

However, these processes are extremely fast, some changes of properties after photoexcitation last only picoseconds if not femtoseconds or attoseconds. Traditional recording of time-series events with clocked digital data acquisition, such as digital cameras, does not even come close to those time-scales. Time-resolved spectroscopies address this problem by exploiting the fact that we can repeat the excitation events rapidly at kilohertz rates for amplified mode-locked

laser, and megahertz rates for unamplified mode-locked lasers. The high repetition rate allows us to only take one snapshot per event, which is gated by ultra-short excitation and probe laser pulses. The difference in arrival time between these pulses, which can be controlled by altering their optical path lengths, gives us the time resolution needed.

Most spectroscopies mentioned in the last chapter have their time-resolved counterparts, but the light sources are severely restricted as time-resolved spectroscopies require coherent ultrafast light pulses. Ultrafast hard X-rays are usually obtained by free electron lasers (XFEL). High-harmonic-generation (HHG) is employed to generate soft X-ray and extreme ultraviolet (EUV). Visible and NIR light is readily available from mode-locked lasers, and supercontinuum in visible and NIR range is obtained by white light generation with ultrafast lasers. MIR can be obtained via differential frequency generation (DFG) from mode-locked lasers.

1.2.3 Transient Absorption Spectroscopy

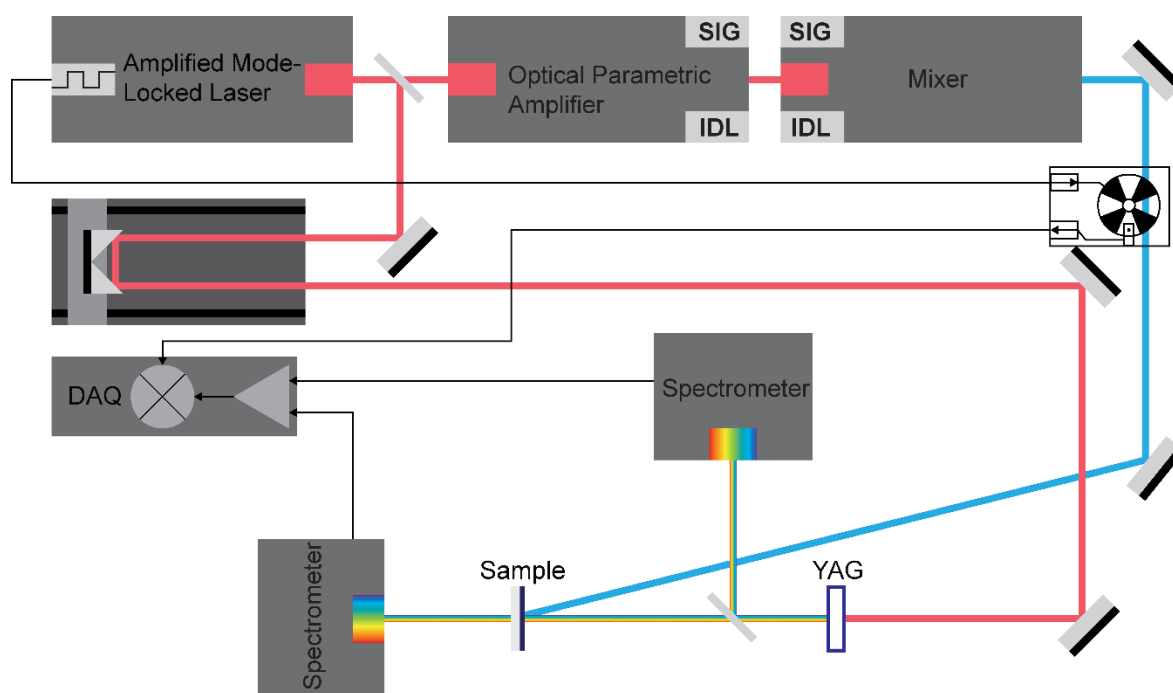


Fig. 5 Illustration of a typical pump-probe TAS system powered by amplified mode-locked laser.

Transient absorption spectroscopy (TAS) is the most popular and mature time-resolved spectroscopy due to its simple pump-probe scheme and only involving visible and NIR light, which is readily available from mode-locked lasers and optical parametric amplifiers (OPA).

The probe pulse is usually broadband white light generated by self-focusing of ultrafast laser pulses inside sapphire (visible band) or YAG (NIR band) crystals and detected by cameras or photodiode arrays. The probe pulse usually repeat at the laser repetition frequency and the pump pulse repeats at half of that. This allows us to capture alternating spectra of pumped and unpumped sample, and thus producing time-resolved differential absorption spectra.

TAS spectra contain rich information about quasiparticles such as excitons and polarons, as different quasiparticles have different spectral and temporal signatures. For example, quasiparticles have different contributions to ground state bleach (GSB), stimulated emission (SE) and photoinduced absorption (PIA) regions that are typically observed with supercontinuum probes. This will be further explained in the next chapter. Unfortunately, those signatures are all summed into a matrix with highly degenerate low-rank approximation, which is difficult to interpret. This issue will be addressed in chapter 5 with a novel method.

1.2.4 Time-Resolved Terahertz Spectroscopy

Terahertz radiation is electromagnetic radiation with frequency around 1 THz, and shares properties with far infrared and microwave radiation. The energy of terahertz radiation is not high enough to promote interband activities in most semiconductors. Instead, it behaves more wave-like in semiconductors acting as a transient electric or magnetic field passing through the medium. When it encounters charged particles, change of terahertz radiation waveform can be described by Maxwell equations, and thus allowing us to obtain the dielectric function of the material. The derivation is detailed in chapter 3.1.

However, the terahertz region is difficult to access as it cannot be generated from conventional or commonly available light or radio frequency generation methods. While terahertz radiation can be generated at high cost from synchrotrons, free electron lasers and quantum cascade lasers. Recent advancement in ultrafast mode-locked laser has enabled table-top generation of coherent single cycle terahertz pulses through optical rectification, photoconductive antenna and air-plasma.

The detection of terahertz radiation is even more challenging than generation, as its energy is too low to be visible to all types of photodetectors and its intensity, depending on the source, is usually too weak to be reliably detected by pyroelectric sensors. The detection of terahertz radiation utilises the inverse physical processes of the generation methods, for example, electro-optical sampling (EOS), air biased coherent detection (ABCD)⁶⁷, and photoconductive detection⁶⁸, which are the inverse processes of optical rectification, air-plasma emission and photoconductive emission receptively.

Terahertz spectroscopy has been gaining momentum recently due to its ability to probe conductivity and charge carrier mobility without electrical contact.⁶⁹⁻⁷² Measuring intrinsic conductivity or carrier mobility in semiconductor materials are complex tasks with electrical methods especially when reliable interference between electrode and substrate is difficult to establish. The free electric field of terahertz radiation can be used to probe semiconductor materials without contacts, producing reliable and reproducible results and allows access to dielectric response at terahertz range, which is impractical to measures with electrical methods.

Coupled with optical excitation, time-resolved terahertz spectroscopy (TRTS) is a powerful tool to study charge carrier dynamics in optoelectronic materials. The most rudimentary and popular application is optical-pump-terahertz-probe (OPTP), which is the terahertz analogue of pump-probe TAS.

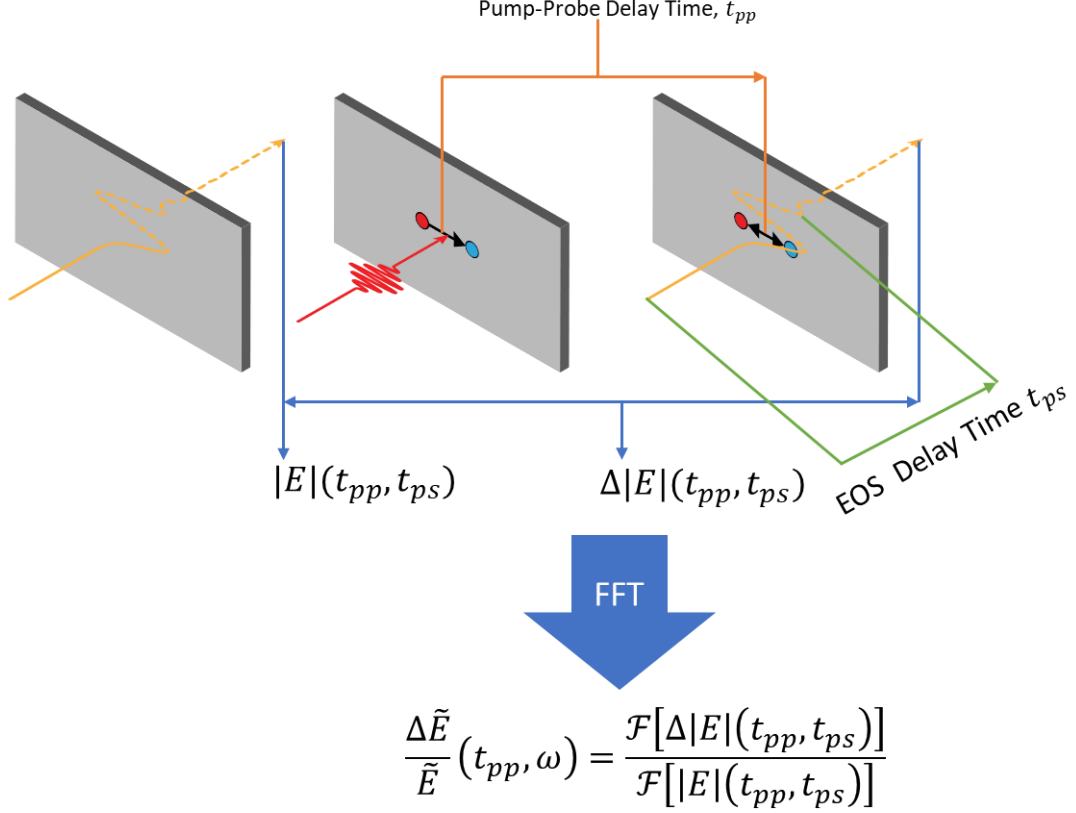


Fig. 6 Time-domain diagram for OPTP experiment. For each pump-probe delay, the terahertz pulse is scanned by the EOS beam.

TRTS becomes increasingly popular to study perovskites semiconductor properties.⁷³⁻⁸⁷ However standard TRTS is still inherently a pump-probe technique which suffers the difficulty interpreting the rising curve as its convoluted with various high-order physical processes and IRF. Tab. 1 shows general interpretations of supercontinuum probe, NIR probe, and terahertz probe. $\frac{\Delta T}{T}(t, \omega)$ is time (and frequency in the case of supercontinuum probe) resolved differential transmission recorded by pump-probe spectroscopies using visible-NIR probe. Signals produced by supercontinuum probes are broadband so they often include multiple quasiparticles. Therefore, it can be expressed as the sum of the population $N_i(t)$ weighted by their spectral signature $A_i(\omega)$. It has been demonstrated that NIR probe is sensitive to mobile carriers in perovskites.⁸⁸⁻⁹⁰ Thus narrowband NIR probe signals $\frac{\Delta T}{T}(t)$ is indicative to the population of mobile carriers N_{mobile} . In terahertz probe, the data obtained through Fourier transform of time-domain signals are differential complex electric field $\frac{\Delta \tilde{E}}{\tilde{E}}(t, \omega)$, which is

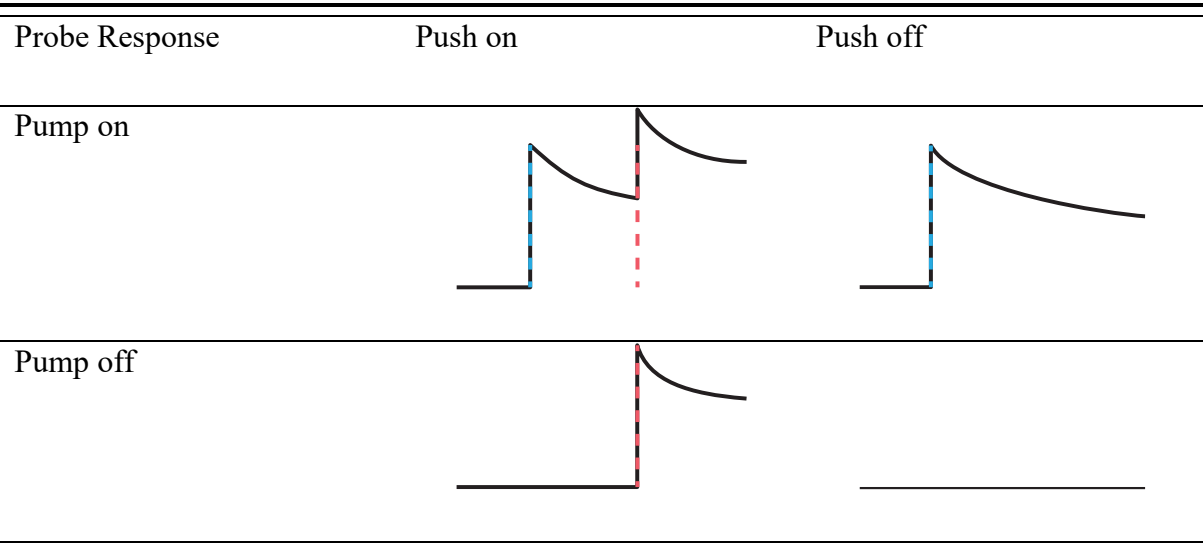
directly related to the photoconductivity $\Delta\tilde{\sigma}$ as shown in chapter 3.1. Intrinsic carrier mobility can also be calculated.

Probe type	Interpretations	
Supercontinuum probe: (TAS)	$\frac{\Delta T}{T}(t, \omega) \propto \sum_i A_i(\omega) N_i(t)$	Mixed population of excited electron quasiparticles
NIR probe:	$\frac{\Delta T}{T}(t) \propto N_{mobile}$	Population of mobile carriers (in perovskites)
Terahertz probe:	$\frac{\Delta \tilde{E}}{\tilde{E}}(t, \omega) \propto \Delta\tilde{\sigma}, \Delta\tilde{\sigma} \propto \mu$	Complex photoconductivity, mobility (proportional only in thin-films)

Tab. 1 Physical interpretations of probes in time-resolved spectroscopies.

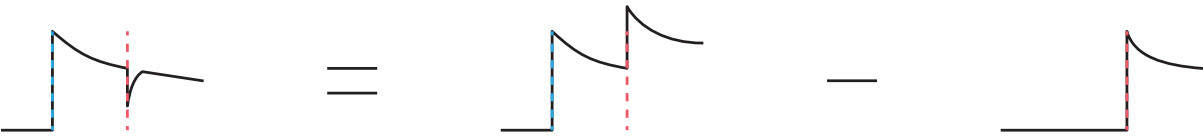
1.2.5 Pump-Push-Probe Spectroscopy

Recently, pump-push-probe (PPP) spectroscopy has become popular to study hot carriers as it does not rely on the initial photoexcitation to extract hot carrier dynamics.^{56-58, 91, 92} The additional push pulse, which is followed by the pump pulse after certain time delay, excites existing carriers to higher energetic states, effectively heating up carriers. The push pulse energy is selected to be much lower than the bandgap so the push excitation does not create additional carriers.



Tab. 2 Typical probe response to NIR push of processible optoelectronic martials in pump-push-probe spectroscopy. The push pulse illustrated here is intense enough to create new carrier population by MPA.

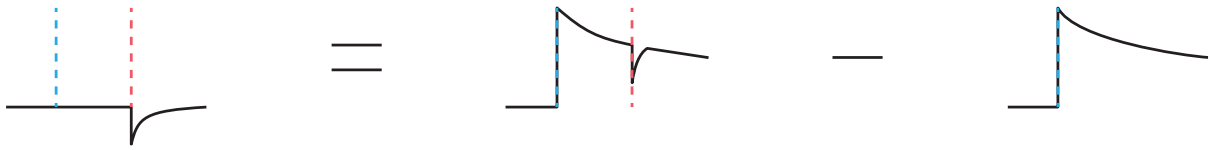
The PPP technique does come with challenges. As the push signals are typically small, NIR push pulse far more intense than the pump pulse is usually required to perform such experiments, resulting in significant multi-photon absorption artifacts (MPA). Therefore, careful modulation of the pulses with multiple optical choppers are required to extract emergent effect of the push pulse while subtracting the MPA. Firstly, the material response to pump and probe excitation can be extracted by subtraction the overall three-pulse signal with push-only signal.

$$\text{[Pump + Push + Probe Signal]} = \text{[Pump + Push Signal]} - \text{[Push-Only Signal]}$$


$$\Delta S_{\text{PumpPush}} = S_{\text{PumpPushProbe}} - S_{\text{PushProbe}}$$

eq. 1

Then, the emergent effect of the push excitation can be extracted by subsequent subtraction with pump-induced signal:



$$\Delta \Delta S_{\text{push}} = \Delta S_{\text{PumpPush}} - (S_{\text{PumpProbe}} - S_{\text{Probe}})$$

eq. 2

The NIR push tends to render carriers less absorptive to visible or NIR probe as the carriers are pushed deep into the band and became hot carriers. One other effect is stimulated emission or “dump” where the hot carriers undergo emissive recombination. Those two effects are easily distinguishable by observing the kinetics after push excitation. If the signal recovers, the hot carrier has emitted the excessive phonon and returning to the band edge. If the signal does not recover or flatlines then the carriers are lost. Those processes are not mutually exclusive, as partial carrier heating and partial stimulated emission has been observed in conjugated polymers.⁹²

PPP has been used to study hot carrier cooling in halide perovskites and it was discovered that interfacial hot carrier extraction can be much faster than hot carrier cooling.⁵⁷ A related technique is pump-push-photocurrent replacing the optical probe with photocurrent detection,^{93, 94} which is preferable in device physics investigation.

Multi-Pulse extension of TRTS can probe hot carrier cooling without interference from nonlinear processes. To this day, publications of Multi-Pulse TRTS are scarce.

1.3 THz Spectroscopy of Perovskites

Perovskites has been extensively studied with terahertz spectroscopies using OPTP method in the past decade.^{73-87, 95-99} In this sub-chapter studies for optoelectronic perovskites utilising OPTP of the past decade are reviewed in chronological order. The review will emphasis on their treatment of time and frequency resolution of photoconductivity obtained from OPTP.

1.3.1 Optical-Pump-Terahertz-Probe of Perovskites

One of the first OPTP study of perovskite in 2014 by C. Wehrenfennig, *et al.* from L. Herz group has determined carrier mobility of spin-coated hybrid mixed halide perovskite MAPbI_{3-x}Cl_x to be around 10 cm² V⁻¹ s⁻¹.⁸⁵ In the same year, the same group published the OPTP of the same material but vapor deposited, with carrier mobility around 30 cm² V⁻¹ s⁻¹.⁹⁵ The studies focused on recombination kinetics, which was analysed using a parametric model:

$$\frac{d}{dt}n = -k_1n - k_2n^2 - k_3n^3$$

eq. 3

The first order k_1 term represents monomolecular trap-assisted recombination, the second order k_2 term represents bimolecular recombination and the third order k_3 term describes high-order processes including Auger recombination. Their transport property was attributed to long diffusion length.

In 2015 temperature-dependent OPTP studies of perovskites were published.^{79, 96} C. La-o-vorakiat, et al. measured OPTP (50 fs, 400 nm excitation pulse) of MAPI at 15-285 K,⁷⁹ and fitted frequency-domain data with parametric Drude-Smith model eq. 4, which did not account for the peak features in the data.

$$\Delta\sigma = \frac{\varepsilon_0 \omega_p^2}{\Gamma - i\omega} \left(1 - \Gamma \frac{c}{\Gamma - i\omega} \right)$$

eq. 4

Where $\Gamma = 1/\tau$ is the scattering rate and τ is the mean free time between collisions. The plasmon frequency $\omega_p = \sqrt{\frac{e^2 n}{m}}$ is related to carrier density n and effective mass m . The c parameter is related to back scattering rate. eq. 3 was also used to analyse kinetics in this research. They concluded that the carrier diffusion length of MAPI is heavily affected by temperature-induced phase change through k_3 Auger recombination term, and low temperature at tetragonal phase perform best.

Similar research by R. L. Milot, *et al.* from L. Herz group with more comprehensive temperature and fluence dependent OPTP measurement (35 fs, 550 nm excitation pulse) from 8-370 K was published the same year.⁹⁶ They also adopted the three-order parametric model eq. 3. Both mobility and diffusion length decreases with temperature regardless of phases and the temperature dependence agrees with model that assume band-like transport limited by phonon scattering.¹⁰⁰ For frequency dependence, they quantified the likeness to Drude model by taking the L2 norm of the ratio between the real part and the modulus of the frequency-resolved complex differential transmission.

$$f_D = \frac{1}{N} \left\| \frac{\Re(\Delta T(\omega)/T(\omega))}{|\Delta T(\omega)/T(\omega)|} \right\|_2$$

eq. 5

Apparently, the imaginary part (AC contribution) was considered non-Drude. Using this criterion, they found that the frequency response is more Drude-like with increasing temperature.

In 2016, M. B. Johnston, *et al.* from L. Herz group published fluence-dependent OPTP measurement (50 fs, 550 nm excitation pulse) with vapour-deposited MAPbI_{3-x}Cl_x.⁷⁷ They

analysed the kinetics using eq. 3 and assumed only k_2 term recombination is radiative. Photoluminescence quantum yield was calculated using fitted rate constants and they concluded trap-assisted recombination k_1 is a significant energy loss pathway.

H. Yan, *et al.* performed fluence-dependent OPTP measurement (400 nm excitation pulse) with drop-cast MAPI.⁸⁶ They noted similar early-time dynamics for different fluences, which suggested absence of high-order processes, and found linear correlation between peak conductivity and fluence. They also measured OPTP with 800 nm excitation, which produced significantly slower decay compared with 400 nm excitation. They attributed first order decay rate measured with 400 nm and 800 nm excitations to surface and bulk recombination respectively. They fitted frequency-resolved conductivity with Drude-Smith model and found mean free time to be 5 ps.

In 2017 T. W. Crothers, *et al.* from L. Herz group measured fluence-dependent OPTP (400 nm excitation) on vapor-deposited MAPI films between 50 and 533 nm.⁷⁵ They observed photon recycling effect where the photons from radiative recombination are partially absorbed, resulting in slowed apparent recombination rate, as evidenced by that k_2 decrease exponentially with increasing film thickness. They proposed modified eq. 3 to account for photon recycling mediated by carrier diffusion.

$$\frac{\partial}{\partial t}n = D \frac{\partial^2}{\partial z^2}n + G - k_1n - k_2n^2 - k_3n^3$$

eq. 6

where z is the film thickness and G is the initial charge generation rate by photoexcitation to account for rising part of the carrier kinetics. Using this model, they were able to extract intrinsic k_2 for films of all thickness, and found them to be identical, which suggests bimolecular recombination rate is invariant from film thickness.

In the same year, exciton-phonon interaction in excited halide perovskites has been gaining interests. L. Lou, *et al.* performed OPTP (399 nm and 790 nm excitation) on solution-processed MAPI on PMMA substrate.⁸² They constructed a model consists of quantified excitonic Rydberg states transitions, phonon bleaching on top of Drude-Smith model to explain frequency

response of conductivity. While the fit to frequency-resolved conductivity is excellent, there are too many parameters in this model, and no regularisation terms were introduced nor the model cross-validated.

In 2018, C. L. Davies, *et al.* from L. Herz group performed temperature-dependent OPTP (400 nm excitation) of vapour-deposited FAPI at 100-300 K temperature, and compared with the MAPI counterpart.⁷⁶ They observed that the frequency-resolved photoconductivity with prominent phonon features at low temperature, but more Drude-like at 300 K. They also fitted temperature-dependent mobility of FAPI with power law and found $T^{-0.5}$ dependency, which is in agreement with Fröhlich electron-phonon coupling model. In contrast, MAPI exhibits $T^{-1.5}$ dependency.

The same year, M. Monti, *et al.* performed excitation-energy-dependent OPTP of $\text{Cs}_{1-x}\text{Rb}_x\text{SnI}_3$ from 470 nm to 790 nm, to study hot carrier dynamics.⁸⁴ They analysed the rising time of pump-probe data as a function of excitation energy and found that the rise is slower with higher excitation energy, which is plausible as the hot carriers require finite amount of time to cool down, *i.e.*, become more mobile and thus more visible to terahertz probe. They assigned excitation energy dependency of rise time to transitions inside the band structure of $\text{Cs}_{1-x}\text{Rb}_x\text{SnI}_3$ calculated by DFT, and concluded that the hot carrier cooling is strongly mediated by Fröhlich electron-phonon coupling.

In 2019, E. Cinquanta, *et al.* performed OPTP (790 nm excitation) on solution-processed CsPbBr_3 nanocrystal film.⁷⁴ The frequency-resolved conductivity exhibit obvious Lorentzian response and they found excellent fit with Drude-Lorentz model:

$$\sigma(\omega) = \frac{ne^2}{m_p} \frac{1}{\Gamma - i\omega} + \sum_m \frac{g_m \omega}{i(\omega_m^2 - \omega^2) + \Gamma_m \omega}$$

eq. 7

Where the second term accounts for Lorentz oscillations associated with phonon modes. Their findings quantitatively illustrated strong Fröhlich electron-phonon interaction with Lorentzian harmonic approximation.

Y. Lang, *et al.* utilised ultra-broadband OPTP (band edge excitation, up to 10 THz presented in data, generated by air-plasma with ABCD) ⁸⁰ to directly observe coherent lattice motion in MAPbI₃. In addition to TO phonon oscillation at 1.2 THz, they also observed coherent oscillation in time-domain at around 7.5 THz. They detrended then Fourier transformed the kinetics and found oscillation centred at 3.7 THz associated with LO phonon.

Mixed-ion PSC has been gaining attention since 2019. D. Zhao, *et al.* measured temperature-dependent OPTP (790 nm excitation, 15 K, 65 K, 285 K) of FA_{0.85}CS_{0.15}Pb(I_{0.97}Br_{0.03})₃ film. ⁸⁷ They fitted the frequency-resolved conductivity measured at 15 K with Lorentzian function and found TO phonon modes at 0.88 THz and 1.76 THz, and LO modes at 1.15 THz and 3.57 THz (extrapolated). They modelled the kinetics via eq. 3 enhanced with spectral weights and explained the charge carrier dynamics with phonon absorption and phonon emission via two LO phonon modes.

In 2020, M. Monti, *et al.* measured composition-dependent TAS and OPTP of Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb_xSn_{1-x}I₃ (x=1.0, 0.5, 0), ⁹⁷ and fitted the kinetics with dual-exponential (excitation and recombination) model. They analysed the rise times and concluded the hot carrier has high mobility comparable to cold carriers.

A. M. Ulatowski, *et al.* from L. Herz group performed fluence-dependent OPTP (400 nm excitation) on solution-processed MAPbBr₃ films ⁹⁸ to investigate the effect of doping with bismuth (0.1%, 0.5%, 1%, 5%), which is intended to induce more trapping states. They fitted the kinetics with modified eq. 3 excluding the second-order and third-order terms, and treating the electron and hole conductivity separately (mathematically a biexponential fit) even though OPTP cannot discriminate contributions from electrons and holes. They found the electron contribution to the first-order kinetics is independent from Bi doping, but the hole contribution to first-order recombination rate increases with Bi doping. The carrier mobility significantly dropped with Bi doping at 0.1% but remain constant after that. They concluded that Bi doping enhance carrier trapping by inducing energetic disorders.

In 2023, H. Zhang, *et al.* performed fluence-and-temperature-dependent OPTP (400 nm excitation) of various lead halide perovskites (MAPbI₃, CsPbBr₃, γ -CsPbBr₃) from 78 K to 286 K. ⁹⁹ They found that late carrier conductivity (from late-time kinetics, 80 ps) for all three samples saturates with increasing excitation density (from fluence). The saturation carrier densities agree with the Mott polaron density from Feynman polaron model. For γ -CsPbBr₃,

the saturation carrier densities are in good agreement with Mott polaron density from 78 K to 286 K, which increase near linearly with temperature. They attributed the phenomenon to Mott polaron transition and thermal disorder at high temperature inhibits phonon emission. They fitted the frequency-resolved conductivity (0.2-1.6 THz) with Drude model and found out that the mean free time decreases with excitation density and remain constant after Mott polaron density. They concluded that Mott polaron state protects carriers from recombination and thus the existence of saturation carrier densities.

From the publication history we can see the understanding of photophysics of halide perovskite photovoltaics evolved from complete denial of excitonic and polaronic coupling to more sophisticated models that acknowledge and account for those effects. Recently the reports of long-lived (>100 ps) hot carriers in halide perovskites have gained much research attention.^{[49-55, 97](#)}

However, most OPTP studies of perovskites heavily favours the use of eq. 3 and its variations (usually with more parameters) to analyse carrier dynamics, which may not be statistically suitable as the model is obviously far too general and over-parametrised. For frequency-dependent conductivity, the use of Drude-Smith model eq. 4 is heavily favoured. While Drude model explains metallic conduction and some traditional semiconductors well, its applicability in processible semiconductors is questionable, especially nanomaterials where quantum confinement kicks in.

On the other hand, with the exact physical model being unknown beforehand there is not much choices in modelling kinetics. Conjectures were used to refine models which yield results, but it is questionable that the fitted results justify the conjectures, especially when the models were never cross-validated. To address this problem, more sophisticated experiments need to be designed in order to overcome the model over-fitting problem, and provide clearer picture of underlying photophysics.

1.3.2 Pump-Push-Probe TRTS of Perovskites

In 2021 we published one of the first pump-push-probe TRTS to study hot carrier dynamics of halide perovskites¹⁰¹, which is presented in chapter 4. Two more studies utilising PPP-THz were independently published around the same time.

H. Zhang, *et al.* performed optical-pump-infrared-push-terahertz-probe (400 nm pump, 800 nm push, ~ 8.2 ps pump-push delay to ensure complete thermalisation of initial hot carriers) on solution processed $\text{Cs}_2\text{AgBiBr}_6$ (bandgap 571 nm) to study hot carrier dynamics.¹⁰² They observed increased conductivity upon push and thus suggested highly mobile hot carrier. They fitted the frequency response of conductivity with Drude-Smith model eq. 4 and the frequency-dependent conductivity appeared to be Drude-like within 0.2-1.6 THz window. In time-domain, upon push excitation, the mean free time reached 150 fs with $c \approx -1$ parameter. The mean free time remain constant after 2 ps ($\tau \approx 50$ fs, $c \approx -0.63$). Therefore, they attributed the high mobility of hot carriers to efficient ballistic transport (low collision rate).

A. M. Ulatowski, et al. from L. Herz group reported PPP-THz (800 nm pump, 1450 nm push) study of $\text{FA}_{0.83}\text{Cs}_{0.17}\text{SnI}_3$ thin film.¹⁰³ They found linear relationship between time-domain peak push-induced photoconductivity and push excitation density. They further performed push-energy-dependent PPP-THz from 1200 nm to 2000 nm, and fitted the post-push recovery curve with Gaussian-convoluted mono-exponential decays, whose lifetime increases with decreasing push energy. They argued that carrier cooling is dominated by carrier-carrier scattering as opposed to carrier-phonon scattering, in which case the cooling would slow down with increasing push energy. They fitted the frequency-resolved push-induced photoconductivity with Drude model, despite the clear presence Lorenz oscillator in the 0.5-2.5 THz frequency range.

H. Zhang, *et al.*'s work excellently demonstrated Drude response from 0.2-1.6 THz of $\text{Cs}_2\text{AgBiBr}_6$ film photoconductivity and the mean free time retrieved from each time slice after push excitation corresponds well with highly mobile hot carrier theory. Their choice of push excitation (800 nm, fundamental harmonic of Ti:Sapphire mode-lock laser) energy is quite different from our measurement with 2000 nm.¹⁰¹ Also, the material system is double perovskite while our system is hybrid metal halide perovskites. While we employed similar novel technique (THz-PPP), our results are opposite to each other. Further investigations, potentially a cross-experiment with double perovskite pushed at 2000 nm and MHP pushed at

800 nm, are required to explain the exact nature of the change in photoconductivity upon push excitation.

1.4 Research Objectives

1.4.1 Part 1: Construction of a TRTS System with PPP-THz Capability

TRTS is a powerful tool to study charge carrier dynamics, but the OPTP technique has limitations that make analysing data difficult. The first part of the thesis objective is described in detail in chapter 2. In addition, validation of the setup by preliminary experiment with graphene is included in chapter 3.

1.4.2 Part 2: Studying Hot Carrier Dynamics of Halide Perovskite with PPP-THz

The PPP-THz capable TRTS setup construct in Part 1 will be used to investigate hot carrier dynamics of halide perovskites (chapter 4). The PPP technique greatly simplifies modelling of conductivity kinetics during hot carrier cooling, allowing models with fewer parameters and assumptions to be applied to the conductivity kinetics.

1.4.3 Part 3: Developing non-Parametric Model-Free Analysis Software for Time-Resolved Spectroscopy Data

A part of the thesis project is to develop a GUI software for exploratory, non-parametric and model-free analysis of high-dimension time-resolved spectroscopy data, which is described in chapter 5. Unfortunately, phase-aware analysis (processing complex data without separating real and imaginary part) is not within the scope of this project, and thus does not directly benefit TRTS experiment. However, other time-resolved techniques often accompanying TRTS, such as TAS and 2DES benefit greatly from such analytic approach.

2 Construction of Multi-Pulse Time-Resolved Terahertz Spectroscopy System

In this chapter, the construction of a multi-pulse TRTS system is described. The TRTS setup consists of three subsystems: the optical system, the electronic system and the control system, which are introduced separately.

The optical system is the physical optics setup on the optical table, including a 35 fs amplified Ti:Sapphire mode-locked laser, two OPAs, and a compact THz radiation generation and detection system.

The electronics system contains a half-bridge driver providing bias to the photoconductive antenna while synchronised with the laser pulses, and a quadrature decoder that processes positional data from the delay stage on-the-fly and sends the data to DAQ with very low latency.

The control system is mostly software that handles scanning schedules and real-time signal processing concurrently. It also handles inter-instrumental communications on hardware level, and together with the optical and the electronic system forms an all-hardware-triggered control loop.

The TRTS setup is designed for fast acquisition rate by using a synchronous-continuous scanning scheme as opposed discrete single value acquisitions. It also minimizes any overhead by utilizing hardware communications instead of software APIs wherever possible. The performance of the TRTS setup is also evaluated.

The goal of this chapter is to provide reproducible construction of a multi-pulse TRTS system. Researchers with reasonable optical, electronic, and software engineering background should be able to reproduce the multi-pulse TRTS system with information in this chapter.

2.1 Overview

To address the challenges in time-resolved spectroscopic measurement outlined in chapter 1.3, a novel multi-pulse time-resolved terahertz spectroscopy setup was developed as part of this thesis, which incorporate an additional infrared pulse to manipulate charge carrier temperature after the initial photo-excitation (PPP-THz). This is essentially the broadband terahertz probe analogue of previously used Vis-pump-IR-push-IR-probe spectroscopy, except the terahertz probe itself requires an additional delay line and modulation for EOS detection. Thus, PPP-THz is technically a quad-pulse, triple-delay, dual-modulation setup, which is challenging to implement.

Implementing additional pulses increases the measurement time drastically due to SNR issue in the push-induced signal. Lengthy measurement often degrades the sample before the measurement is completed, which is a serious problem as one cannot distinguish spectral features caused by sample degradation from intrinsic features. Therefore, a fast, well-optimised setup is needed to perform such task.

With the above-mentioned objectives in mind, the setup should be able to perform PPP-THz experiment with enough SNR for halide perovskite samples. The setup should have at least 100 ps temporal range and 0.5-2.5 THz frequency range in order to produce data comparable to most of the literature (chapter 1.3). In addition, the setup should support OTP experiment, and switching to OTP configuration should be trivial for streamlined measurements of different samples. Finally, the data acquisition should be as fast as possible to avoid sample degradation during the experiment.

In this chapter, the detailed construction of a fast, reliable, and highly autonomous multi-pulse TRTS system is described. The setup features automatic scanning and bandwidth control and continuous synchronous acquisition mechanism which are explained in detail in this chapter. The setup consists of three subsystems: optical system, electronic system and control system.

2.2 TRTS-Optical System

2.2.1 Terahertz Radiation Generation and Detection:

Generally, there are three well-known methods available for terahertz generation with mode-lock pulsed laser: Optical rectification in non-linear crystals, air-plasma, and photoconductive antennae.^{24, 72} The first two methods require substantial power ($>1\text{mJ}$ in general) which is not available in this particular setup, as the majority of the power is permanently fed into two OPAs responsible for generating excitation pulses. Therefore, this TRTS system opts for photoconductive antenna for terahertz radiation generation. A commercially available (TeraSed) LT-GaAs antenna with 1cm^2 square active area was chosen.

Since the terahertz pulse field strength is limited by the antenna, the most sensitive coherent terahertz radiation detection method available was chosen, which is electro-optical sampling (EOS) using a ZnTe crystals which has highest electro-optical constant. The downside is that ZnTe has strong absorption near 3 THz, at which the bandwidth of the TRTS is clamped.

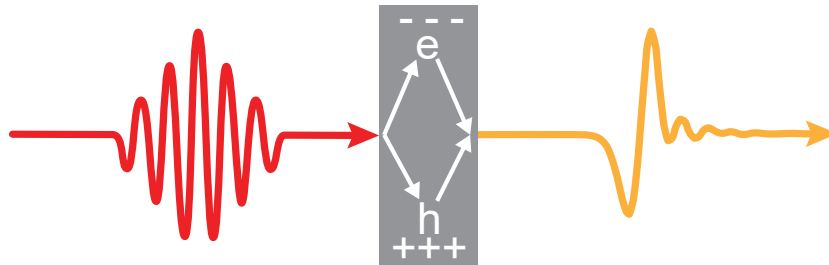


Fig. 7 Illustration of terahertz pulse generation by biased PCA through coherence transfer from the 800 nm pump laser.

The single cycle terahertz pulse is generated by a photoconductive antenna (TeraSed). The antenna is made of low-temperature-grown GaAs (LT-GaAs), which has large amounts of defects. When bias voltage is applied and the antenna is illuminated by fs-pulse, the excited charge carriers undergo trap-assisted recombination with lifetime close to 1 ps. This in turn emits terahertz radiation peaked around 1 THz. The GaAs also blocks the 800 nm beam eliminating the need for filtering afterwards. The PCA is tested up to 40V bias voltage. In

amplified mode-locked lasers, the laser spot should cover as much area of the PCA as possible, while not exceeding saturation pulse energy.

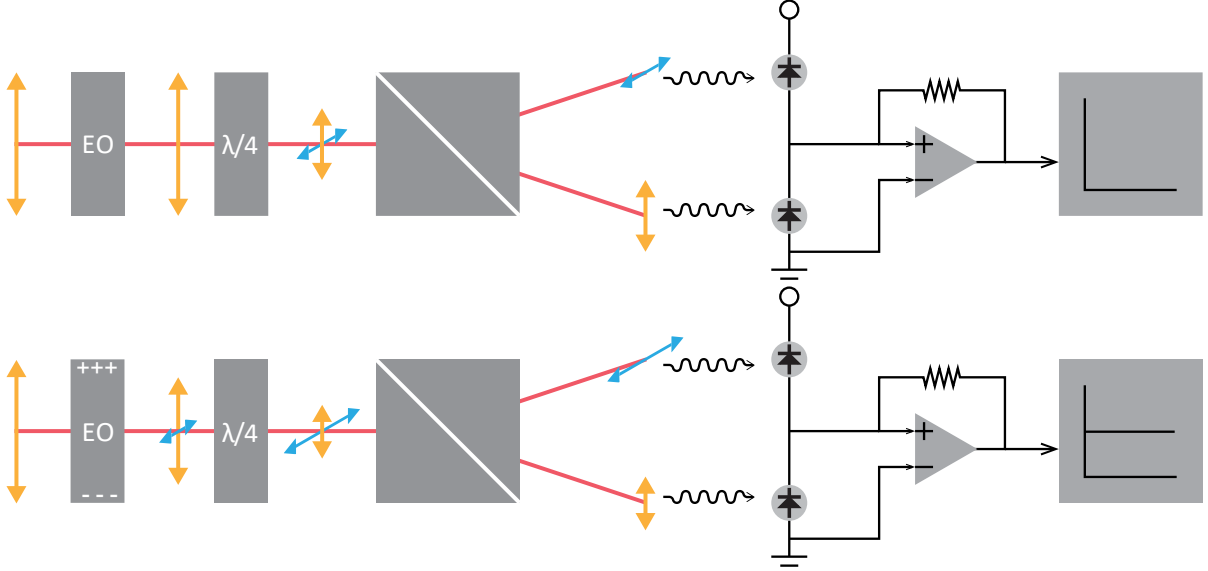


Fig. 8 Illustration of EOS detection method with balanced photodiodes. Upper row: calibrated EOS with zero differential photovoltage. Lower row: EOS producing differential photovoltage when the EO crystal is polarised by the electric field from the terahertz pulse.

The single cycle terahertz pulse is detected by electro-optical sampling (EOS). An 800 nm sampling beam is made colinear to the terahertz beam and both are focussed onto a 0.5mm thick ZnTe crystal. When the EO crystal is exposed to electric field by the terahertz pulse, its birefringence changes and rotates the polarisation of the passing 800 nm pulse. This phenomenon is well-known as the Pockels effect. The 800 nm sampling pulse then pass-through a quarter-wave plate (QWP) and a polarising beam splitter where its orthogonal components are spitted into two beams. The two orthogonal beams are then sent into a balanced photo diode with transimpedance amplifier. The differential voltage produced by the photo diode is proportional to the terahertz pulse electric field strength.

The quarter-wave plate calibrates the detection system by producing a static polarisation rotation. When the terahertz pulse is not present, the QWP should be rotated so that the balanced photodiodes produce the same voltage, and thus the differential output should be net zero.

2.2.2 Optical-Pump-Infrared-Push-Terahertz-Probe Configuration

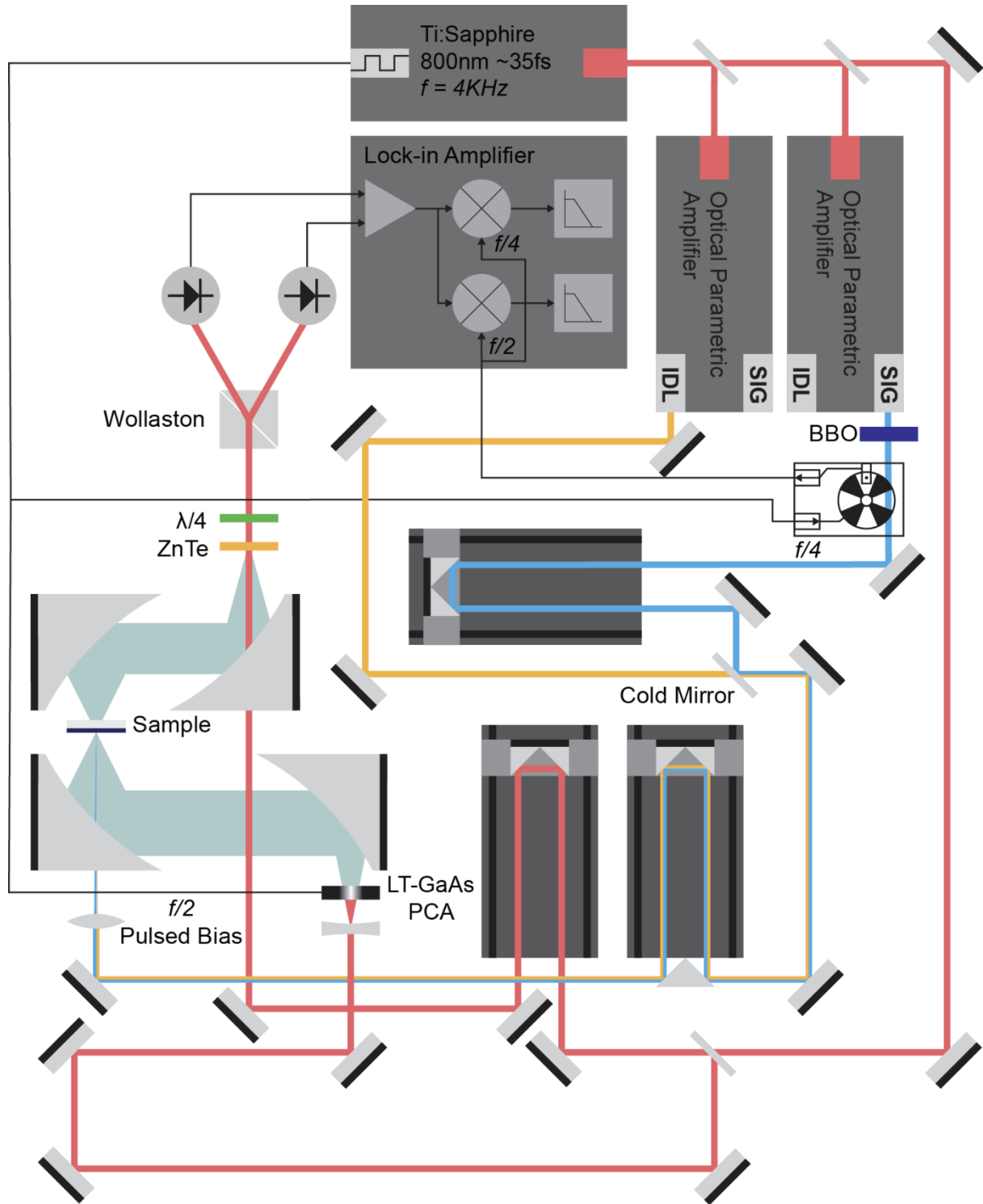


Fig. 9 Simplified diagram of the multi-pulse TRTS setup. The TRTS system is entirely powered by a 35-fs amplified Ti:Sapphire laser (Coherent Astrilla) with fundamental harmonics centred at 800 nm.

2.2.3 Multi-Pulse Signal Modulation

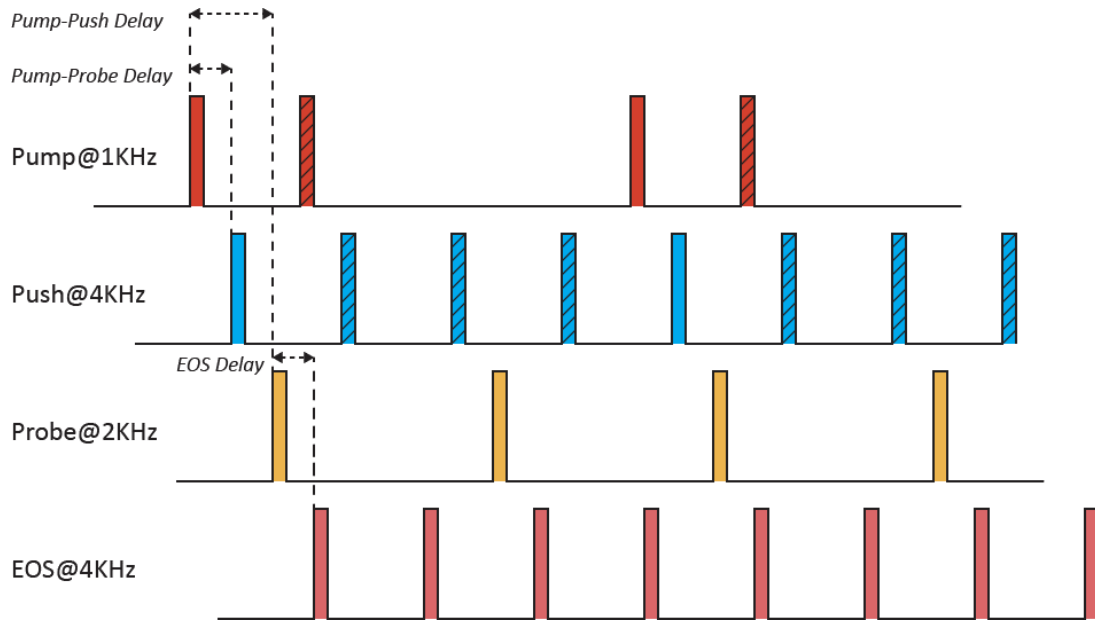


Fig. 10 Signal Modulation for multi-pulse TRTS. The push and EOS pulse repeats at $f = 4\text{KHz}$ which is the repetition rate of the amplified mode-locked laser. The probe pulse (THz) is modulated at $f/2$ electronically by the antenna driver. The pump pulse is modulated mechanically at 1 KHz. Unneeded pulses are marked in slashes.

In multi-pulse mode, 4 pulses need to be synchronised and modulated to ensure the acquisition of push-induced spectra change. The fastest repetition ($f = 4\text{KHz}$) pulse should be the EOS since it is used to detect the terahertz pulses, which repeat at half of the EOS frequency ($f/2$). The terahertz pulse is the probe in the pump-push-probe topology, and thus the pump pulse repeats at half of the terahertz probe frequency ($f/4$). Due to the 50% duty cycle of the mechanical chopper, a second pump pulse is allowed through, but it does not affect the signal because it arrives after the current probe, and is too far away from the next probe.

The push pulse can be left as-is at f because it only affects the signal when probe pulse is present. This modulation scheme is the simplest and only requires one optical chopper, while producing MPA-corrected pump and push response (eq. 1). The down side is that the sample is exposed to increased thermal load from unneeded pulses, which can be alleviated by using 25% duty chopper blade on the pump line, and adding a 25% duty chopper to the push line. However, this will make the timing exceedingly more complex as the choppers have to be phase-correct with much lower margin.

Complementary OTP is optional to retrieve emergent push effect (eq. 2). However, since the push effect is much faster than the recombination, it can be retrieved by software detrending without the need to perform complementary OTP.

2.2.4 Lite mode (OTPT) Configuration

When multi-pulse extension is not needed, the TRTS setup can be switched to lite mode that is powered entirely by a single 800 nm source. In lite mode, part of the 800 nm input beam is split and doubled by a pre-cut BBO crystal ($\Theta = 29.2^\circ$ $\Phi = 90^\circ$) into 400 nm beam, which is used to excite the sample. The setup can be switched to lite mode simply by placing a beam splitter on a magnetic mount and tick the box in the controlling software, which automatically reconfigure itself to the accommodate lite mode.

mechanical stage, then decode and send them to the DIO of the lock-in amplifier. The antenna driver applies biased to the PCA when needed (when there is laser pulse).

2.3.2 Photoconductive Antenna Driver

The photoconductive antenna (PCA) responsible for generating the terahertz pulse is driven by low-duty pulses at half of the laser repetition frequency. This approach has two major benefits: (1) Optical chopper on the terahertz beam is not needed. (2) The pulsed bias voltage can be much higher than constant bias voltage while only producing a tiny fraction of thermal dissipation power (TDP).

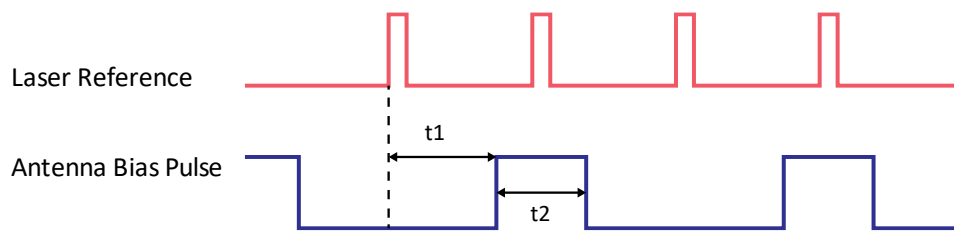


Fig. 12 Timing diagram of PCA driver synchronised with pump laser pulse. The delay parameters $t1$ and $t2$ ensures the pump pulse is inside the driving envelope while ensuring the envelope is as small as possible to reduce thermal stress on the antenna.

The bias voltage pulses are synchronised to the laser with the laser beam appearing at the centre of the pulse. The driver adopts push-pull topology to ensure that any remaining charge is drained during off-time and allows the driving pulsed to be ground-referenced as opposed to single N-FET low side switching, which would create an additional ground plane that needs to be insulated.

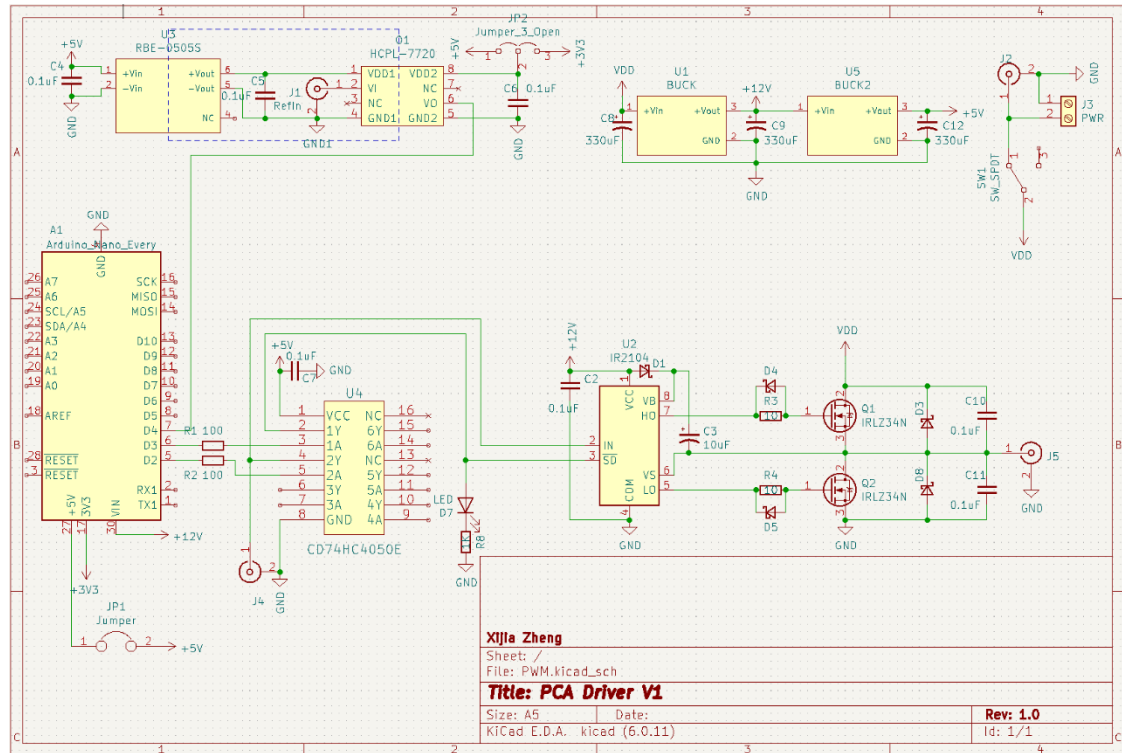


Fig. 13 Circuit diagram of the PCA driver.

The PCA driver is a piece of home-made electronics designed solely by the author of this thesis. The board is a carrier for Arduino Nano series boards, and carries an ATmega4809 (Arduino Nano Every) by default but compatible to all Arduino Nano series boards. The driver is synchronised with the laser reference, and operates at half of the laser repetition frequency. The PCA driver consists of 4 stages to produce the desired waveform:

Input Stage

The input stage contains a dual-supply opto-coupler and an isolated SMPS to power the input side of the opto-coupler. The high input impedance of the opto-coupler and galvanic isolation protect the laser reference, with only 10uA maximum current draw.

Digital Stage

The output of the opto-coupler is fed into an on-board microcontroller for frequency division, duty adjustment and phase shifting. The laser reference frequency is halved and shifted so that the reference pulse overlaps with the next laser pulse. Arduino nano series microcontroller boards are supported. Since the repetition of the amplified laser is rather slow compared with

the clock of the microcontrollers, software PWM was used for ease of implementation. However, should the need of MHz repetition laser arise, the timing can be offloaded to timer/counter peripherals of the microcontrollers.

Switching Stage

The digital signal needs to be amplified to drive the antenna. A Push-Pull topology with two N-MOSFETs was selected for high driving capability and allowing coupling the driver to earth ground. The MOSFETs are driven with a floating-channel gate-driver (IRS2104) with digital inputs fed by the microcontroller.

Output Stage

The output stage contains a snubber network to minimise switching noise.

Power Supply

Three power rails with different voltages are required for the operation of the antenna driver. The MCU operating voltage, either 3.3V or 5V; The NFET gate-driving voltage, typically 10-15V for a MOSFET to fully open ($R_{DS\ on} \rightarrow \min.$); The antenna bias pulse voltage: 20-40V.

The driver was designed to run on single supply for ease of operation. A BUCK module is used to convert antenna driving voltage to 12V, suppling the gate driver and the half-bridge. It also supplies the MCU board, which has integrated BUCK or linear regulator. Both 3.3V and 5V MCUs are supported on the driver.

2.3.3 Synchronous Continuous Data Acquisition

Ideally, data acquisition for experiments with mode-lock pulsed lasers, which are low duty square-wave modulated, should be discrete. For example, a boxcar can be programmed to sum the discrete pulses signal at each pulse window. However, instead of discrete DAQ, the use of lock-in amplifiers, which is intended for continuous sinusoidally modulated signals, is popular because they seemly produce better apparent SNR, while the users are often unaware of the consequences of aggressive low-pass filters integrated in the lock-in amplifiers.

Since observing the sharp rising edge following photoexcitation is a common objective of time-resolved spectroscopy, inappropriate programming of data acquisition software can introduce huge IRF, rendering the observation, and subsequent model fitting inaccurate if not inadmissible. In point-by-point signal acquisition scheme with lock-in amplifiers, sufficient time should be allowed to pass in order for the low-pass filter to settle. For example, for a third order low-pass filter to settle 90%, 6 times the time constant should be allowed to pass before measuring the next point. This makes lock-in amplifiers especially slow with pump-probe type experiment where infinite bandwidth is required.

During the construction of the multi-pulse TRTS setup, the time frame does not allow programming a DAQ or FPGA from scratch, and an existing lock-in amplifier is ready to use. Therefore, the data acquisition of the TRTS setup must be based on the lock-in amplifier.

Fortunately, while measuring time-domain terahertz signal, contentious acquisition of samples is possible because the terahertz spectrum has finite bandwidth, and thus the time constant of the lock-in amplifier's lowpass filter can be set to match that bandwidth. The continuous synchronous acquisition method is superior than discrete points acquisition in terms of acquisition speed and signal quality, as the software correctly compute acquisition low-pass filter and sampling frequency.

Let f_{TDS} to be the bandwidth of the terahertz pulse, v to be the velocity of the mechanical stage, q to be the mechanical-to-optical delay coefficient, and f_{NEP} to be the lock-in amplifier low pass filter bandwidth in noise equivalent power:

$$q = \frac{\tau}{L} = \frac{2}{c} \quad v = \frac{L}{t} \quad f_{TDS} = \frac{1}{\tau}$$

eq. 8

Where L is the traveling distance of the delay stage during a TDS scan, v is the velocity of delay stage, τ is the theoretical time-domain sampling period and t is the real sampling period at the cut off frequency f_{cut} . The cut off frequency can be calculated as:

$$f_{Cut} = \frac{1}{t} = \frac{v}{L} = \frac{qv}{\tau} = qvf_{TDS}$$

eq. 9

The low-pass filter cut-off frequency represented by noise-equivalent power f_{NEP} must be sufficiently large than the calculated cut-off frequency. The sampling frequency should be considerably larger than twice of the low-pass cut-off frequency (super-sampling) to suppress aliasing.

$$f_{NEP} \gg f_{Cut} \quad f_s \gg 2f_{NEP}$$

eq. 10

2.3.4 TRTS-Mechanical Stage Decoder

However, the continuous acquisition of data needs to be interpolated against a time-domain reference. In interferometry, this is typically acquired from the interferogram of a reference laser with known wavelength. TDS-THz could adopt this approach but the complexity of the optical construct will increase significantly. Alternatively, the time domain reference can be obtained directly from the quadrature encoder of the mechanical stage, which has 32-bit resolution. The lock-in amplifier also has mixed-signal ability with 32 digital channels that can be used to received 32-bit data. A 32-bit quadrature decoder (QDEC) board is designed to convert raw encoder pulses to 32-bit positional data and send it to the DIO of the lock-in amplifier.

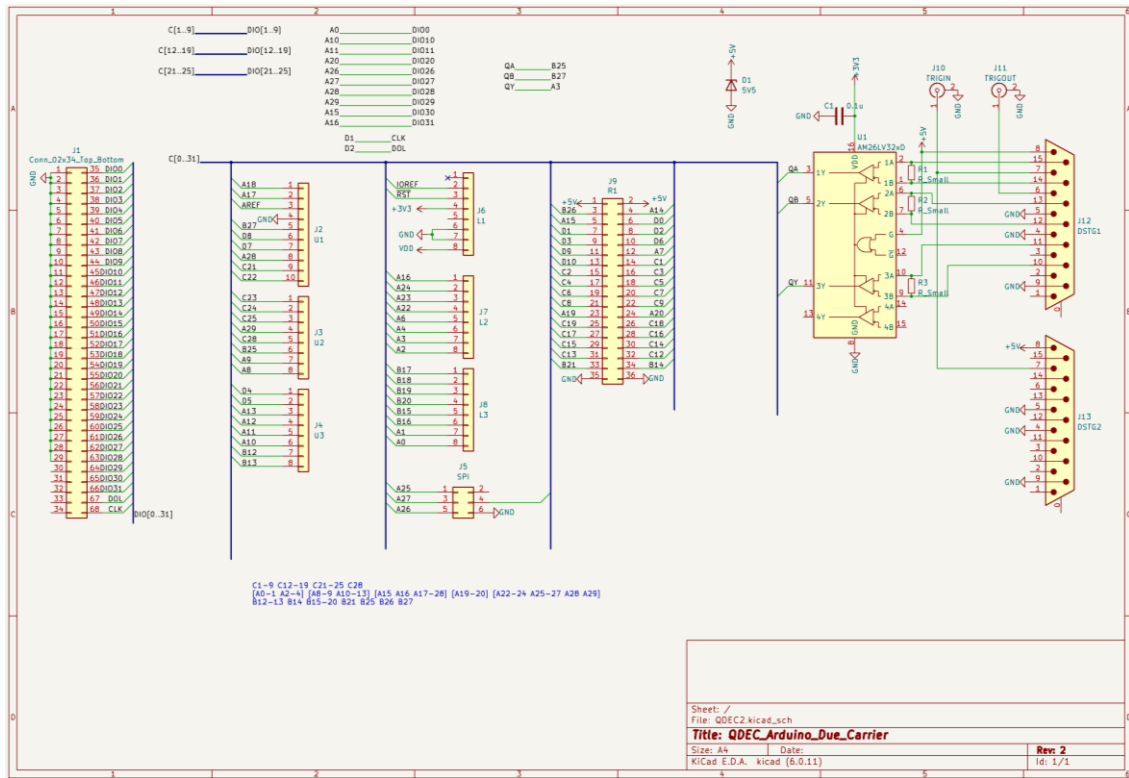


Fig. 14 Circuit diagram of the QDEC board.

The QDEC board contains two D-SUB connectors to directly interact with the mechanical stages at the lowest hardware level. The encoder signal from the mechanical stage is transferred as differential pair with RS422 protocol, which is received by a RS422 transceiver on the QDEC board with 100Ohm termination. The signal is then routed to the quadrature decoder peripheral of SAM3X8E ARM Cortex M3 MCU (Arduino Due). The board also contains two BNC connectors that are connected to the trigger-in and trigger-out DIO of the mechanical stage controllers.

The board is designed as an Arduino Due carrier, where the 32-bit output of the quadrature decoder peripheral along with the latch signal is routed to the PIOs as directly as possible, and connected to the 68-pin output plug that goes into the DIO port of the lock-in amplifier.

2.4 TRTS – Scanning and Sampling Control System

2.4.1 Hardware Control loop

As mentioned in the last chapter, for the contentious scan, the positional data is acquired via MCU-assisted decoding of the 32-bit quadrature encoder, and recorded synchronously by the lock-in amplifier. The MCU reads the raw quadrature encoder pulses from the delay stage controller and converts them to 32-bit counter value. This is accomplished by the quadrature decoder (QDEC) peripheral of the ARM Cortex M3 MCU. To minimise propagation delay, the 32-bit value is sent to the lock-in amplifier's digital IO (DIO) in raw form without any encoding. This uses up all 32 digital channels from the lock-in amplifier.

The demodulated analogue photodiode signal and the digital positional signal are synchronously gated and acquired by the lock-in amplifier's DAQ module using the same time-base. In post-processing the acceleration and deceleration part of the signal is cropped leaving only the linear part. This helps the interpolation of signal to the pre-defined position value.

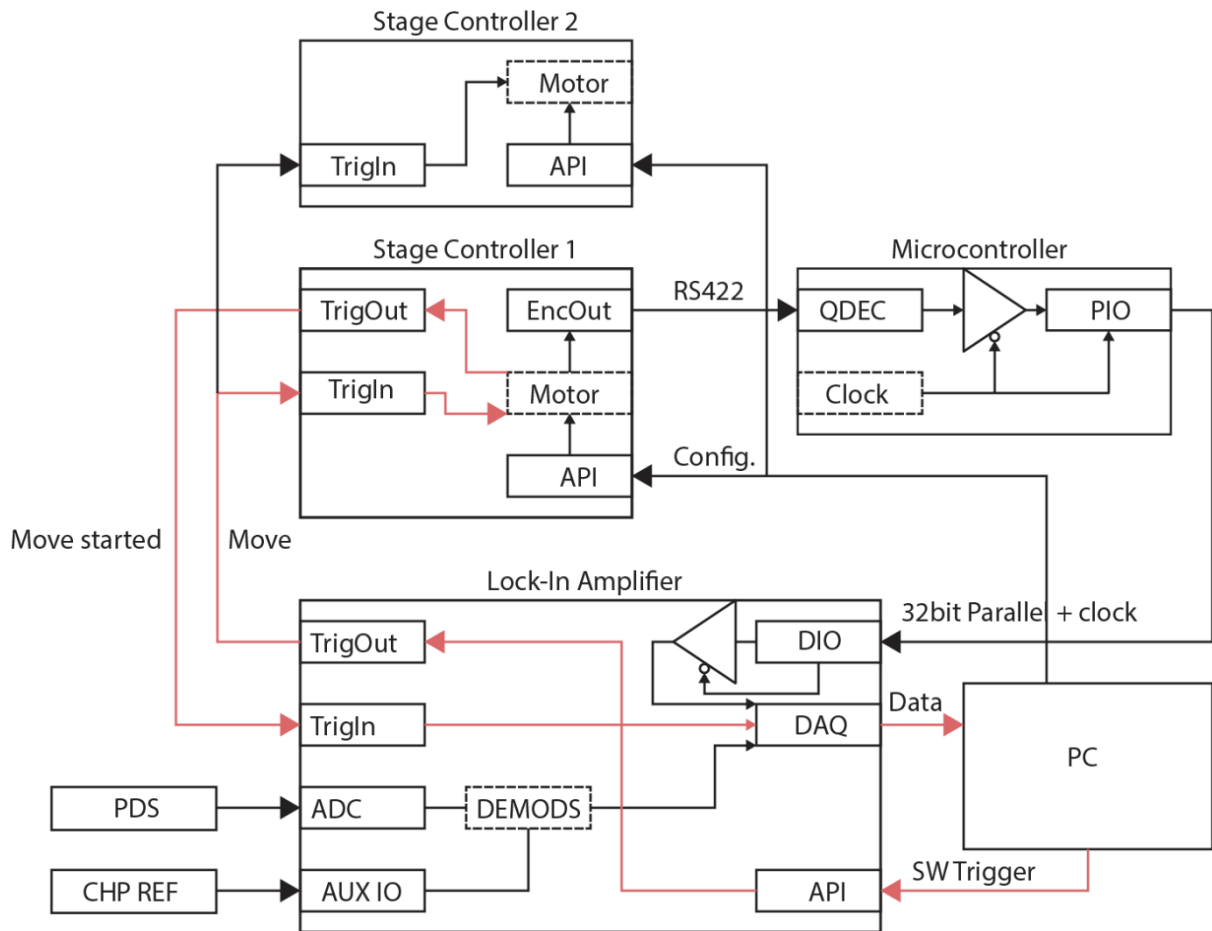


Fig. 15 Control loop diagram of the TRTS setup. The red arrows indicate chain of triggers that drive the loop.

- A software command to the lock-in amplifier sends an external HW trigger to start both delay stages simultaneously.
- As the stage start to move, the delay stage controller sends a HW trigger to the lock-in amplifier to start the data acquisition.
- At the same time, the microcontroller decodes pulses from the quadrature encoder of the delay stage at real time and sends raw 32-bit counter value to the lock-in amplifier data acquisition module.
- The PC software control loop pulls the DAQ result and enqueue it to the data processing loop.
- Software commands are sent to adjust the instrument parameters such as delay stage target positions, for the next scan.

2.4.2 Software Architecture

The instrument control software was written in LabVIEWTM and adopts a three-block design similar to the commonly used code architecture for dual-core embedded systems, where the first block initializes the system, the second block (the producer) control the instruments and collect data, and the third block (the consumer) process the data communicated via first-in-first-out buffer (FIFO) with the second block. The producer and consumer are executed in parallel and synchronously because the consumer is usually faster and waits for data coming out of the FIFO.

This architecture eliminates the data processing time as the consumer block is almost always faster than the producer block, which defines the loop time. The system exploits every hardware interface available to facilitate inter-instrumental communications at hardware level to reduce loop time.

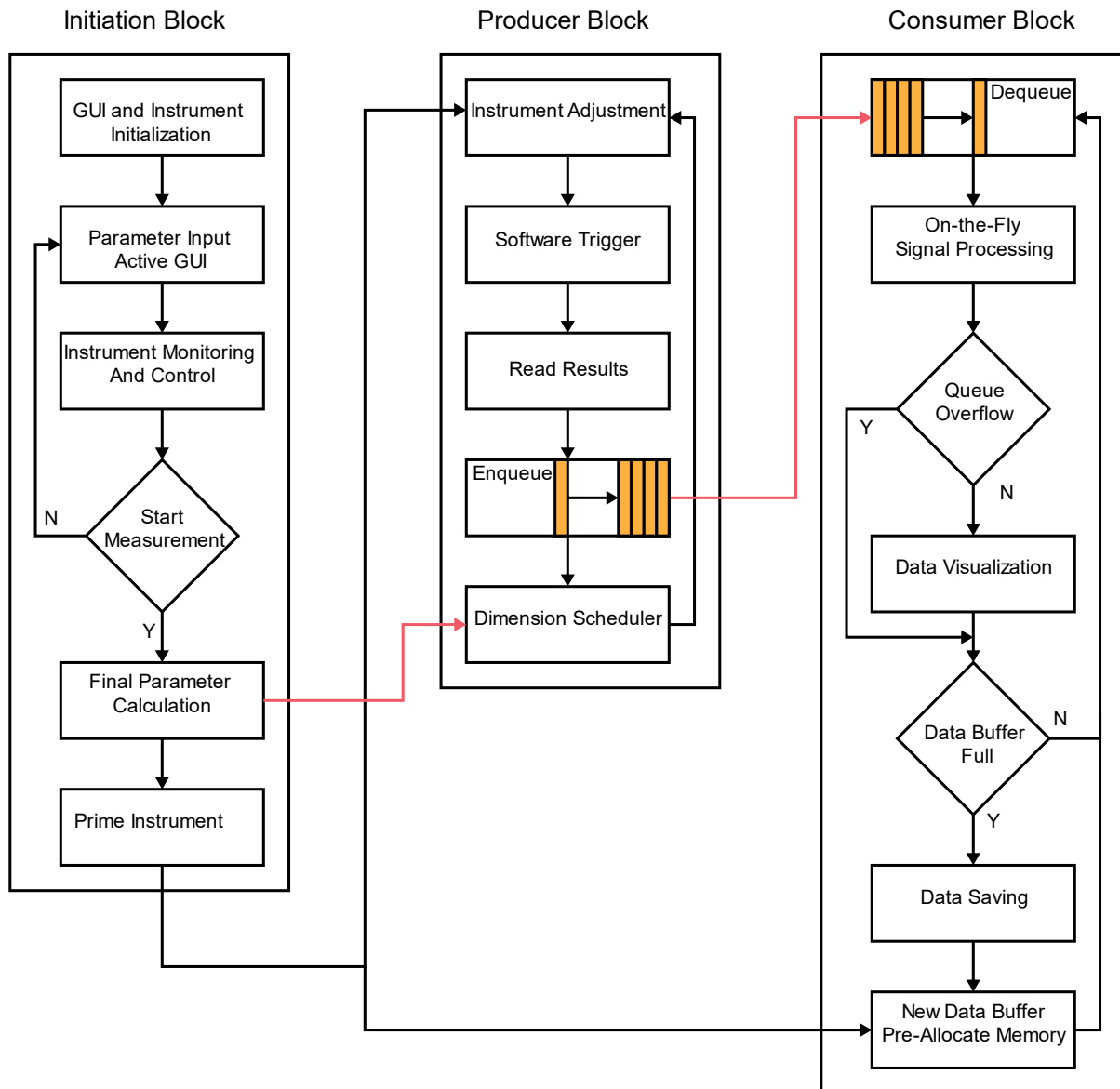


Fig. 16 Block diagram of the instrument control software on PC.

2.4.2.1 Initiation block

The software is designed in a way that it interreacts with instruments via API as less as possible during the measurement loop to maximise scanning speed. Therefore, most instrument configuration is done in advance in the initiation block, where all instruments are initialised and properly configured. This is followed by an event-driven loop allowing users to control and monitor the instruments while preparing parameters for the scans.

A concurrent loop retrieves real-time data from the instruments and display them on the GUI. Once the loop is exited, the calculation of parameters and instrument adjustment is finalized. A queue operation is initiated creating two threads (producer and consumer) that execute concurrently on different CPU cores.

2.4.2.2 Producer block

The producer block is responsible for adjusting instrument parameters, sending software triggers, and collecting data. The instrument parameters are retrieved via dimension orchestrator, which flattens the multi-dimensional parameters prepared in the initialisation block, and shift them out one by one for measurement.

Then, a software command is sent to the lock-in amplifier instructing it to send a hardware trigger to the sampling delay stage. The delay stage sends back a trigger to start the DAQ module when it starts moving. The producer block monitors the progress of the DAQ and retrieve the data, which is then sent to the FIFO.

2.4.2.3 Consumer block

The consumer block is responsible for on-the-fly data processing, visualisation and data logging. When a data stripe is retrieved from the queue, the differential photodiode data from the lock-in amplifier is interpolated against positional data (Fig. 17) to produce TDS.

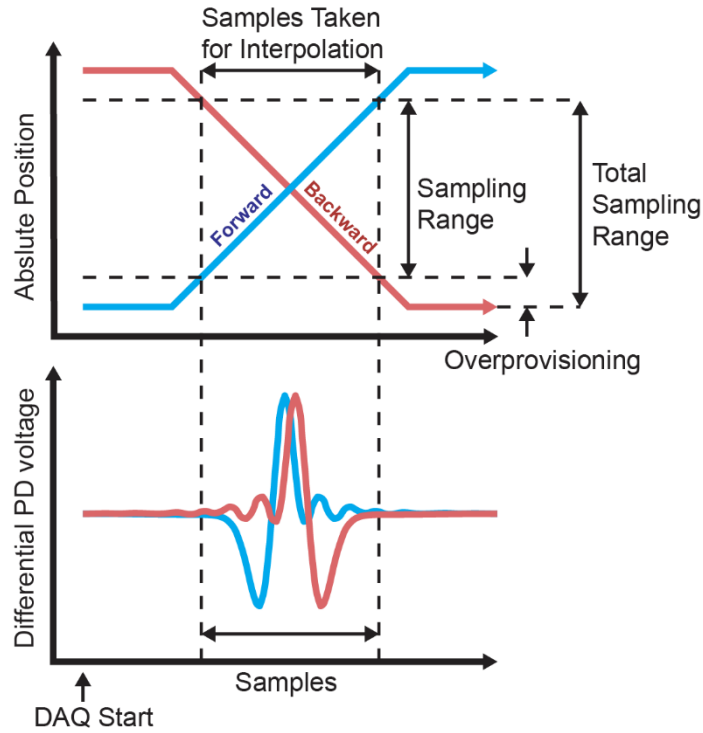


Fig. 17 Illustration of bidirectional synchronous photodiode and positional data acquisition. The upper graph shows the absolute position of the mechanical stage in both scanning directions. The lower graph shows differential photodiode voltage collected by lock-in amplifier.

The samples are collected in a continuous manner as described in chapter 2.4.1. To increase acquisition rate and reduce measurement time, the samples are taken when the delay stage travels in either direction so there is no waiting time for the delay stages to reset. Any hysteresis, including mechanical backlash from the delay stage is compensated in the controlling software. The peak position of each scan is collected and their standard deviation is calculated for debugging purpose. In addition, overprovisioning of scanning range is implemented to ensure all the samples are captured in the linear region of the mechanical stage positions. The overprovisioning also ensures that the DAQ always starts before the delay stage entering the sampling range. The data outside sampling range is discarded during interpolation.

For the comprehensiveness of the data visualisation, a 3D buffer, where repeated scans of time-and-frequency-resolved spectra are stored as pages, is used. The buffer is pre-allocated to ensure there is enough system memory to support the entirety of the scan and prevent memory leaks. The TDS stripe is pulled from the FIFO and then inserted into the 3D buffer by the consumer block as illustrated in Fig. 18.

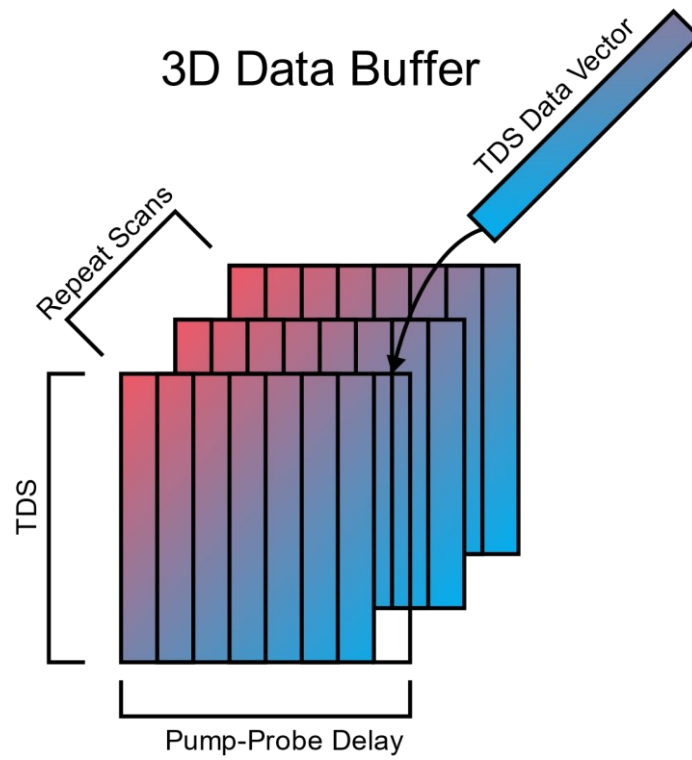


Fig. 18 Illustration of the 3D data buffer used in the TRTS software. Columns are TDS data, rows are pump-probe data, and pages are repeated data.

In the rare event of FIFO overflow (the consumer block becomes slower than the producer block, which may happen if the 3D data buffer is configured exceptionally large), the visualisation code, which is the slowest part of the consumer block, is skipped (Fig. 16, right). This ensures the FIFO is quickly cleared and all data is saved.

2.5 System Characteristics

TRTS systems found in literatures generally uses optical rectification/EOS. Our system opted for PCA/EOS to overcome input power constrains, while producing similar bandwidth to optical rectification/EOS systems. The downside is that terahertz field strength is limited in our system, and only samples with conductivity comparable or greater than that of halide perovskites can be measured with acceptable SNR.

The easiest way to improve terahertz field strength is replacing the 1cm^2 PCA with larger area and higher dielectric strength. Alternatively, if higher input power available, we can switch to optical rectification with emerging organic terahertz crystals.

Characteristics	Value	Condition
Static Time Domain Peak SNR	45 dB	RH<1%
Max Tested PCA Bias Voltage	40 V	Pulse Duty<1%
Min Effective Frequency	0.1 THz	RH<1%, EOS=ZnTe
Max Effective Frequency	3 THz	RH<1%, EOS=ZnTe
Focal Point FWHP	430 μm	
PCA Saturation Pulse Energy	10 nJ	$\lambda_{PCA} = 800\text{nm}$
Pump Pulse Length	<100 fs	
Pump Wavelength Range	400-1200 nm	OPA with frequency mixer
Push Wavelength Range	1200-2000 nm	IDL output of OPA
PCA Driver		
Max Input Voltage	75V	
Min Input Voltage	15V	
Time Resolution	1 μs	Software PWM
Tested Laser Repetition	4 KHz	
Max Reference Current Draw	10 μA	

Tab. 3 Characteristics of the multi-pulse TRTS setup.

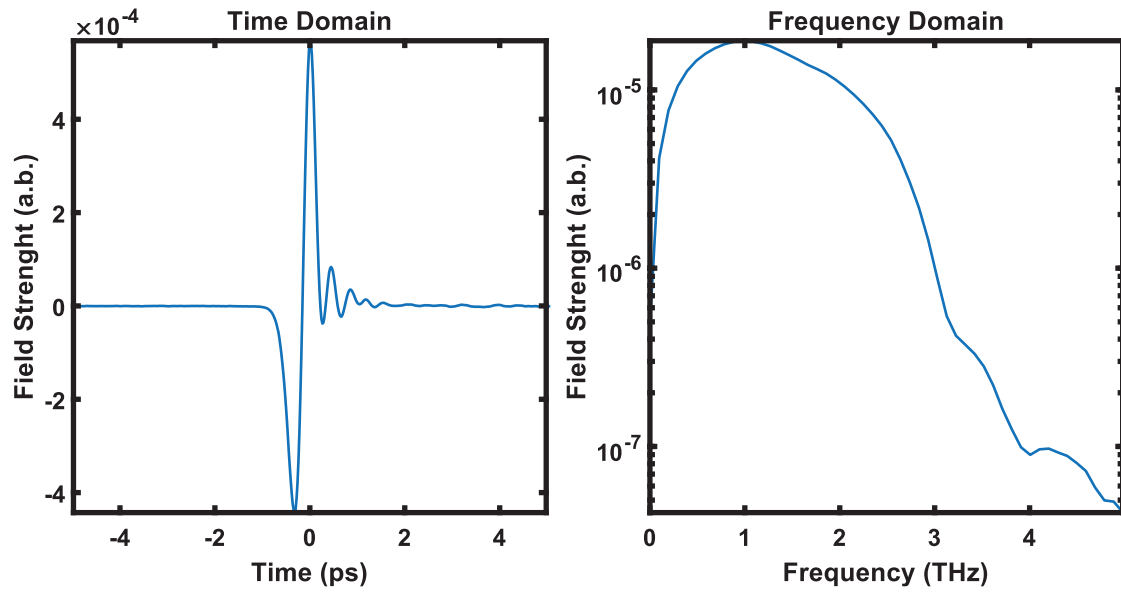


Fig. 19 THz pulse measured in dry air ($RH < 1\%$) with ZnTe EOS: (Left) time-domain; (Right) frequency domain.

3 Validation of the Multi-Pulse TRTS Setup with Model Optoelectronic Martial Systems

In this chapter the application of the developed experimental setup in studying charge carrier dynamics in semiconductors is demonstrated.

The relationships between terahertz transmission, refractive index, intrinsic conductivity, and carrier mobility are derived. Material complex conductivity can be related to its complex refractive index by solving the Maxwell equations analytically. Photoconductivity can be retrieved from differential terahertz transmission by accounting for all beam paths for a particular sample-substrate geometry. For thin film on thick substrate, thin film approximation (TFA) can be used to greatly simplify the derivation, which finally arrived at a relationship where photoconductivity is proportional to normalised differential terahertz transmission.

The constructed multi-pulse TRTS system is validated with OPTP experiment of graphene and PPP-THz experiment of perovskites. The photoconductivity dynamics of graphene is negative as expected, and decays within 10 ps at room temperature. The frequency-resolved complex photoconductivity suggest multiple excitonic/polaronic features within 0.1-2.5 THz range.

3.1 Derivation of Complex Conductivity from TRTS Data

3.1.1 Conductivity as a Function of Refractive Index

While TRTS is regarded as non-contact conductivity and mobility probe, the exact relationship between terahertz transmission and sample refractive index in solids is not trivial. In this chapter the relationship between complex conductivity and complex refractive index is fully derived.

The coherent single cycle terahertz probe pulse can be viewed as a traveling electric field act upon charged carriers inside the sample. Refractive index of the material can be extracted from the change in terahertz transmission, and photoconductivity can be retrieved from the refractive index.

In Euclidian space, form Maxwell–Faraday equation:

$$\nabla \times \mathbf{E} = -\frac{\partial}{\partial t} \mathbf{B}$$

eq. 11

Apply $\nabla \times$ on both sides:

$$\nabla \times (\nabla \times \mathbf{E}) = \nabla \times \left(-\frac{\partial}{\partial t} \mathbf{B} \right)$$

eq. 12

Rearrange:

$$\nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\frac{\partial}{\partial t} (\nabla \times \mathbf{B})$$

eq. 13

From Ampère's circuital law (free current only):

$$\nabla \times \mathbf{H} = \mathbf{j} + \frac{\partial}{\partial t} \mathbf{D}$$

eq. 14

Using the definitions $\mathbf{B} \equiv \mu_0\mu_r\mathbf{H}$ and $\mathbf{D} \equiv \epsilon_0\epsilon_r\mathbf{E}$, and substituting eq. 14, into eq. 13 yields:

$$\nabla(\nabla \cdot \mathbf{E}) - \nabla^2 \mathbf{E} = -\mu_0\mu_r \frac{\partial}{\partial t} \mathbf{j} - \mu_0\mu_r\epsilon_0\epsilon_r \frac{\partial^2}{\partial t^2} \mathbf{E}$$

eq. 15

Assuming the medium is homogenous, isotropic, and neutral $\rho = \epsilon_0\epsilon_r \nabla \cdot \mathbf{E} = 0$, eq. 15 becomes:

$$-\nabla^2 \mathbf{E} = -\mu_0\mu_r \frac{\partial}{\partial t} \mathbf{j} - \mu_0\mu_r\epsilon_0\epsilon_r \frac{\partial^2}{\partial t^2} \mathbf{E}$$

eq. 16

Using the relationship between current density and conductivity $\mathbf{j} \equiv \sigma \mathbf{E}$, eq. 16 becomes:

$$\mu_0\mu_r\epsilon_0\epsilon_r \frac{\partial^2}{\partial t^2} \mathbf{E} + \mu_0\mu_r\sigma \frac{\partial}{\partial t} \mathbf{E} - \nabla^2 \mathbf{E} = 0$$

eq. 17

Using inverse Fourier transform integral to remap $\mathbf{E}$ from time and Euclidian space to frequency and vector space:

$$\mathbf{E}(x, t) = \frac{1}{4\pi^2} \int d^3\mathbf{k} \int d\omega \mathbf{E}(\mathbf{k}, \omega) e^{i\mathbf{k}x - i\omega t}$$

eq. 18

Substituting eq. 18 into eq. 17 yields:

$$\int d^3k \int d\omega \mathbf{E}(\mathbf{k}, \omega) e^{i\mathbf{k}\cdot\mathbf{x} - i\omega t} \left[-\mu_0 \mu_r \varepsilon_0 \varepsilon_r \omega^2 - \mu_0 \mu_r \sigma i\omega + \mathbf{k}^2 \right] = 0$$

eq. 19

with the definition of complex wavevector:

$$\mathbf{k} \equiv \frac{\omega}{c} \mathbf{n} = \sqrt{\mu_0 \varepsilon_0} \omega \mathbf{n}$$

eq. 20

eq. 19 becomes:

$$-\mu_0 \mu_r \varepsilon_0 \varepsilon_r \omega^2 - \mu_0 \mu_r \sigma i\omega + \mu_0 \varepsilon_0 \omega^2 \mathbf{n}^2 = 0$$

eq. 21

Rearrange eq. 21

$$\mathbf{n}^2 = \mu_r \varepsilon_r + \frac{i\mu_r \sigma}{\varepsilon_0 \omega}$$

eq. 22

Assuming charge carriers have no significant magnetic moment:

$$\sigma(\omega) = (\mathbf{n}^2 - \mu_r \varepsilon_r) \frac{\varepsilon_0 \omega}{i\mu_r} \approx i\omega \varepsilon_0 (1 - \mathbf{n}^2)$$

eq. 23

Finally, we arrive at the relationship between complex conductivity and refractive index.

3.1.2 Thin Film Approximation

While we have established the general relationship of complex conductivity and complex refractive index in the last chapter, retrieving complex refractive index from the actual TRTS data is not trivial either. In this chapter we establish the relationship between terahertz transmission and sample refractive index via thin film approximation.

The attenuation of light inside the analyte is not the only process that occurs. Because of the transverse wave nature of light, at any interface between two different materials partial transmissions and reflections occur. In addition, Fabry–Perot reflections will cause inseparable echoes embedded in the transmitted pulse if the medium is thin enough.

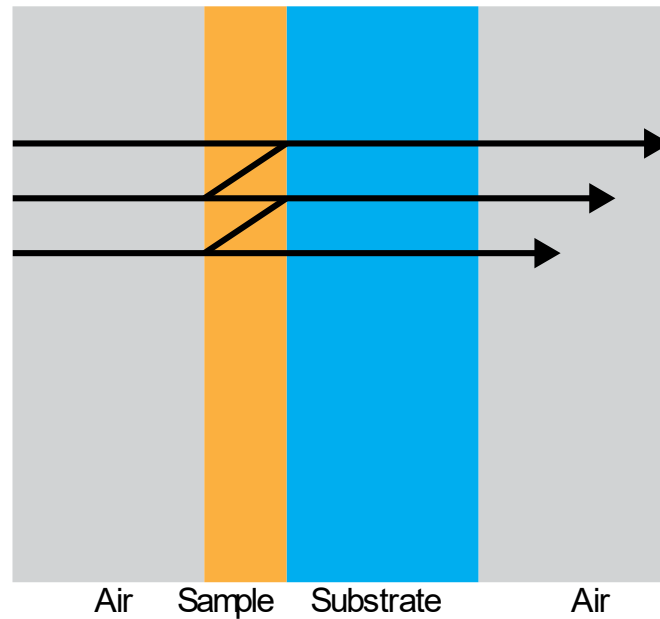


Fig. 20 Illustration of light propagation through thin film on substrate system.

The relationship between $\Delta\tilde{E}/\tilde{E}$ and differential complex conductivity $\Delta\tilde{\sigma}$ is obtained by solving Fresnel equations for the sample-substrate system, which consists of a thin material layer on top of a substrate surrounded by air or nitrogen ($n \approx 1$). The terahertz wave is assumed to be p-polarised to the sample. The following processes are considered: **(1)** transmissions in

and out of the material layer, **(2)** internal reflections inside the material layer, and **(3)** attenuation inside the material layer. The length of internal reflections inside the substrate is far greater than the period of a single terahertz cycle, thus they can be easily truncated from collected time-domain data.

The terahertz transmission and refractive index is related by:

$$T(\omega) = \frac{2n(n_{sub} + 1) \exp\left[-\frac{i\omega d}{c}\right]}{(1 + n)(n + n_{sub}) \exp\left(n\frac{-i\omega d}{c}\right) - (n - 1)(n - n_{sub}) \exp\left(n\frac{i\omega d}{c}\right)}$$

eq. 24

Where n and n_{sub} are the complex refractive index of the sample and the substrate respectively. d is the sample thickness. If the film thickness is sufficiently small $d < 500nm$, eq. 24 can be simplified by Tylor expansion of the exponential terms to the first order at zero point:

$$\frac{i\omega d}{c} \approx 0, \quad \exp\left(\frac{i\omega d}{c}\right) \approx 1 + \frac{i\omega d}{c}$$

eq. 25

$$T(\omega) \approx \frac{(1 + n_{sub})\left(1 - \frac{i\omega d}{c}\right)}{(1 + n_{sub}) - (n^2 + n_{sub})\frac{i\omega d}{c}} \approx \frac{1 + n_{sub}}{1 + n_{sub} - n^2\frac{i\omega d}{c}}$$

eq. 26

Using the relationship between dielectric function and optical conductivity $\sigma(\omega) = i\omega\epsilon_0(1 - n^2)$ the expression of complex transmission as a function of complex conductivity can be retrieved, and rearranged into:

$$\sigma(\omega) = \frac{1 + n_{sub}}{Z_0 d} \left(\frac{1}{T} - 1 \right)$$

eq. 27

In differential measurement such as OPTP, only T changes following the excitation. Therefore, differential conductivity is obtained by keeping only the term with T :

$$\frac{\Delta T}{T} = \frac{T_{ext} - T}{T} = \frac{E_{ext} - E}{E} = \frac{\Delta E}{E}$$

In OPTP, transmission is not actually measured, instead, for simplicity only transmitted electric field strength in arbitrary unit is measured.

Finally, the widely used thin film approximation of differential complex conductivity is obtained:

$$\Delta\sigma(\omega) = -\frac{1}{Z_0 d} \frac{\Delta E(\omega)}{E(\omega)} (1 + n_{sub})$$

eq. 28

While TFA has been extensively used for thin samples^{73, 76, 104-108}, the applicability of TFA is still debated^{109, 110}. TFA is attractive because it makes the relationship between photoconductivity and differential electric field explicit and linear. Also, TFA does not require the material thickness to calculate photoconductivity.

3.2 Typical TRTS Responses for Semiconductors

Various materials were measured on the multi-pulse TRTS system (Fig. 21) and the results were compared with literatures as the first-stage general validation of the multi-pulse TRTS setup. A comprehensive literature review and discussion of findings are not included, as the purpose of this chapter is to validate the setup with (extrapolation of) existing results, and introduce exploratory results of the three-pulse extension.

PPP-THz were performed on SLG, single-crystal silicon and halide perovskites. The SNR of measurements with organic crystal and organic conjugated polymer is too low to perform PPP, but OTP is possible and their responses were collected.

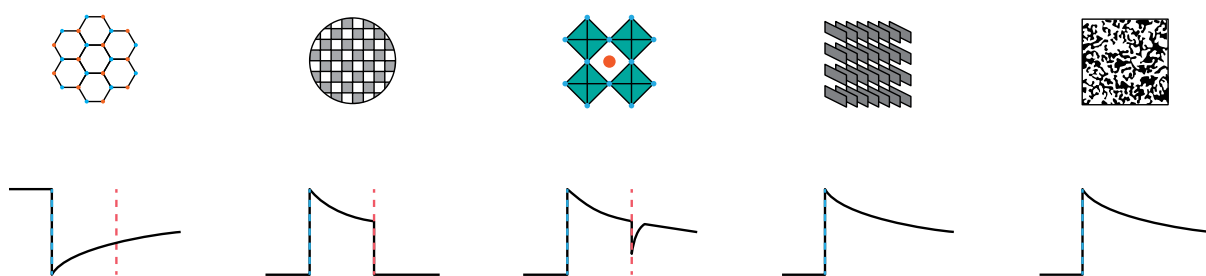


Fig. 21 Typical photoconductivity response of semiconductor material in terahertz frequencies. The blue dashed line indicates pump pulse and the red dashed line indicates push pulse at 2000 nm. From left to right (1) Graphene (2) Silicon (3) perovskites (4) organic crystals (5) polymer organic semiconductors

The response of graphene was consistent with literature.¹¹¹⁻¹¹⁶ Its signatures such as negative photoconductivity, and ~ 10 ps fast decay at room temperature are observed. However, the NIR push pulse has no emergent effect because the intrinsic bandgap of SLG is well below the energy of the NIR push pulse. The experiment with 400 nm pump and 2000 nm push produced no effect on MPA-corrected signal.

Interestingly, while the response to pump excitation of silicon is as expected, the push excitation reduced the conductivity to zero. This phenomenon may be attributed to stimulated emission by the intense NIR pulse since it explains the total loss of conductive carriers. Further experiments, possibly pump-push-probe with infrared supercontinuum probe, where stimulated

emission can be spectroscopically observed, are required to find out the exact nature of the extinction of mobile carriers.

In perovskites, the push excitation reduced the conductivity, which eventually recovers to previous level. While this is contrary to the expectation that push excitation would liberate trapped carriers thus increasing conductivity, the decrease of conductivity can be attributed to carrier heating¹⁰¹. This is presented in chapter 4 in great detail.

Organic crystals (rubrene) and organic NFA (Y6) have been measured on the setup. Despite low SNR due to low field strength limited by the size and dielectric strength of the PCA, Positive photoconductivity is observed in these organic systems, which is consistent with increased photocurrent observed in time-resolved pump-probe-photocurrent experiment.⁹³

3.3 OPTP Experiment on Graphene

Graphene has been extensively studied with OPTP^{[111-121](#)} due to its high conductivity and potential optoelectronics applications. In addition, graphene has potential for terahertz emission and detection applications. The terahertz photoconductivity of graphene is very characteristic with signatures such as negative photoconductivity and short carrier lifetime. Those signatures make graphene an excellent sample to test the TRTS setup.

In 2008 P. A. George, *et al.* from F. Rana group established carrier equilibration timeframe (10 fs-150 fs for thermalisation, 150 fs-1 ps for carrier cooling, and 1 ps-15 ps for carrier recombination) for epitaxial graphene through excitation-energy-dependent OPTP.^{[115](#)}

Intrinsically doped single layer graphene (SLG) was selected as test material because of its characteristic negative photoconductivity and very fast decay. OPTP was performed on the SLG with 400 nm excitation. As indicated in Fig. 22, the notable negative conductivity of graphene was observed, and the time scale is consistent with literatures.^{[112](#), [113](#), [115](#), [116](#)}

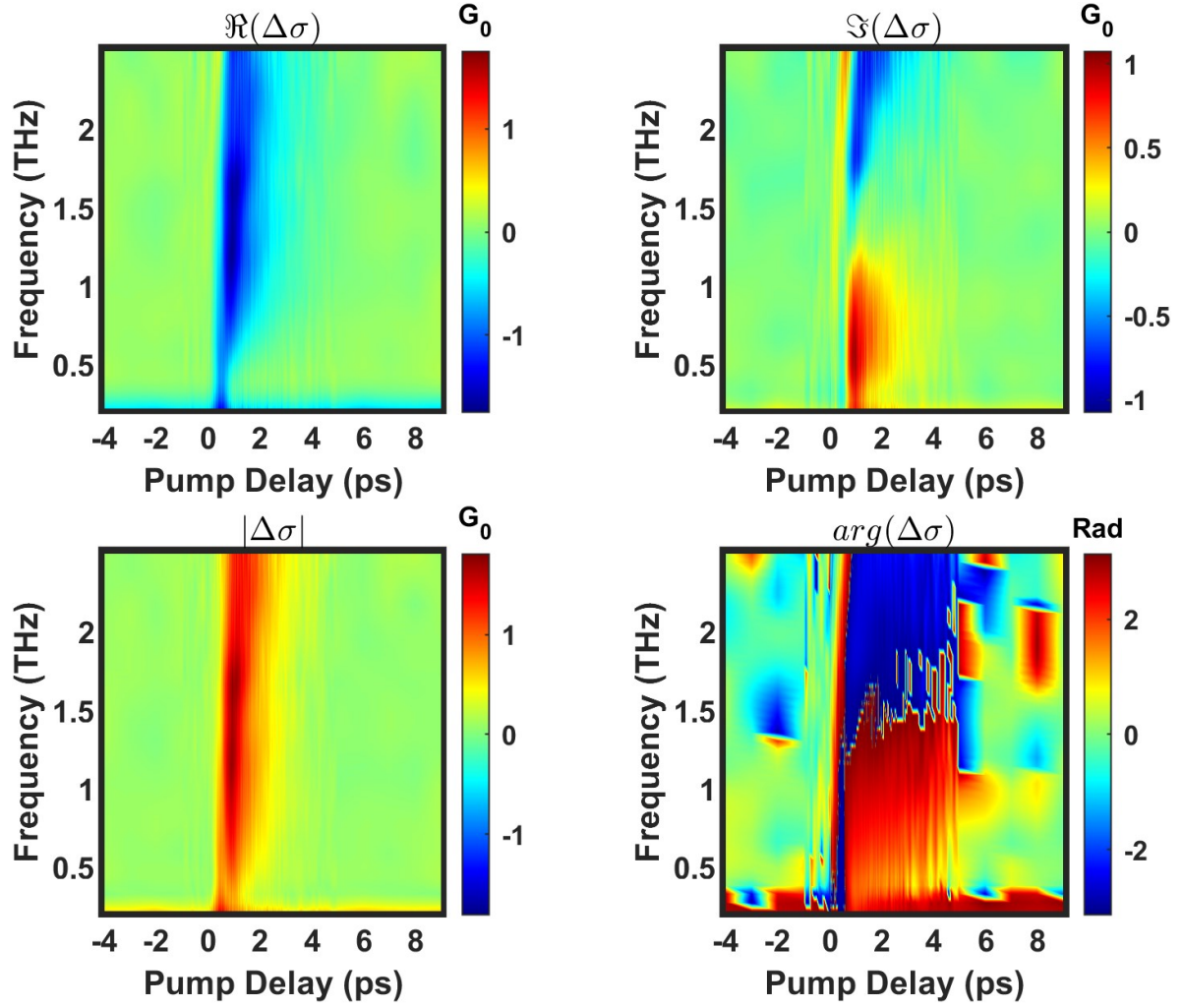


Fig. 22 Time and frequency resolved sheet photoconductivity of intrinsically doped SLG. UL: Real part of the complex conductivity. UR: Imaginary part of the complex conductivity. LL: Amplitude of the complex conductivity, LR: Argument (phase angle) of the complex conductivity.

In addition, a Lorenz oscillation occurred at $f = 1.25 \text{ THz}$ as evidenced by an extremum of the real part and a zero-crossing of the imaginary part of the photoconductivity (Fig. 23 Left), which is consistent with the frequency dependence of photoconductivity of SLG reported in literature.¹¹³

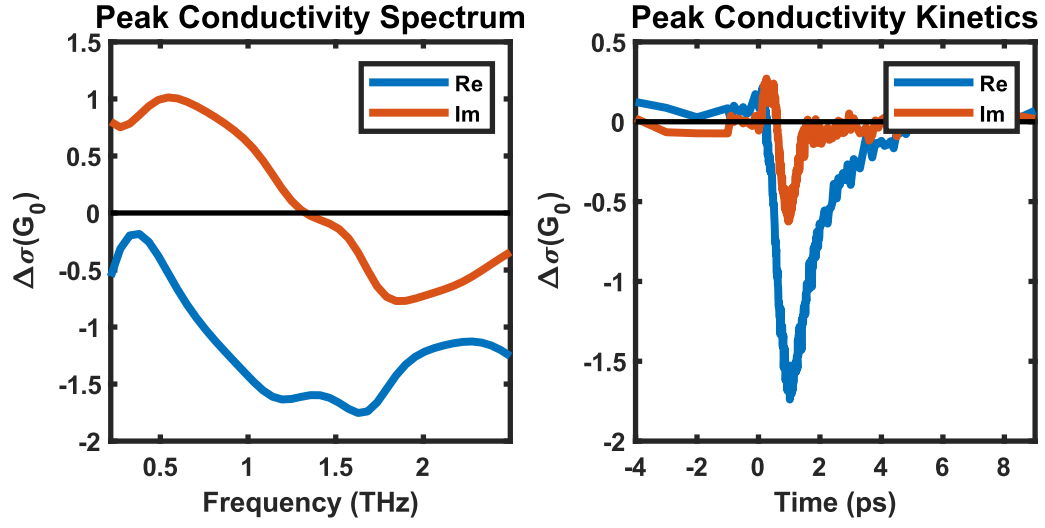


Fig. 23 Peak photoconductivity of intrinsically doped SLG. L: Conductivity Spectrum at pump-probe peak. R: Conductivity dynamics at frequency domain peak.

3.4 PPP-THz Experiment with Perovskite

The PPP-THz scheme, which involves 4 laser pulses of 3 different colours, 3 modulation frequencies, and 3 moving mechanical stages, needs to be carefully tested. While graphene is an excellent material system at terahertz frequencies as illustrated in the last chapter, it is gap-less and therefore existing carriers cannot be excited without creating new carriers (see chapter 3.2). Instead, solution-processed MAPI film was chosen as test device for PPP-THz experiment (Fig. 24) due to its high conductivity, fast cooling, and slow recombination rate.

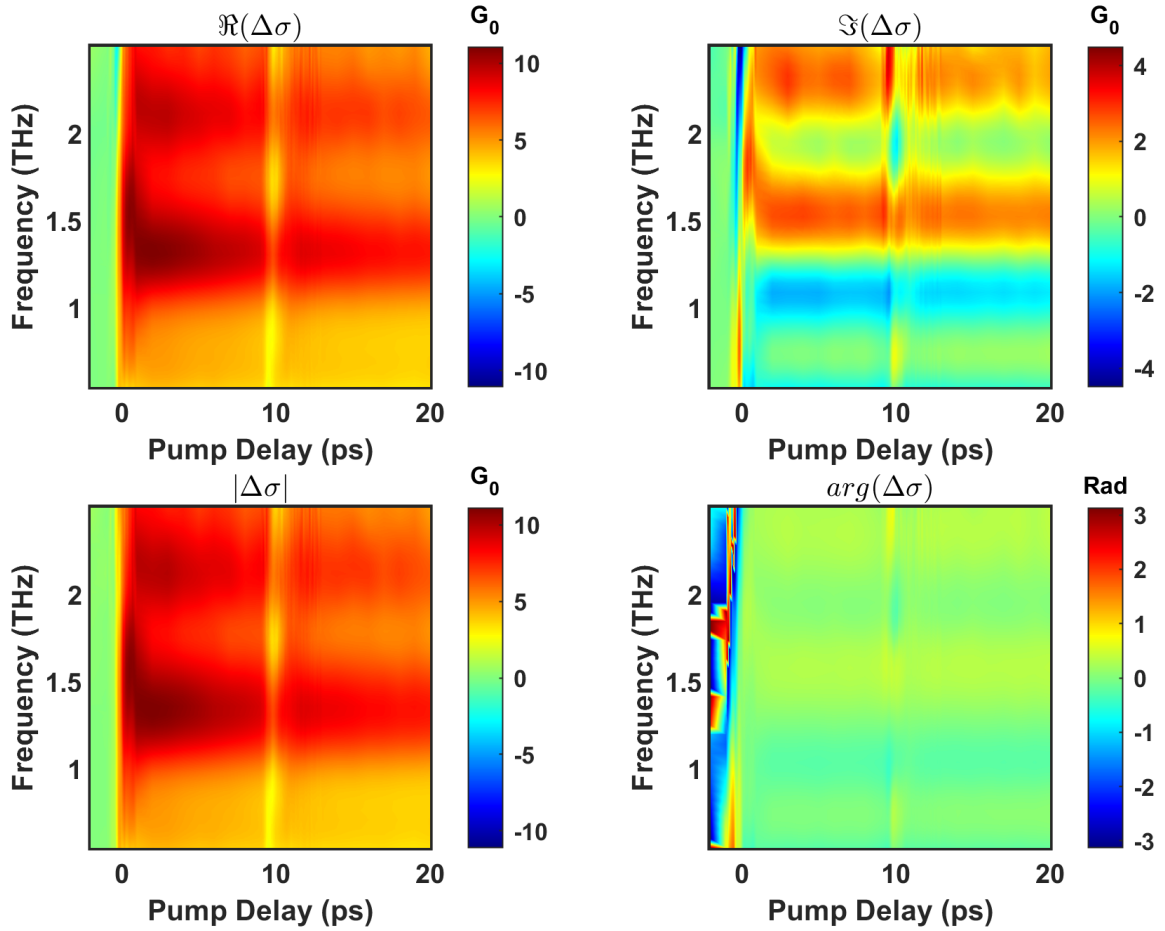


Fig. 24 PPP-THz measurement of MAPI film on z-cut quartz substrate $\lambda_{\text{pump}} = 650 \text{ nm}$, $H_e^{\text{pump}} = 1.47 \text{ Jm}^{-2}$, $\lambda_{\text{push}} = 2073 \text{ nm}$, $H_e^{\text{push}} = 12.5 \text{ Jm}^{-2}$

As expected, MAPI exhibited prominent response to push excitation at 10 ps, followed by fast and complete recovery. This response validates the PPP-THz capability of the multi-pulse TRTS system. The detailed photophysics of MAPI studied by PPP-THz is discussed in chapter 4.

3.5 Determination of Charge Carrier Mobility

TRTS is also known as a contactless probe for charge carrier mobility, which greatly improve measurement accuracy compared with contacted device measurement as it directly interreact with the active material without the interference of the electrode. As a result, terahertz contactless probe only requires a sample film instead of a functional device.

The carrier mobility can be derived from its definition and expressed as a function of sheet photoconductivity as follows:

$$\mu = \frac{\Delta\sigma}{ne} = \frac{\Delta GA}{Ne} = \frac{hc}{\Phi_{EQE} Q_e^{pump} \lambda_{pump}} \frac{\Delta GA}{e} = \frac{hc}{e} \frac{\Delta G}{\Phi_{EQE} \lambda_{pump} H_e^{pump}}$$

eq. 29

Where $\Delta\sigma$ is the photoconductivity, ΔG is the differential sheet photoconductivity (conductance), n is the eletron density at the excitation site, A is the pump and probe beam overlap area, N is the number of photoelectrons created and H_e^{pump} is the pump fluence.

Eliminating the reflected and transmitted pump power the equation becomes:

$$\mu = \frac{hc}{e} \frac{\Delta G}{\Phi_{IQE} \lambda_{pump} H_e^{pump} (1 - R_{pump} - T_{pump})}$$

eq. 30

If the internal quantum efficiency cannot be estimated, we can at least obtain the lower bound of the mobility:

$$\mu_{LB} = \frac{hc}{e} \frac{\Delta G}{\lambda_{pump} H_e^{pump} (1 - R_{pump} - T_{pump})}$$

eq. 31

A slice of frequency-resolved complex photoconductivity (Fig. 25) was taken from the time-domain peak of the MAPI data (Fig. 24, 5 ps, after carrier cooling from initial excitation is completed). Form eq. 31, the conductivity is calculated to be $\mu_{LB} = 13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which is within an order of magnitude compare with literatures using TRTS to obtain mobility⁹⁶.

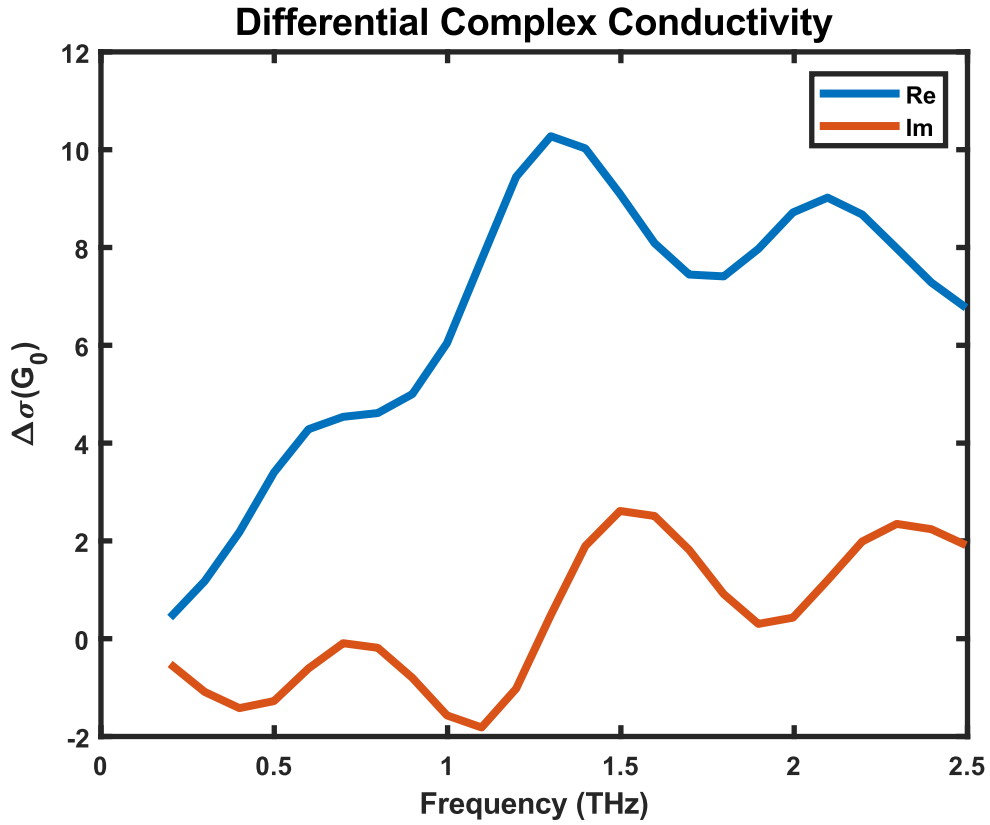


Fig. 25 Frequency-domain slice of complex conductivity at 5 ps pump-probe delay.

4 Multi-Pulse TRTS of Metal-Halide Perovskite

Hot carriers in metal-halide perovskites (MHPs) present a foundation for understanding carrier-phonon coupling in the materials as well as the prospective development of high-performance hot carrier photovoltaics. While the carrier population dynamics during cooling have been scrutinized, the evolution of the hot carrier properties, namely mobility, remains largely unexplored. Here we introduce novel ultrafast visible pump–infrared push–terahertz probe spectroscopy to monitor the real-time conductivity dynamics of cooling carriers in methylammonium lead iodide. We find a decrease in mobility upon optically re-exciting the carriers, as expected for band transport. Surprisingly, the conductivity recovery is incommensurate with the hot carrier population dynamics measured by infrared probe and exhibits a negligible dependence on the hot carrier density. Our results reveal the importance of localised lattice heating toward the hot carrier mobility. This collective polaron-lattice phenomenon may contribute to the unusual photophysics of MHPs and should be accounted for in hot carrier devices.

4.1 Introduction

Metal-halide perovskites (MHPs) are the subject of intense optoelectronic research on account of their efficient light-absorbing and emitting characteristics,^{122, 123} composition-tunable bandgaps,¹²⁴ relatively high carrier mobilities^{125, 126} and surprisingly long carrier lifetimes/diffusion lengths.¹²⁷⁻¹²⁹ These outstanding optical and electronic properties have prompted exhaustive investigations into the fundamental nature of the electronic excitations.^{130, 131} A common finding across these works is the importance of strong carrier-phonon coupling, which can be understood as being due to the soft and polar nature of the MHP lattice.¹³² By and large, the onset of carrier-phonon coupling in semiconductors occurs on the ultrafast timescale where the electronic and structural degrees of freedom are far from equilibrium.^{133, 134} The nature of this coupling is therefore particularly salient to carrier cooling and polaron formation; two processes wherein electronic excitations exchange their energy with vibrations of the lattice to minimise the overall energy of the system.

Research into these interrelated phenomena in MHPs has been extremely active over the past decade. The remarkable properties of highly energetic (hot) carriers in MHPs were first identified in the photophysical studies that followed the discovery of highly-efficient MHP solar cells.^{135, 136} One of these early characterisations by Xing et al. highlighted that the lifetimes of hot carriers in MHPs spanned hundreds of femtoseconds, well beyond the timescale of internal vibrational relaxation in most organic semiconductors.¹²⁸ Even longer hot carrier lifetimes have been reported for MHPs, which has been ascribed to the screening of the energy losses via carrier-phonon scattering (cooling) by the polar response of the lattice surrounding the carriers (polarons).^{137, 138} A great deal of reports have shown that cooling can be further protracted at high excitation densities, (re)invigorating discussions about the potential harvesting of hot carriers to surpass the Shockley-Queisser efficiency limit of single-junction photovoltaics.¹³⁹⁻¹⁴¹ The slowed cooling effect at high excitation density is usually explained through some manifestation of a “hot-phonon bottleneck”, where the cooling of many hot carriers produces an excess of non-equilibrium phonons that are continually reabsorbed by the charges.¹⁴²⁻¹⁴⁴ A growing number of works implicate polarons in this aspect of the hot carrier behaviour too, owing to the enhanced spatial extent, strong coupling to phonons and sharing of phonon subpopulations inherent to overlapping polarons.¹⁴⁵⁻¹⁴⁸

The interpretation of the transient optical signals that convey the aforementioned relaxation processes in MHP-based materials must be taken with care, especially when pumping far above the bandgap and at high fluences. These conditions can favor a myriad of processes that obfuscate the intraband relaxation, including, but by no means limited to: interband transitions between distinct electronic/spin states,¹⁴⁹⁻¹⁵¹ exciton formation/dissociation,^{133, 152-154} energy/charge migration,¹⁵⁵⁻¹⁵⁷ bandgap renormalisation,^{142, 158} refractive index changes,^{142, 159} Stark shifting,^{160, 161} and many-body (Auger) processes.¹⁶² The interpretation is complicated further still by the lack of established analysis procedures for even the most widely used transient absorption (pump-probe, PP) methods.^{163, 164} To circumvent these challenges and provide new insight into the carrier relaxation dynamics of MHPs we recently developed a visible pump – infrared push – infrared probe experiment (PPP-IR) to pump the material into the lowest-energy (cold) excited state, excite (“push”) these carriers into a higher-energy (hot) state optically and probe their intraband relaxation.¹⁴⁶ This experiment allowed us to establish the material parameters that control cooling in MHP-based materials, and also demonstrate the interplay between carrier-carrier and carrier-phonon relaxation mechanisms.^{165, 166} The technique has since been adapted to elucidate the extent and dynamics of hot carrier trapping¹⁶⁷ and extraction¹⁶⁸ in MHPs.

While all-optical PP and PPP approaches have been successful in unravelling the population dynamics and density of state distribution for hot carriers in MHPs, they do not provide explicit information on the properties of the carriers and lattice during relaxation. This could potentially be realised by monitoring the mobility of the carriers and the structure of the lattice as function of time. Recent developments in ultrafast microscopy¹⁵⁵⁻¹⁵⁷ and X-ray/electron diffraction approaches are highly encouraging in this regard,^{169, 170} but tend to require considerable investment both in terms of experimental resources and data analysis.

A robust table-top method to ascertain the evolution of carrier mobilities and associated lattice response in semiconductors is time-resolved THz spectroscopy. This is another form of transient absorption spectroscopy employing ultrashort (sub-ps) pulses, but with a low energy probe (on the order of meV). The electric field of this THz radiation accelerates the motion of (unbound) charge carriers, thus providing a means to track the electrical mobility of the photoexcited states, as well as resolving the low-energy phonons in the material that can couple to the carriers.^{171, 172} The technique is commonly employed to study charge recombination and transport in MHPs.^{125, 173-176} Early reports focusing on the time-domain data established

moderate mobilities (on the order of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and slow bimolecular recombination constants for the materials.⁴ Ostensibly, these aspects signify the existence of polarons, but contradictory values for the mobilities have surfaced depending on the conditions of the experiment and sample,¹⁷⁷ and effects such as photon recycling have also been shown to play an important role in the observed dynamics.¹⁷⁵ More recent studies have focused on the sub-ps timescale with a view to explore the carrier cooling dynamics.¹⁷⁸⁻¹⁸¹ Generally, these reports echo the results of the aforementioned transient absorption studies in that they show a delayed build-up of the signal for higher energy excitations. Bretschneider et al. showed that this build-up cannot be solely attributed to carrier cooling, and contains an intrinsic term for polaron formation ($\sim 400 \text{ fs}$ in the case of MAPbI_3).¹⁷⁹ On the other hand, frequency-resolved THz measurements have pointed toward the emergence of polarons in the form of a non-Drude spectral response^{176, 182} and/or coherent beating at particular resonances,¹⁸³⁻¹⁸⁵ but are seldom able to fully distinguish this self-localisation of the charge from the cooling of the carriers.

Herein, we introduce a novel ultrafast visible pump – infrared push – THz probe pulse sequence (PPP-THz) to combine the advantages of pump-push-probe and THz spectroscopies. We observe a decrease of carrier mobility upon optically energizing the carriers. This agrees with previous THz studies, and the general theoretical understanding that these materials exhibit band transport. Intriguingly, the reduction in carrier mobility does not happen instantly after the IR push, and the subsequent recovery takes longer overall ($\sim 800 \text{ fs}$) than the observed intraband carrier relaxation measured by PPP-IR (a few hundred fs). The THz conductivity also shows a negligible push fluence dependence, whereas the strong push fluence dependence in PPP-IR has been ascribed to the hot-phonon-bottleneck effect.¹⁴⁶ We interpret this behaviour as a two-step relaxation which includes intraband carrier cooling leading to a local (polaron) lattice heating effect. This local lattice heating is short-lived but has a substantial effect on the mobility of cooling carriers.

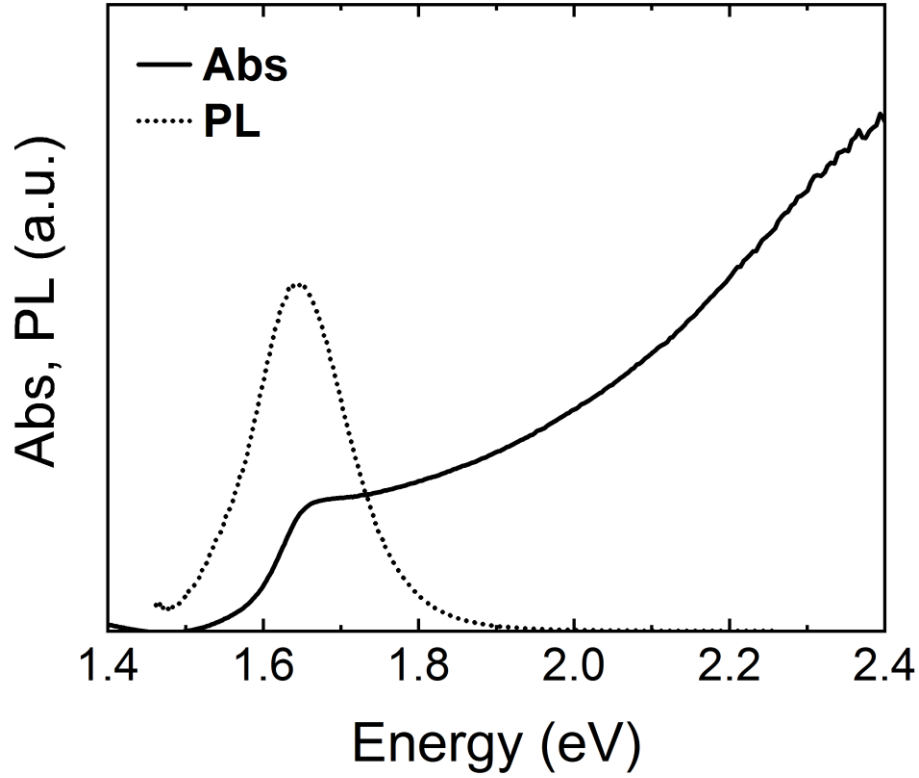


Fig. 26 Linear optical spectra for the MAPbI₃ sample.

In this work we chose to study the prototypical MHP methylammonium lead iodide (MAPbI₃) as a thin film on a THz-transparent *z*-cut quartz substrate (see Supporting Information for full sample preparation details). Although better-performing MHP compositions now exist for optoelectronic applications,^{[123](#)} MAPbI₃ is still used as a workhorse for spectroscopic investigations. Fig. 26 shows the absorption and photoluminescence spectra for the sample. Based on the overlapping absorption onset and emission peak of the sample, we estimate the optical bandgap to be around 1.6 eV, in accordance with literature values for the material.^{[124](#)}

4.2 1D Pump-Push-Probe

To explore the photoexcitation dynamics in the MAPbI₃ sample we complement the PPP-IR experiment presented in our previous work¹⁴⁶ with a new variant of time-resolved THz spectroscopy, PPP-THz. Fig. 9 depicts the latter experimental setup. The full technical details are elaborated in chapter 2, but in essence there are four beams of femtosecond pulses to consider. The first three are typical of time-resolved THz spectroscopy rigs based on commercial femtosecond regenerative amplifiers, and comprise of: (i) a visible pump pulse, used to photoexcite the sample; (ii) a THz probe pulse, used to interrogate the behavior (i.e. population and conductivity dynamics) of the photoexcitations; and (iii) the gate pulse, used to modulate the electro-optic detection. Each point in the time domain of the THz waveform contributes to every frequency of the THz radiation in Fourier space. By fixing the gate delay to the peak of the THz waveform, one can obtain the weighted-average or frequency-integrated response as a function of the pump-probe time delay. Alternatively, the gate can be scanned along each time point in the THz waveform to relay the full transient spectral response as a function of the pump-probe delay.¹⁷¹ For simplicity, we will focus on the former frequency-integrated scheme, and return to the latter frequency-resolved results toward the end of this report. The ultrashort and broadband nature of the THz probe pulses are corroborated by Fig. 27, which evince the ~ 130 fs instrument response function (IRF) of the setup and ~ 15 THz bandwidth of the THz radiation, respectively. Note that the PPP scheme is designed to eliminate artifacts of the initial excitation such as Auger heating⁵⁰, which could protract the carrier heating dynamics beyond 100 ps. Therefore, our result in Fig. 27 only shows few-ps hot-carrier dynamics.

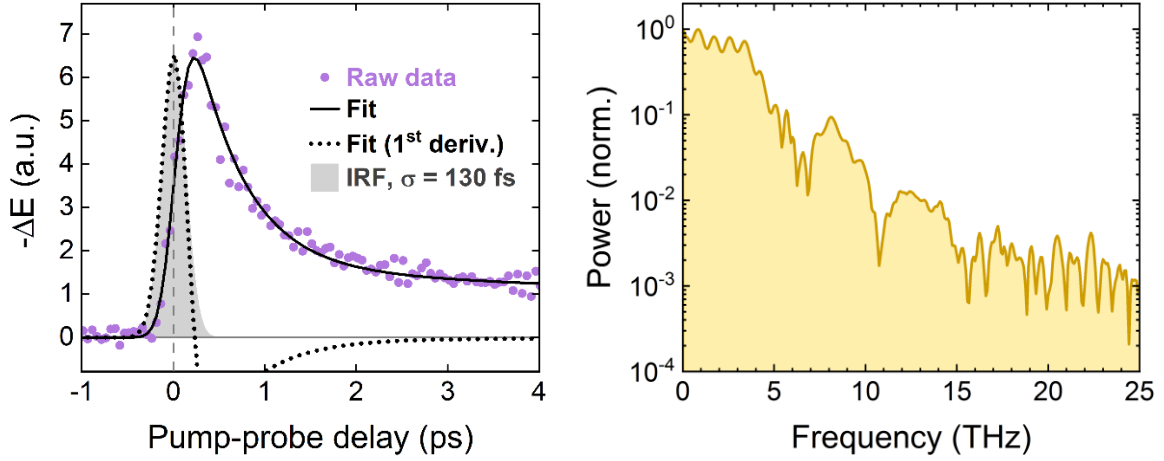


Fig. 27 [left] Instrument response function (IRF) of the time-resolved THz setup. Here a conductive 6,13-bis(triisopropylsilylethynyl)pentacene crystal was pumped at 3.1 eV ($740 \mu\text{J cm}^{-2}$) and the response was recorded at the peak of the THz waveform. The solid line is a Gaussian-convoluted exponential fit. The dotted line shows the first derivative of this fit. The “time-zero” at 0 ps is defined by the center of the Gaussian component and peak of the pump-probe first derivative. The width parameter of the extracted Gaussian function (grey) reveals an IRF of 130 ± 15 fs. **[Right]** Power spectrum of the ultra-broadband THz probe pulses used in this work, as detected by a $50 \mu\text{m}$ -thick GaP crystal. The bandwidth is estimated to be at least 10 THz based on the position of the noise floor. In the experiments we focus on the 0.5-2.5 THz region using a ZnTe crystal for detection (see experimental details above).

Fig. 28 shows the frequency-integrated pump-probe kinetics as a function of the pump fluence. Unless specified otherwise, all experiments in this work were performed at low pump fluences ($< 60 \mu\text{J cm}^{-2}$) where the early (ps) and late-time (ns) amplitudes match and scale linearly with the pump fluence. For higher intensity excitation (corresponding to carrier densities $> 3 \times 10^{18} \text{ cm}^{-3}$) we observe prominent signatures of Auger recombination in the time-resolved data, and find that the overall dynamics are dominated by many-body interactions between carriers. To this end, we have previously experimentally established that the collisions between hot and cold carriers can in fact accelerate the intraband relaxation dynamics in MHP materials.^{165, 166} Our ability to restrict the cold carrier population to ignore the contributions from these processes is not practicable for standard transient spectroscopies deploying a single excitation pulse.

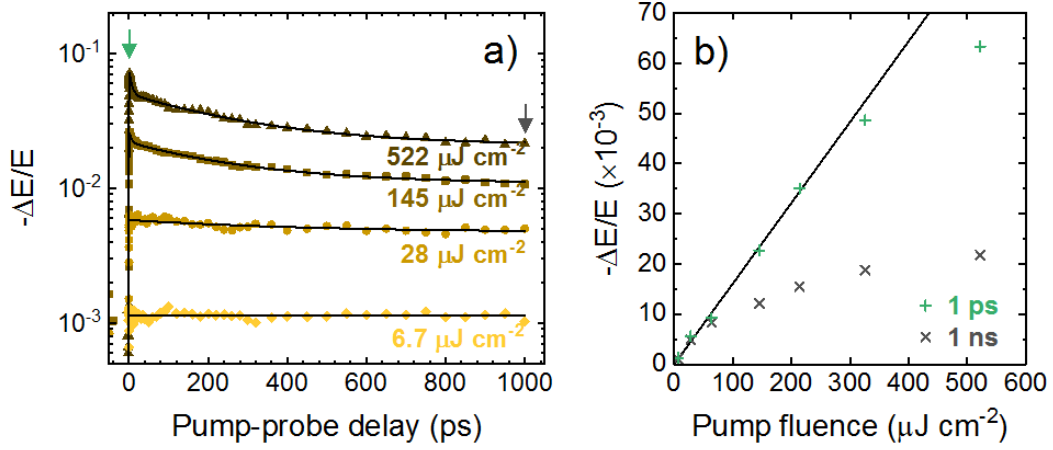


Fig. 28 (a) Fluence-dependent 1.9 eV pump – THz probe kinetics for MAPbI₃, obtained at the peak of the THz time-domain signal. Multiexponential fits are shown as a guide to the eye. (b) Pump-probe signal amplitude as a function of the fluence. Below 60 $\mu\text{J cm}^{-2}$ the early and late-time amplitudes match and scale linearly with fluence (regression shown as solid line). Above 60 $\mu\text{J cm}^{-2}$, the late-time signal saturates due to annihilation of the carriers via Auger recombination.

The unique feature of our experiment is the IR push beam spectrally tuned to a broad photoinduced absorption by the electrons and holes in MAPbI₃.^{186, 187} This beam arrives at the sample after the pump to optically re-excite the relaxed “cold” states with appreciable excess energy (600 meV) without populating higher-lying electronic bands,^{149, 158, 188} thereby providing a means to control the number of hot states and directly track the intraband relaxation dynamics. Fig. 29 (a) shows that the introduction of the push ~ 12 ps after the pump arrival momentarily reduces absorption of the THz probe, which subsequently recovers within 1 ps. As an additional control measurement, we varied the delay between the pump and push pulses but observed no effect on the recovery dynamics (see Fig. 30). This indicates that the moderate excess energy (~ 300 meV) from the above-gap pump (1.9 eV) is dissipated before the push arrives.

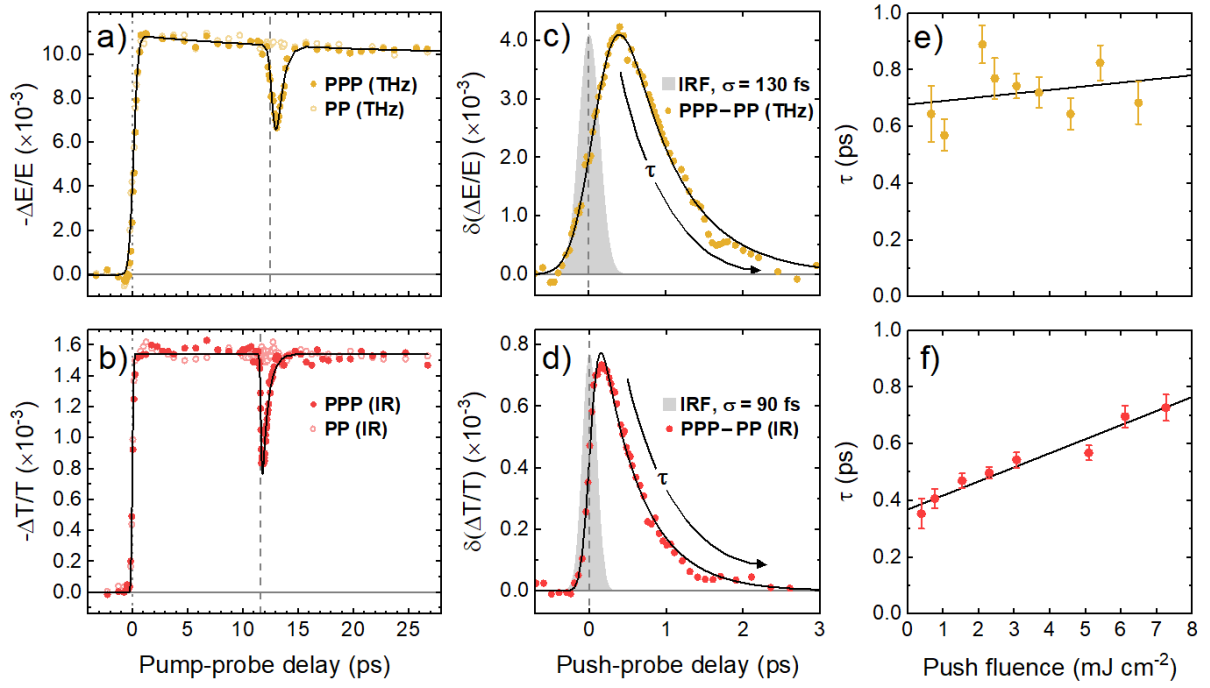


Fig. 29 Representative pump-push-probe transients (left), push-induced kinetics (middle) and overall probe recovery dynamics (right) for the PPP experiments with THz and IR probes (top and bottom, respectively). The grey-shaded areas depict the Gaussian instrument response function for the experiments.

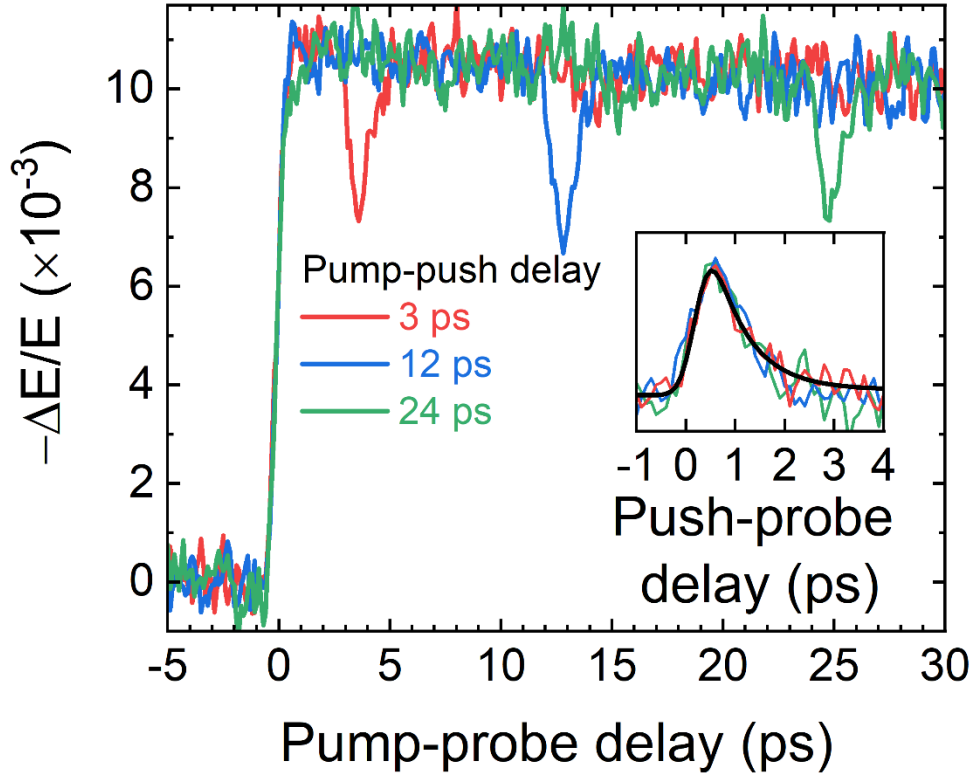


Fig. 30 Visible pump – IR push – THz probe transients for MAPbI_3 , obtained at the peak of the THz waveform for pump-push delays of 3, 12 and 24 ps. Pump: 1.9 eV, $60 \mu\text{J cm}^{-2}$, push: 0.6 eV, 6.5 mJ cm^{-2} in all cases. The dynamics of the push-induced signal in the inset are not affected by the pump-push delay. The thick black line is a Gaussian-convoluted monoexponential fit.

The overall action of the push pulse on the THz absorption is qualitatively similar to what we observe in the analogous PPP-IR experiments^{146, 165, 166} where the probe is resonant with the push transition (i.e. IR push and probe pulses have the same energy). This is shown in Fig. 29(b) for the sample under study. To scrutinise the differences between the THz and IR data, we compare the push-induced kinetics by subtracting the pump-probe traces (PP) for each experiment from the corresponding pump-push-probe transients (PPP). There are two key differences between the THz and IR responses in Fig. 29(c-d). Firstly, the IR response emerges within the IRF, whereas the THz response lags behind by at least 100 fs. Secondly (for low push fluences), the overall probe recovery time (τ) to the pre-push condition is almost twice as long in the THz case. Fig. 29(e-f) reveal a third discrepancy in the responses when τ is measured as a function of the push fluence; the THz dynamics barely change, whereas the IR dynamics do.

From our prior works on MHPs using the PPP-NIR experiment, we can assign the absorption of the IR probe as the intraband absorption by cold carriers. We can also interpret the prompt (within IRF) change in the signal due to the push as the impulsive (re)-excitation of the cold carriers into a higher-energy hot state. The amplitude of the push-induced signal increases with the incident push fluence, and for the highest push fluence, the NIR probe absorption is almost totally depleted by the push (Fig. 31), attesting to the depopulation of the cold state. This cold state and the IR absorption are restored as the carriers cool. The slowing of the carrier cooling dynamics at higher push fluences (hot carrier densities) can be understood through the framework of the hot-phonon bottleneck mechanism,¹⁴²⁻¹⁴⁴ where the energy deposited into phonons through cooling is continually re-absorbed by overlapping polarons.¹⁴⁵⁻¹⁴⁸

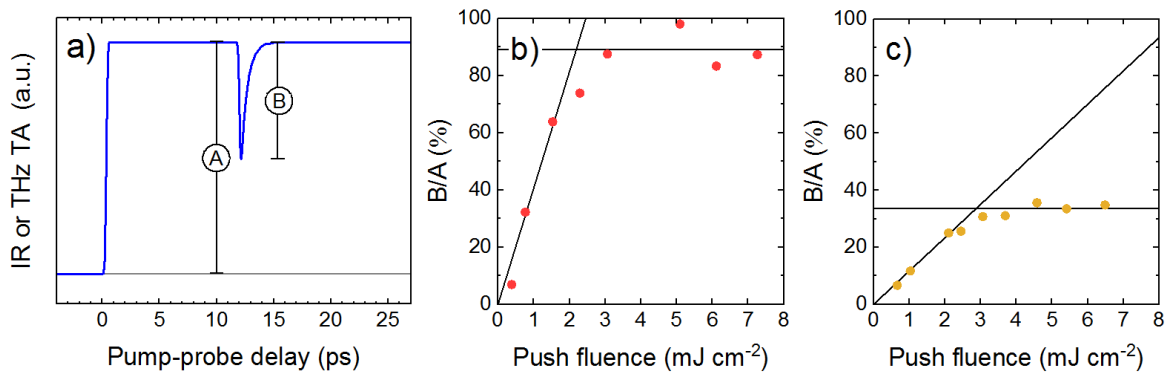


Fig. 31. (a) Schematic of the IR or THz absorption transients in a PPP experiment. Here the relative amplitude of the push-induced signal is obtained from the ratio between ‘B’ (the maxima of the push-induced TA bleach just after the arrival of the push) and ‘A’ (the pre-push TA amplitude). B/A as a function of the push fluence for the (b) IR and (c) THz PPP experiments. In the latter case, the push never fully depletes the absorption of the probe.

Generally, the low-energy THz probe ought to be sensitive to all carriers (cold and hot), regardless of their energy within the electronic band. The push is not capable of interband excitation and therefore does not change the overall concentration of the photoexcited carriers. Since the absorption of THz radiation by charges is sensitive to both their concentration and mobility, it follows that the reduced THz opacity caused by the push is due to the lower mobility of the pushed (hot) carriers compared to the unpushed (cold) carriers. We estimated 0.6 eV energy of hot carrier is transferred to heat. The reduced mobility of the hot states may be due to an increase in their effective mass, as outlined in recent works.^{181, 189} However, taking the

delayed response of the THz dynamics following the IR push, we suggest that this reduced mobility is instead caused by a temporary localised heating¹⁹⁰ of the MHP lattice, associated with the immediate vicinity of the localised charge-carrier (polaron). The small volume of this polaron leads to a high effective lattice temperature, and substantial reduction of the carrier mobility. On a timescale of ps, heat flows out of the polaron volume (equivalently, the polaron moves) and the effective temperature equilibrates with the surrounding ambient lattice, thus restoring the mobility to the pre-push level. This thermal process causes the lifetime of the signal recovery to be constant regardless of the push fluence. Unlike in the NIR experiment, the THz probe absorption is never fully “bleached” by the push, and instead gives an overt saturation (Fig. 31). From this, the push induced reduction in mobility can be quantified from the THz response as being a 35% reduction. From our previous model of temperature-dependent mobility,¹⁸⁹ this reduction from ambient occurs at an effective temperature of 700 K. Equating the 0.6 eV push with this 400 K uplift, we can estimate that there are 18 degrees of freedom which make up the local heat bath around the charge carrier.

To capture the dynamics from the experimental data in a more quantitative manner, we propose the three-state kinetic model depicted in Fig. 32(a). Here, cold polarons (n_c) are re-excited by the push to form hot polarons (n_h). The hot polarons undergo intraband cooling, transferring the excess energy from the carrier to phonons within the polaron volume to form the hot polaron lattice state (n_{hl}). The system returns to the initial cold polaron state after the local lattice heat is equilibrated with the lattice beyond the polaron volume. We emphasise that, though this kinetic model is ostensibly similar to one proposed in the work of Bretschneider et al.,¹⁷⁹ the nature of intermediate state is different. Their model concerns the relaxation of the pre-polaron (free carrier) state and synchronous formation of the polaron, which has also been proposed in other notable works.^{137, 191} In our experiment, we assume that initial pump pulse forms the polaron several ps before it encounters the push. In the case that polaron formation in MAPbI₃ takes ~400 fs, it is unlikely to be ‘unformed’ within a ~100 fs push pulse based on the principle of microscopic reversibility. We therefore exclude a polaron formation time in our analysis and attribute the observed relaxation processes to intraband cooling and polaron-lattice cooling. The system of rate equations for the three-state model is shown below. We assume that PPP-IR tracks the n_h population while PPP-THz principally follows the n_{hl} population.

$$\frac{d}{dt}n_h = I_{push} \cdot n_c - k_c n_h$$

eq. 32

$$\frac{d}{dt}n_{hl} = k_c n_h - k_l n_{hl}$$

eq. 33

$$\frac{d}{dt}n_c = -I_{push} n_c + k_l n_{hl}$$

eq. 34

Fig. 32(b) shows representative global modelling of PPP-IR and PPP-THz data obtained at the same pump and push fluence. The full datasets obtained across a range of push fluences are displayed in Fig. 33. In all cases, the delayed rise of the PPP-THz signal is well reproduced by the intraband cooling process that is observed as a decay of PPP-IR. The summary of extracted time constants for all push fluences is presented in Fig. 32(c). Interestingly, the model suggests that polaron-lattice cooling has a constant timescale around 450 fs regardless of the n_h population density. Meanwhile, the carrier intraband cooling timescale k_c increases with this population density from 400 to 650 fs, as was previously observed and attributed to the hot-phonon bottleneck effect.^{142-144, 146-148, 164} The observed timescales of both cooling processes are in excellent agreement with Bretschneider et al.¹⁷⁹ However, the fact that a ~ 450 fs local lattice cooling timescale k_l is observed in our experiment where polaron formation precedes (and is therefore ruled out from) the observed dynamics may point toward an alternative interpretation of their results.

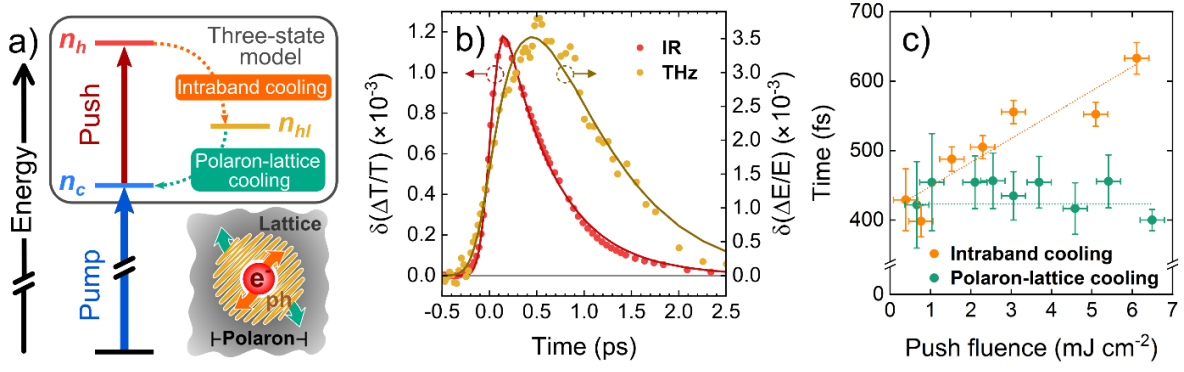


Fig. 32 (a) Energy diagram of the three-state model used to interpret the PPP-THz data. n_c , n_h and n_{hl} represent the cold polaron, hot polaron and polaron-hot lattice populations, respectively. The inset provides a microscopic depiction of the model, where e^- and ph represent an electron and the surrounding phonons. (b) Experimental PPP-IR and PPP-THz push-induced transients at comparable push fluences (5.1 and 5.4 mJ cm^{-2} , respectively), with fits from the system of coupled rate equations. (c) Intraband cooling and polaron-lattice cooling times extracted from the model fits of the experimental data (see Fig. 33). Dotted lines are linear fits as a guide to the eye.

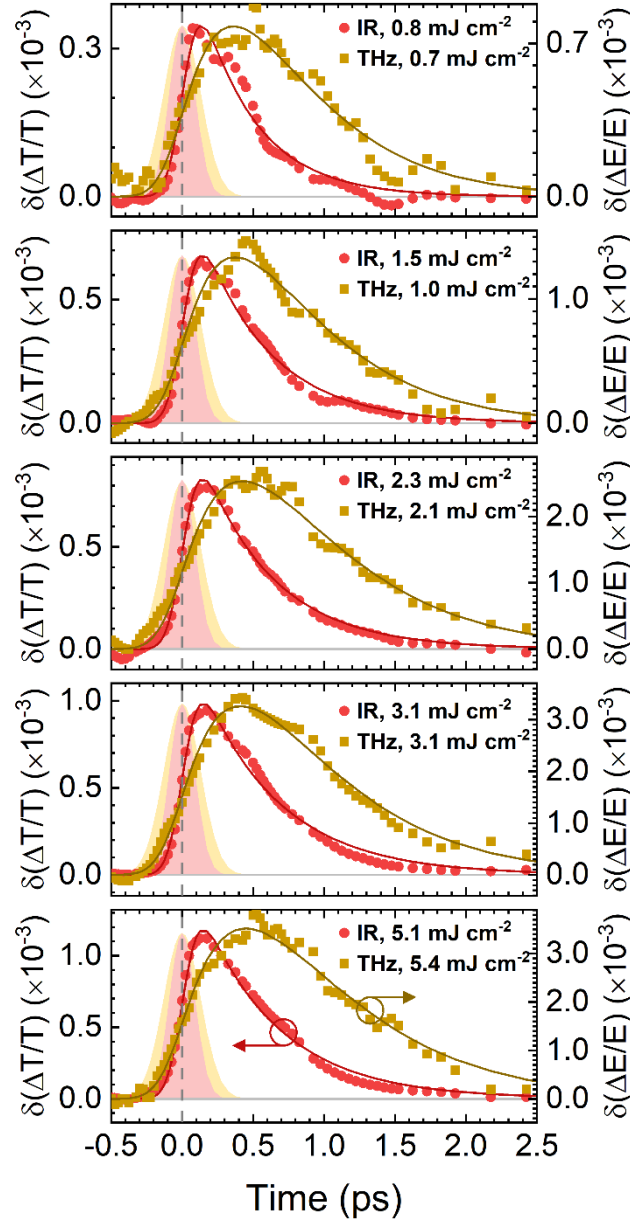


Fig. 33 Global fitting of the experimental PPP-IR and PPP-THz transients for MAPbI_3 across a range of IR (0.6 eV) push fluences (see legend). In all cases the pump was set to 1.9 eV, with a fluence below the Auger threshold at $60 \mu\text{J cm}^{-2}$. The pump-push delay was 12 ps in all cases. The pink and yellow shaded areas at $t=0$ ps depict the instrument response function for the PPP-IR and PPP-THz experiments, respectively. The fit (solid lines) were produced from the system of rate equations presented in the main text. Extracted time constants are presented in Fig. 32(c).

4.3 Time-and-Frequency-Resolved Pump-Push-Probe

To verify our model further, we perform the frequency resolved PPP-THz experiments (scanning both the THz probe and gate delays at each pump delay) to reconstruct the evolution of the dielectric response during carrier relaxation. The results are shown in Fig. 34(a). Upon pumping the sample we observe two strong resonances at ~ 1.25 and 2.25 THz which can be attributed to two groups of optical phonons associated with the bending and stretching of the Pb-I bonds that strongly couple to the carriers.^{[173](#), [174](#), [176](#), [192-195](#)} When the push arrives (in this case ~ 10 ps after the pump), the THz absorption across the whole spectrum is diminished, with the most pronounced reduction at the two aforementioned peaks. This is also shown in Fig. 34 (b), which breaks down the complex photoconductivity spectrum into real and imaginary components. The non-Drude like spectral response tentatively precludes free (non-polaronic) carriers as being the sole origin of the signal.^{[176](#), [182](#)} The evolution of this response as a function of time is non-trivial and will likely require an elaborate analysis of the relevant carrier-phonon couplings at various degrees of quasi-thermal equilibration which is beyond the scope of this work. Notwithstanding the rich spectral behaviour, the dominant effect is a drop in conductivity upon pushing the electronic states to a higher energy level. The interplay between the polaron dynamics and lattice is further corroborated by Fig. 34 (c), which shows that the conductivity recovery dynamics (fitted with Gaussian-convoluted mono-exponential decay at each frequency) are strongly dependent on the THz probe frequency, with the slowest dynamics patently occurring at the peaks. This observation is fairly intuitive in the case that the underlying phonons are strongly coupled to the carriers. In such a scenario, the phonons will be directly heated by the carriers during cooling and before the heat can subsequently dissipate from the modes by scattering into other (non-coupled) phonons. This picture is consistent with our model which essentially conveys the physics as a system of coupled heat baths.

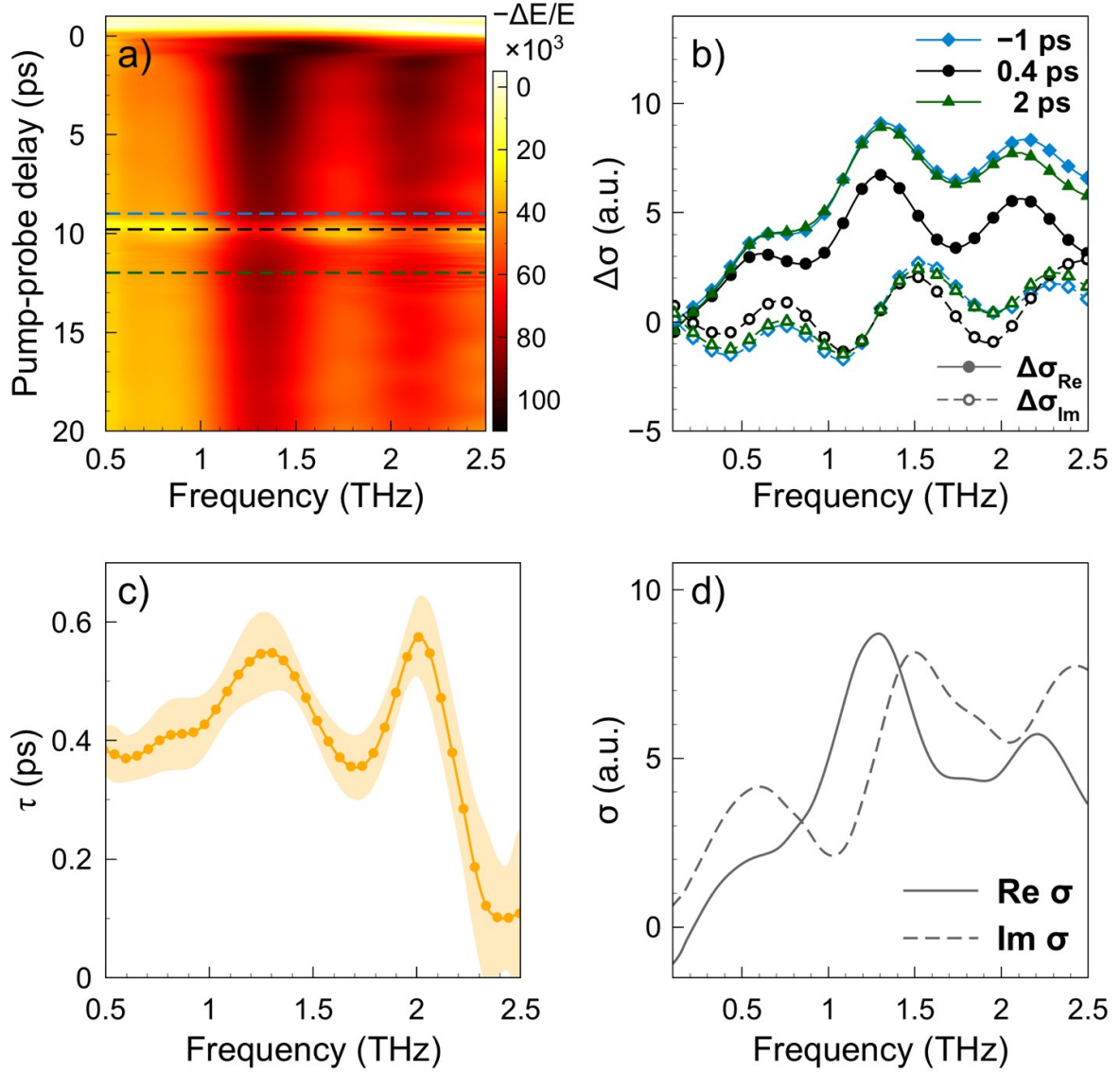


Fig. 34 (a) 2D probe frequency/push-probe delay intensity map for the visible pump-IR push-THz probe experiment, with the pump-push delay set to 10 ps. (b) THz photoconductivity spectra showing the real and imaginary components of the complex conductivity ($\Delta\tilde{\sigma} = \Delta\sigma_{\text{Re}} + \Delta\sigma_{\text{Im}}$) before, at and after the arrival of the push (as depicted by the blue, black and green dashed lines on the intensity map to the left). (c) Overall probe recovery time following the push at different probe frequencies. (d) Simulated frequency-resolved conductivity from the FHIP polaron-mobility theory¹⁹⁶ and an extended version of the material-specific model.¹⁸⁹ The real-component maxima at the phonon group frequencies of 1.25 and 2.25 THz compare well with the measured response, and correspond to a polaron-renormalised interaction with the underlying carrier-phonon coupled modes.

By calculating the full frequency-dependent electrical susceptibility of the polaron in the Feynman-Hellwarth-Iddings-Platzman (FHIP) model,¹⁹⁶ we can simulate the THz response of our lead-halide perovskite model.⁶⁸ This leads to reasonable qualitative agreement with the

observed response. Interestingly we found the best agreement with an effectively zero temperature mobility theory, suggesting that the sub-ps timescale of the THz measurement corresponds to a pre-thermal equilibrium mobility regime. An extended analysis of the frequency-dependent response will be the subject of a future investigation.

In summary, we have developed a novel visible pump – infrared push – terahertz probe spectroscopy (PPP-THz) and used it to uncover obscure aspects of hot carrier relaxation in the benchmark metal-halide perovskite (MHP) methylammonium lead-iodide. The technique allows us to systematically promote band-edge states in semiconductors by means of infrared optical excitation and monitor their subsequent relaxation with a non-contact probe of the photoconductivity. In the case of MAPbI₃, we observe a ~35% drop of the photoconductivity upon supplying the carriers with 600 meV of excess energy. The full recovery of this mobility occurs within a picosecond, but is postponed with respect to the population-only dynamics measured with an ultrafast infrared probe. We show that the observed dynamics can be modelled by a simple two-step sequence involving energy redistribution from the hot carrier to proximate strongly-coupled phonons, and subsequent thermal equilibration of the collective polaron-lattice state with the ambient environment. These results reveal the importance of local lattice heating on the mobility of energetic carriers in MHPs, outlining an additional framework for the design of hot carrier solar cells which consolidate the phononic and thermal properties of the absorber. We envisage that the PPP-THz technique will be instrumental in unlocking other niche optoelectronic applications of MHPs such as ultrafast optical switches,^{[197](#), [198](#)} as well as the characterisation of fundamental excitations (excitons, carriers, charge-transfer states, polarons, trap states) in other emerging materials systems.

5 Non-Parametric Model-Free Analysis for High-Dimension Time-Resolved Spectra

In this chapter, blind signal separation and model-free data analysis for high-dimension multivariate time-resolved spectroscopic data are discussed, along with a GUI software package (Spectrum Decomposition Tool, SDT) written for this purpose. The highlighted capability of the software includes rank estimation via SVD and EFA, spectra decomposition by modified NMF, time-series analysis by SSA with clustering, and dimensionality reduction by ICA.

The traditional data analysis methods for timer-resolved spectroscopy data are questioned and challenged as they are prone to over-fitting, and introduction of empirical parameters to the model.

A modified NMF algorithm is proposed to replace the popular genetic algorithm in the TAS data factorisation. SSA is introduced as a superior time-series analysis and signal separation tool to Fourier analysis, and its capability to extract coherent oscillation from noisy data is demonstrated. High-dimension TAS datasets and time-resolved 2D spectroscopy datasets are analysed with ICA demonstrating the separation of experimental variable dependent and independent data components. All key features of SDT are tested with simulated and real experimental data.

**All Fourier transforms in this chapter are performed with next-power-of-2 length zero padding and Blackman-Harris cosine sum window unless noted otherwise.*

5.1 The Model Fitting Problem

Applying excessive parametric models to experimental data seems to have become a common practice in the ultrafast time-resolved spectroscopy community (Fig. 35 left). Some examples can be found in chapter 1.3. Even theoreticians have added parameters with vague physical meaning to known physical models in order to explain the discrepancy between the data and the original physical model, for example, Drude-Smith model¹⁹⁹. This over-parameterisation practice invites over-fitting, and to this day, publications involving time-resolved spectroscopy data analysis rarely regularise or cross-validated their models.

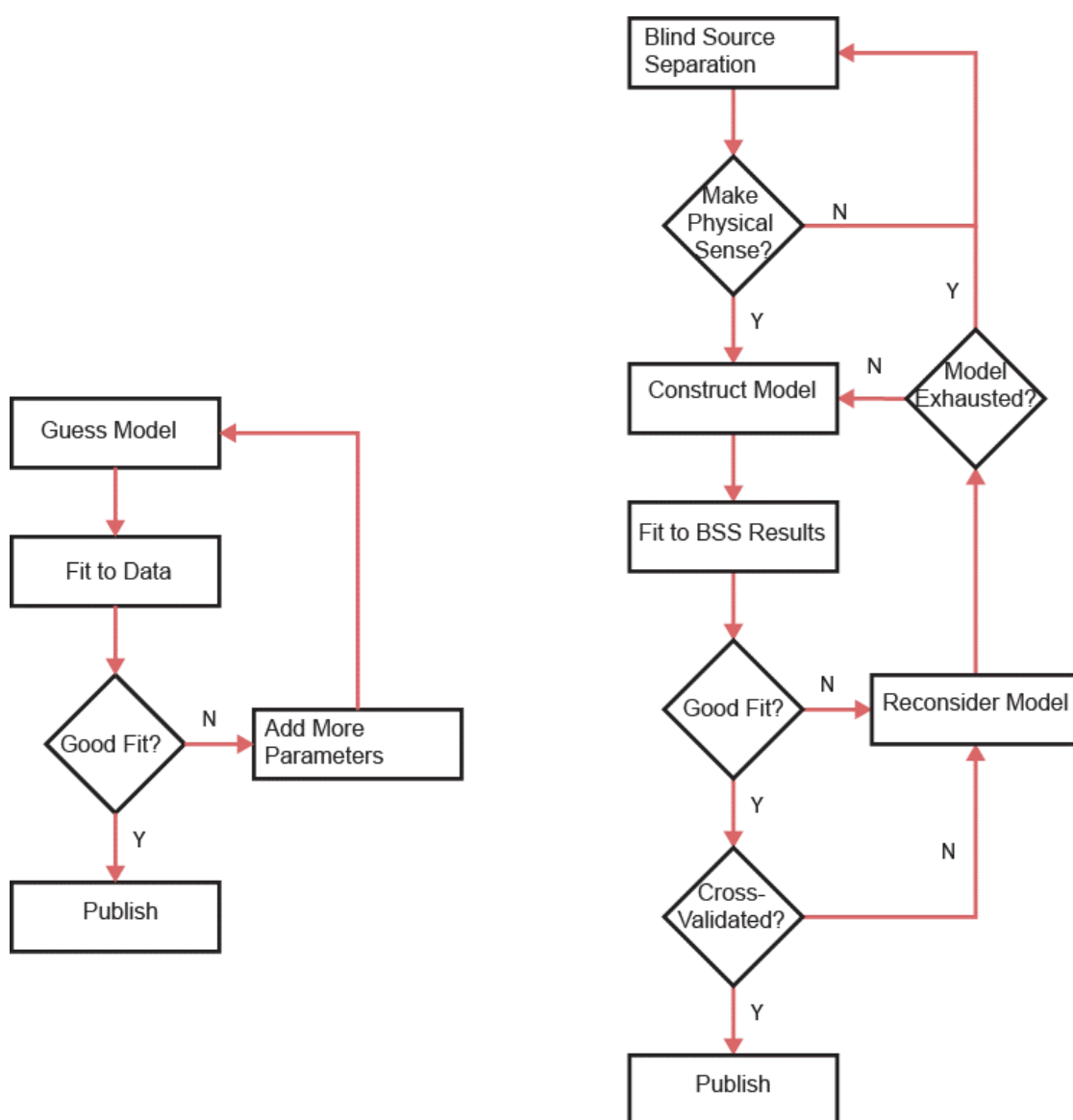


Fig. 35 (left) Common practice of data interpretation. (Right) Proposed practice of data interpretation.

The sheer size and dimensionality of multivariate time-resolved spectroscopy data can be very intimidating at first glance. However, arsenals of statistics and machine learning tools are available to decompose the spectroscopy data with quasi-orthogonal basis without any physical assumption. These techniques are known as blind source separation (BSS), which is especially useful in the ultrafast spectroscopies since most times the physical model is unknown.

The physical model should be inspired from the experimental results, instead of forcing pre-conjectures to the experimental results at the risk of over-fitting. However, it's hard to get "inspiration" when the data encountered in time-resolved spectroscopy is usually multidimensional and multivariate. BSS is able to break them down to physically plausible components and thus reducing dimensionality making the data less intimidating.

Therefore, I propose the analysis of time-resolved spectroscopy data, where the physical model is unknown, starts with BSS to produce physically plausible components. (Fig. 35 right) Then instead of fitting models to partial or whole of the data, fitting should be done to the components, which have reduced dimensionality but still retain almost all of the information from the original data, and thus require less parameters from the model. In addition, all model fittings should be accompanied with cross-validation. While cross-validation is not trivial and even intimidating for high-dimension data, it is a necessary step to rule out over-fitting, which could completely invalidate the model.

The scope of this chapter is limited to BSS, which is already a self-containing complicated topic, and no discussion on physical models is included in the chapter.

5.2 Bilinear Interpretation of Time-Resolved Spectra

Intuitive interpretation of broadband (the size of the spectral dimension is non-unity) time-resolved spectroscopy data, especially those for the blends whose components have large spectral overlap is extremely challenging. This is because the two dimensions of the time-resolved data are almost never independent, and the spectral dimension is the superposition of individual spectrum for all the species, and the time dimension is the combined kinetics for all physical processes. *i.e.*, the data matrices are never physically full-ranked and rarely 1-ranked. However, algebraically they are always full-ranked due to noise, artifacts, and physical non-idealities, which makes data analysis even more challenging.

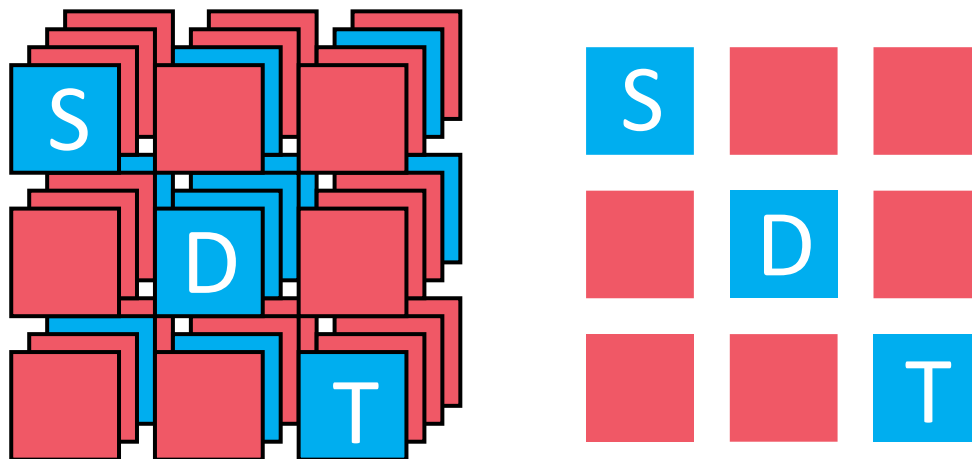
Data matrices are not rectangles of numbers. Rich information such as correlation and covariance are hidden in those rows and columns. However, in literature they are treated interpedently as if the matrices are full-rank, which is not true. Directly forcing an arbitrary model with large number of parameters or using poorly understood but convenient models such as the so-called power law kinetics, onto the data without consideration of overfitting, regularisation or cross-validation is the common practice.

Nevertheless, the 2D data matrices can be decomposed in a sense of solving a system of linear equations or factorised into canonical forms based on eigenvalues. With unknown physically-meaningful models of the system, it is rational to start the analysis with non-parametric approaches *i.e.*, model-independent methods which do not make assumptions about the physical system.

The time-resolved spectra can be viewed as the evolution of population of independent spectral species^{[200](#), [201](#)}. The spectrum can be therefore factorised to the outer product of individual spectral species (spectra) and the time evolution of their populations (kinetics). However, the spectral components are not always the same as the intuitive physical species such as exciton and polaron, because those physical species can have their spectral shape changed over time evolution, which creates additional eigenvalues in the bilinear interpretation.

This problem can be alleviated by introducing physical constrains, such as forcing non-negative kinetics, when factorising data matrix.

5.3 Introduction to Spectrum Decomposition Tool



The Spectrum Decomposition Tool (SDT) is a software package designed for non-parametric data analysis of high-dimension spectroscopic data. SDT is armed with assortments of blind signal separation (BSS) algorithms, dimension reduction techniques, and advanced eigenvector-based time-series analysis with clustering algorithms. The SDT also includes zero-human-intervention signal processing algorithms that automatically recognise and import raw data in various forms, which is followed by completely automatic signal processing including outlier removal, data gap interpolation, *etc.*

The automatic system is supplemented by user-guided artifact removal functions such as background subtraction and group delay distortion correction. It also features rich graphical user interface for rapid inspection, visualisation and navigation of high-dimension datasets. The analytic elements of SDT will be explained in detail in the following chapters.

** SDT is written in MATLABTM and is free and opensource under GPLv3 license. The author of this thesis is the sole developer and maintainer of the SDT.*

5.4 Matrix Rank Estimation and Factorisation

5.4.1 Singular Value Decomposition

It is crucial to find out (or at least estimate) the number of spectral species in the time-resolved spectrum before the data analysis can proceed further. Singular value decomposition (SVD) is a popular approach to address this problem. Unlike eigenvalue decomposition, this generalised eigenvalue-based matrix decomposition method accepts rectangular matrices. SVD calculates full-size singular values sorted in descending order.

$$\mathbf{M} = \mathbf{U} \mathbf{S} \mathbf{V}^T$$

eq. 35

Where $\mathbf{M}$ is the data matrix, $\mathbf{U}$ is the left singular vectors corresponding to independent spectral components, $\mathbf{V}^T$ is the conjugate transpose of the right singular vectors corresponding to the time-resolved amplitudes of the spectral components, and $\mathbf{S}$ is a diagonal matrix containing the singular values sorted in descending order. Since all experimental data matrixes are algebraically full-rank due to physical non-idealities, SVD is particularly useful to calculate the real rank by truncating the cluster of vectors with small singular values. One could observe in $\mathbf{S}$ that the first few singular values are significantly larger than the rest of them. This gives the approximated rank of $\mathbf{M}$ *i.e.*, the number of independent spectral species. The error of this low-rank approximation with first n ranks is conveniently given by the $n + 1^{\text{th}}$ singular value, which equals the spectral (L2) norm of the difference between $\mathbf{M}$ and $(\mathbf{U}\mathbf{S}\mathbf{V}^T)_n$.

$$\|\mathbf{M} - (\mathbf{U}\mathbf{S}\mathbf{V}^T)_n\|_2 = \text{diag}(\mathbf{S})_{n+1}$$

eq. 36

5.4.2 Evolving Factor Analysis

When dealing with noisy data, it is possible some minor components have eigenvalues very close to the noise level and it's not possible to determine whether such components are artifact or physically meaningful components. Singular values of matrix subspaces can be considered to solve this issue. Evolving factor analysis (EFA)²⁰² calculates the SVD for data subsets with

increasing variable range from either the beginning (forward EFA) and the end (backward) of the variable axis, which can be either time or wavelength in time-resolved spectroscopy data. EFA has been successfully and extensively implemented in the spectroscopic peak analysis of chromatography²⁰²⁻²⁰⁶. EFA shows the evolution and emergence of eigenvalues, which could also be used as the initial estimation of the kinetics²⁰⁷. EFA is also a powerful tool to estimate the time region where there is only one significant spectral component, which is a valuable information for the subsequent data decomposition. Using the averaged spectral feature in that time region (often at very early or late time) as one of the basis vectors may lead to the solution that is intuitive to understand.

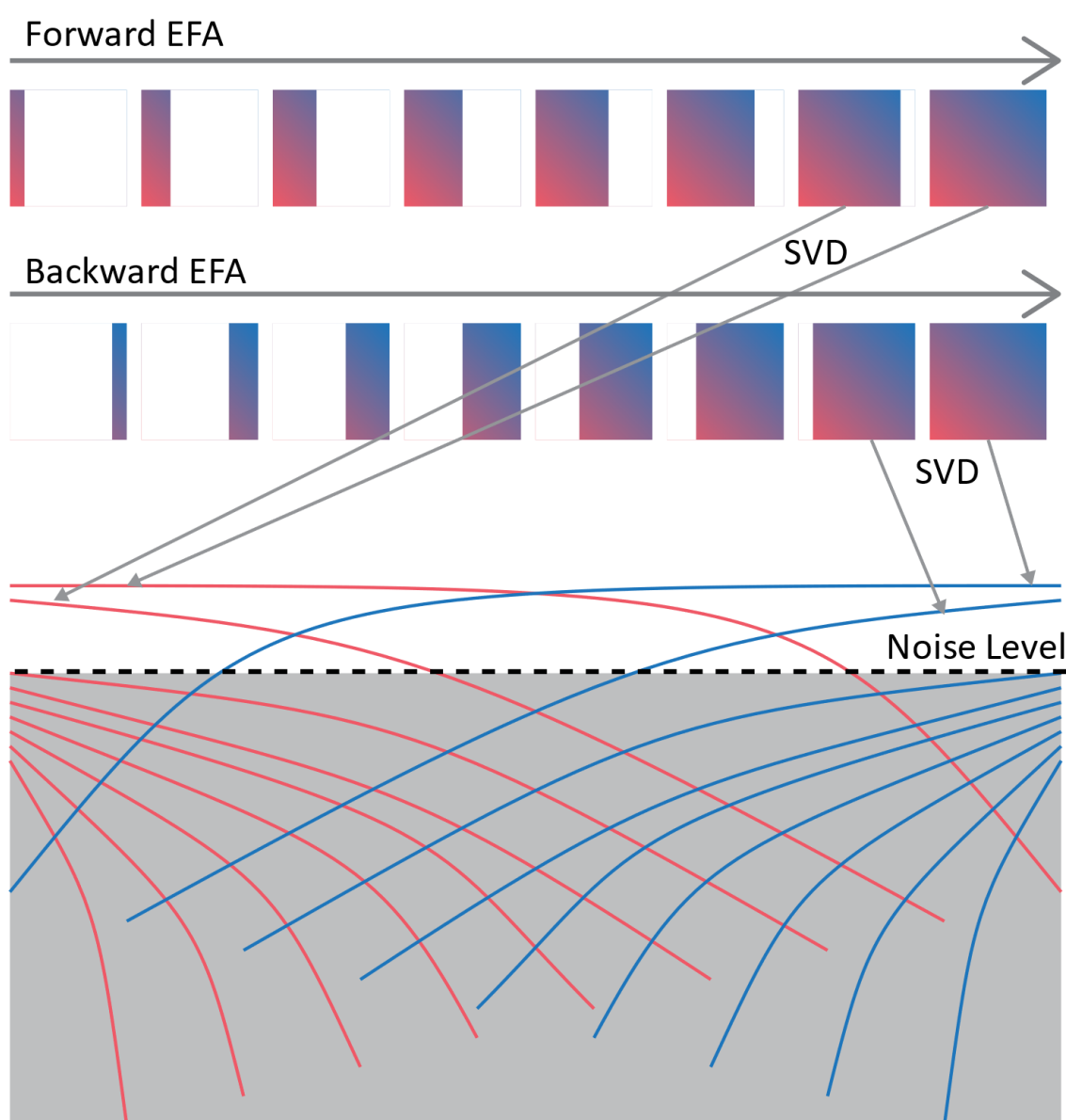


Fig. 36 Illustration of EFA. The data matrix (rank-2) consists of a short-lived component and a long-lived component.

5.4.3 Non-Negative Matrix Factorisation

While SVD is popular in time-resolved spectra analysis, the right singular vectors, which supposedly represent the kinetics of the spectral components (left singular value), are sometimes zero-crossing. This makes SVD unsuitable for spectra decomposition since negative kinetics have no physical meaning.

Non-negative matrix factorisation (NMF) addresses this problem by imposing non-negative constraint on the vectors.

$$\mathbf{M} \cong \mathbf{WH} \quad \min_{\mathbf{W}, \mathbf{H} \geq 0} \|\mathbf{M} - \mathbf{WH}\|_F$$

eq. 37

Where $\mathbf{M}$ is the data matrix containing time-resolved spectra (the columns are spectra and rows are kinetics), $\mathbf{W}$ and $\mathbf{H}$ are matrices containing non-negative vectors that represents the spectral components and kinetic components respectively. The optimisation problem can be solved by either alternating least square (ALS) or multiplicative update.^{[208](#)}

In time-resolved spectroscopy sometimes the spectra can be negative. Semi-non-negative matrix factorisation (SNMF) is a modification of NMF that allows $\mathbf{W}$ to have negative values.

$$\min_{\mathbf{H} \geq 0} \|\mathbf{M} - \mathbf{WH}\|_F$$

eq. 38

This generalisation of NMF is rather trivial to employ and is implemented in the SDT.

5.5 Factorisation of Rubrene TAS Data

As introduced in chapter 1.1.1, singlet fission (SF) is an important pathway for OPVs to recycle excess energy. The kinetic pathway of SF must be understood in order to engineer SF material. For example, a kinetic model that accounts for both non-adiabatic and adiabatic crossing have been proposed.²⁰⁹ Proper validation of such models require discrimination and extraction of singlet and triplet population kinetics. However, the spectral signatures of singlet and triplet states are unknown and they are extremely likely to have overlaps. Therefore, BSS is the obvious choice to proceed.

Here, a dataset of multivariate temperature-dependent TAS measurement of rubrene single crystal in the NIR region was used to test BSS ability of SDT.

The rubrene single crystals (**Fig. 37**) were grown using physical vapour transport method. The sample was measured on a typical TAS setup powered by a Ti:Sapphire mode-locked amplified laser with 800 nm fundamental harmonics and 1 KHz repetition. The pump pulse is generated by OPA (430 nm, 160nJ, 500 μ m) and chopped to 500 KHz. The probe pulse is a supercontinuum generated by YAG crystal and collected by NIR PDAs. (Check chapter 1.2.3 for TAS operation details.) Cryostat was used to control sample temperature from 80 K to 330 K. Polarisation of both pump and probe beams were aligned closely to oA crystal axis. the sample was allowed 20 minutes to reach thermal equilibrium before each measurement.

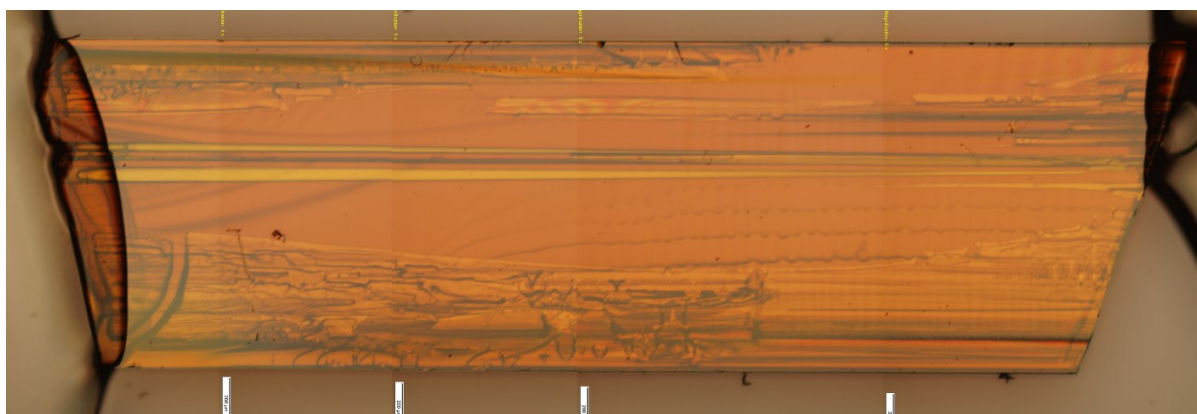


Fig. 37 *Optical microscopy of the rubrene single crystal used in the measurement.*

The first step of BSS is finding out the number of orthogonal components in the TAS data. Here, the TAS data measured at 200 K is selected to demonstrate matrix factorisation. From SVD, the first 2 components already explain more than 95% of the data (Fig. 38, UR). In EFA (Fig. 38, LL and LR), the emergence and disappearance of the first two curves (red and blue), corresponding to the two largest singular values, are in excellent agreement with the peaks seen on the 2D map (Fig. 38, UL). Therefore, we can estimate the rank of the data matrix to be 2, which will be used for spectrum decomposition.

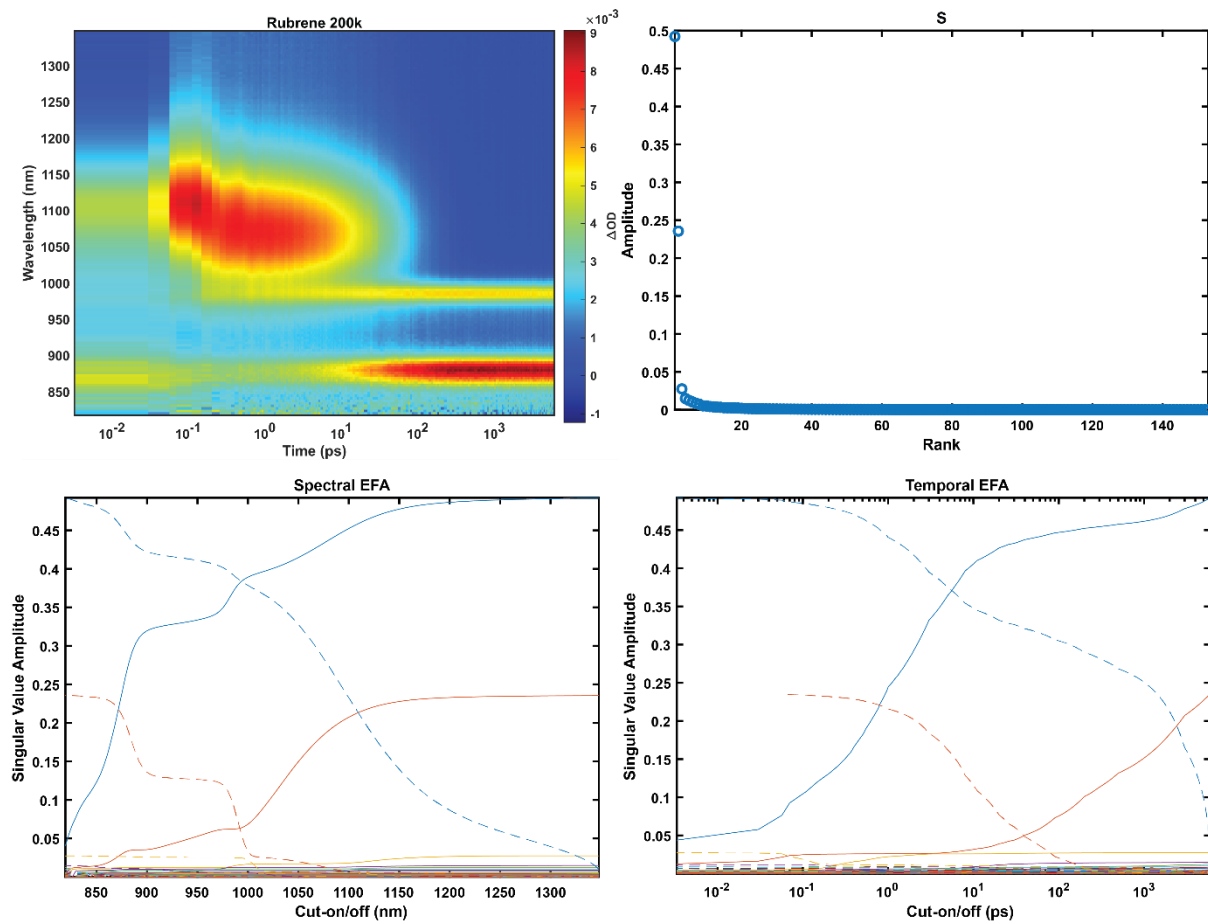


Fig. 38 TAS of single crystal rubrene at 200 K. (UL) The TAS 2D map in NIR region; (UR) Singular value of the full 2D map. (LL) Spectral EFA obtained by slicing the 2D map in the wavelength direction; (LR) Temporal EFA obtained slicing the 2D map in the pump-probe direction.

NMF was performed on the 200 K rubrene TAS data (Fig. 39) with 1000 repetitions and random starting values using ALS algorithm. The optimisation converged in less than 3 seconds. In comparison, genetic algorithm, which is popular in TAS data decomposition²¹⁰, took 15 minutes to converge on the same computer.

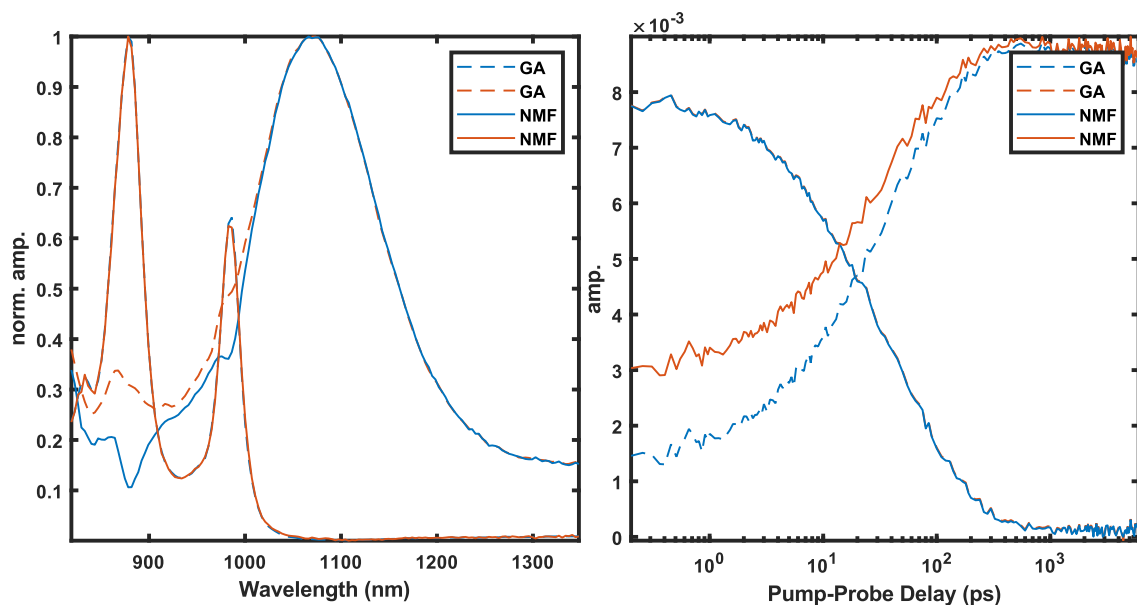


Fig. 39 NMF and GA decomposition of NIR TAS data of rubrene single crystal. NMF converged in 3 seconds with residue RMS of 1.3×10^{-4} . GA converged in 15 minutes with residue RMS of 1.4×10^{-4}

The results of NMF and GA are somewhat similar with one component completely identical. However, NMF is more aggressive and converged at slightly lower residue. The difference in computation cost between GA and NMF is substantial (3sec vs. 15min) making NMF far superior in exploratory data analysis.

5.6 Dimension Reduction for Multivariate Datasets

5.6.1 Independent Component Analysis

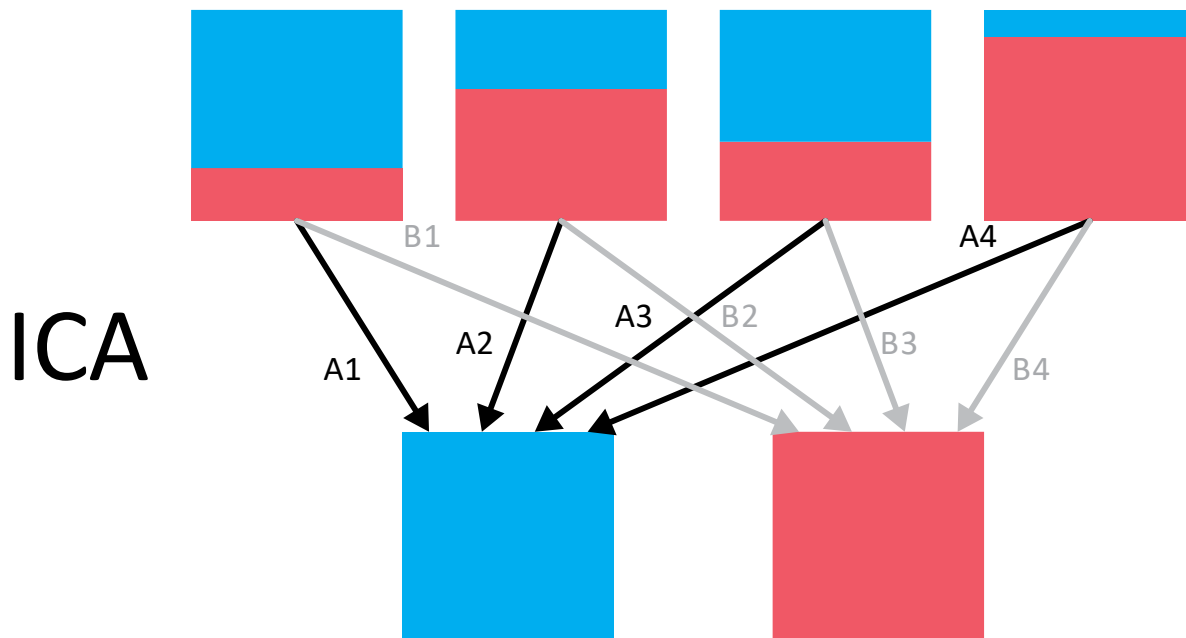


Fig. 40 Illustration of dimensionality reduction via independent component analysis. The original 4 sets of data are unmixed into linear combination of two signatures.

Measuring time and frequency resolved spectra against a third variable is one of the most common experiment in time-resolved spectroscopies. However, in literature the analysis of time-resolved data sets is usually somewhat simplistic, involving extracting certain scalar feature from the time-resolved map such as spectral peak position at certain time delay or rise/decay time at certain wavelength. Again, with unvalidated physical model it is questionable that the criteria of deriving a scalar off a matrix is physically valid as most of the information is lost.

In non-parametric data analysis approach, independent component analysis (ICA)²¹¹ can be employed to extract exact dependency of spectral-temporal features in multivariate datasets. The evolution of the time-resolved picture against the measurement variable can be considered as mixed responses of features to the variable, which can be separated on orthogonal basis.

ICA is an optimisation problem to find nondegenerate transform matrix W , that reduce the data matrix X to independent components Z :

$$X_{m \times n} W_{n \times p} \cong Z_{m \times p} \quad p \ll m$$

eq. 39

The objective function to find W is not trivial and differs from algorithms. Although ICA is a well-established tool in statistics and advanced signal processing, it has yet to make its way into time resolved spectroscopies. Several ICA algorithms, such as FastICA^{[212](#), [213](#)}, JadeICA^{[214](#)}, and Reconstruction ICA(RICA)^{[215](#)} exist with different objective functions and optimisation methods. While FastICA and JadeICA are lite and fast, and even suitable for embedded applications^{[216](#)}, RICA is more robust, designed for more complicated data and is able to produce highly orthonormal transformation. Therefore, despite the high computational costs, RICA was chosen to be implemented here to process high-dimension time-resolved spectroscopic data.

5.6.2 Unmixing Multivariate TAS Dataset

The complete temperature-dependent rubrene TAS dataset was analysed with ICA to separate temperature-dependent and temperature-independent spectral features, and find out the exact temperature dependency in the form of transform weight matrix. In contrast with traditional features such as peak positions at fixed pump-probe delay time, and decay curve lifetimes at fixed wavelengths, each feature here covers the whole of the time and wavelength dimension, i.e., the features themselves can be interpreted as TAS surfaces, where not a single datapoint was omitted.

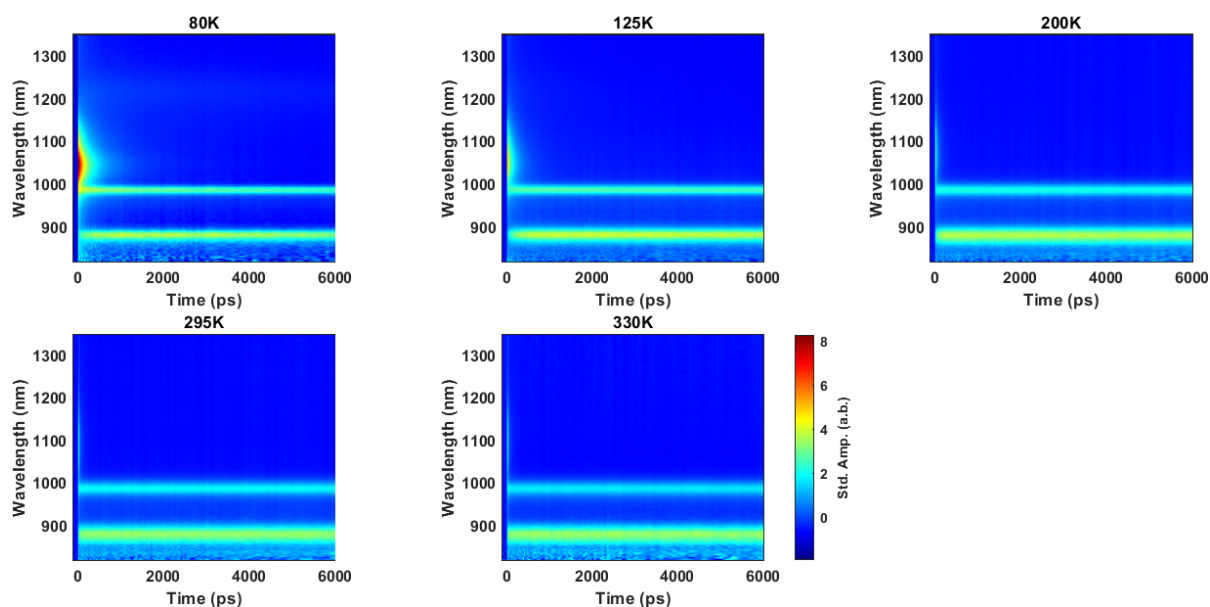


Fig. 41 Standardised temperature-dependent TAS data of rubrene single crystal measured against 5 cryostat temperatures.

As illustrated in Fig. 41, The PIA feature at 1150 nm diminishes and blue-shifts with increasing temperature. While being quite evident, this observation is qualitative and difficult to quantize due to the high dimensionality of the dataset. RICA is able to quantitatively decompose the TA pictures to components with corresponding weight against temperature. Fig. 42

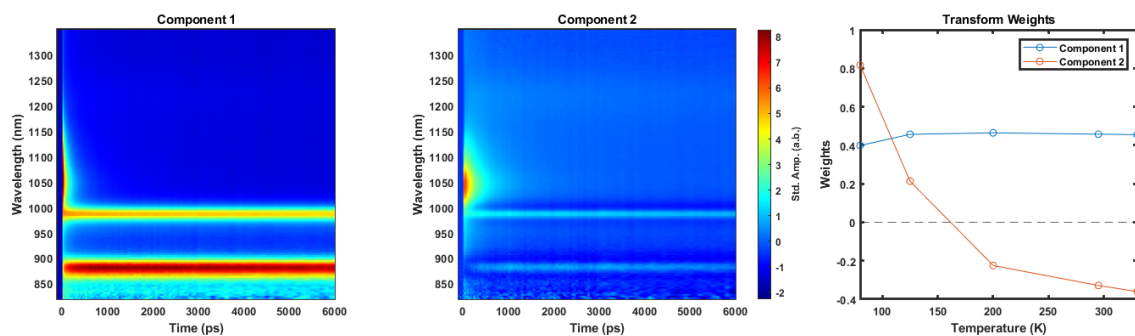


Fig. 42 2-component RICA of rubrene single crystal TAS data clearly showing the temperature-independent (left), component and temperature-dependent component (middle), and the exact temperature dependency (right).

2-component RICA has cleanly separated the dataset into temperature-independent part and temperature-dependent part as indicated by the transformation weight. The two components alone with the transformation weight can quantitatively explain the amplitude change and position shift of the PIA peak and any other feature. Also, original dataset (X) can be reconstructed with very little losses by computing the outer product of the components (Z) and the inverse transform weights (W^{-1}). (Multiply both side of the eq. 39 with W^{-1})

5.6.3 Signature Extraction of Time-Resolved 2D Spectroscopy Data

Time-resolved 2D spectroscopy is more complicated than multivariate time-resolved spectroscopy as the size of every dimension is quite large. Here NFA IEICO, a potential SF material, was measured on 2D electronic spectroscopy (2DES)²¹⁷⁻²¹⁹ in order to extract signatures for various states involved in SF. 2DES uses the same source for pump and probe, and the wavelength range is typically inside UV-VIS-NIR, producing snapshots of 2D spectra at different pump-probe delays.

The results of 2DES may seem overwhelming due to their dimensionality. However, RICA can reduce the stacks of time-resolved 2D maps into just few signature 2D components with a linear transform weight while losing very little information from the original spectra. The transform weights indicate a fast-decaying component (Fig. 43, right column, blue lines) and a fast growing but long-lived component (Fig. 43, right column, red lines). Those components

correspond well with singlet and triplet states and there corresponding signature is also extracted as 2D maps (Fig. 43, first two columns).

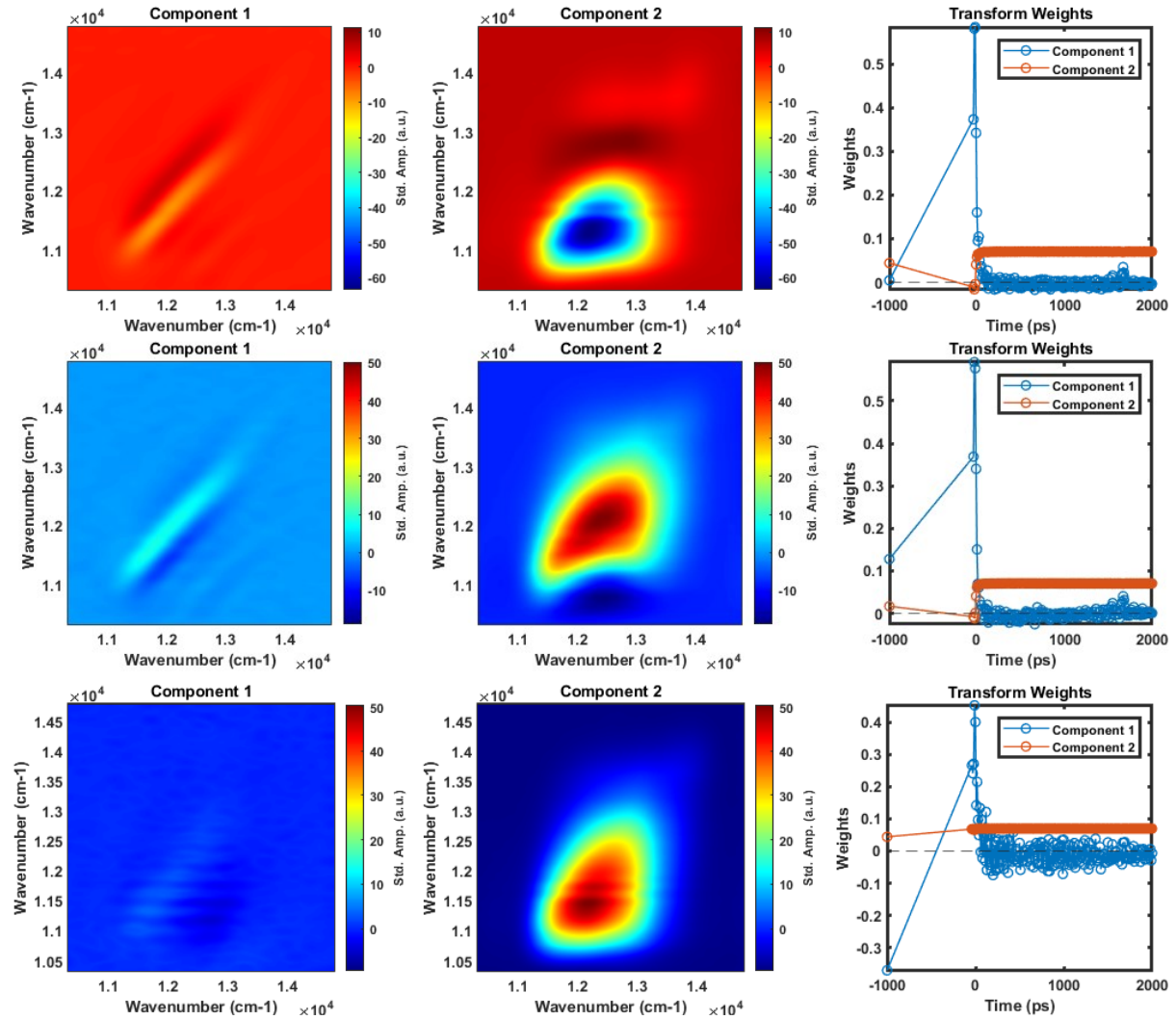


Fig. 43 RICA of IEICO 2DES data. (**upper row**) real part of the spectra reduced to 2 components; (**middle row**) imaginary part of the spectra reduced to 2 components; (**lower row**) amplitude of the spectra reduced to 2 components.

5.7 Coherent Spectra Analysis

Coherent oscillations from lattice motion, vibrionic can be detected by time-resolved spectroscopies if the pulse is sufficiently shorter than the period of the oscillations. The common approach for time-series analysis is simply parametric detrending by curve fitting followed by Fourier analysis.

However, parametric curve fitting requires good initial guess and correct boundary, which may not be available, and/or varies significantly between wavelengths and different samples. Moreover, Fourier analysis require sufficient SNR because everything else is transformed alone with the signal, introducing noises, artefacts and/or baselines at every frequency.

5.7.1 Singular Spectrum Analysis

These problems can be avoided by time series analysis methods that do not depend entirely on frequency space, such as singular spectrum analysis (SSA). SSA is a powerful time-series analysis method with successful applications on physical science.²²⁰ It utilises empirical orthogonal functions (EOF) instead of sinusoidal waves as basis to deconstruct time series.

SSA is essential principal component analysis (PCA) of Hankelised time series. Consider time series X :

$$X = (x_0, x_1, x_2, x_3, \dots, x_n)$$

eq. 40

X can be embedded to a trajectory matrix by stacking up the time series with increasing time delay. (Fig. 44) Let the length of the time series be N , and window size of the embedding be L , and $K = N - L + 1$ is the length of truncated time series. The embedding is essentially stacking up the truncated time series at different offsets. This process can be described as the Hankelisation of vector X since the resultant trajectory matrix is a Hankel matrix. Let H be the Hankelisation operator that embeds the time series as illustrated in Fig. 44:

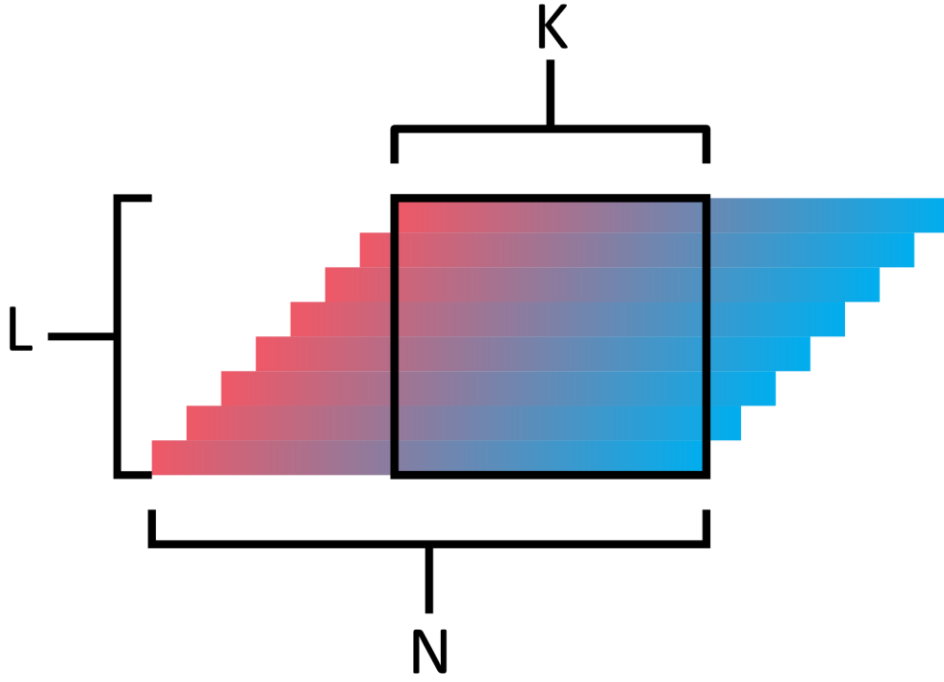


Fig. 44 Illustration of time-delayed embedding (Hankelisation) of time series with length of N , and L copies of the time series were stacked with offset, resulting truncated length K . Note that the anti-diagonal elements are identical.

$$Y = H(X) = \begin{bmatrix} x_0 & \cdots & x_L \\ \vdots & \ddots & \vdots \\ x_K & \cdots & x_N \end{bmatrix}$$

eq. 41

Where, Y is a Hankel matrix containing the trajectory of X . The goal is to extract the principal components of Y , which can be done by eigen decomposition of its covariance matrix:

$$\text{cov}Y = Y^T Y / K$$

eq. 42

Solving the eigenequation:

$$covY = V\Lambda V^{-1}$$

eq. 43

Where V is the eigenvectors and Λ is the eigenvalues. The principal components PC and scores T can be calculated as:

$$PC = VY \quad T = V$$

eq. 44

Alternatively, this can be done via singular value decomposition, which may offer better computational performance because SVD eliminates the need to compute covariance matrix of Y , and SVD also offers the option to process the square subspace of Y only:

$$Y = U\Sigma V^T$$

eq. 45

Where U is the left singular vector, Σ is the diagonal matrix containing singular values, and V is the right singular vector. The principal components PC and scores T would be:

$$PC = U\Sigma \quad T = V$$

eq. 46

Using either method, Y can be decomposed to:

$$Y_i = PC_i * T_i^T \quad Y \cong \sum_{i=1}^L Y_i$$

eq. 47

Reconstructing the original time series from the principal components is simply averaging the trajectory matrix $Y(i)$ anti-diagonally. Let H^{-1} be the reverse Hankelisation operator that revert a matrix to the vector form by anti-diagonal averaging. The reconstructed components $RC(i)$ contains L number of vectors, whose sum is a very close approximation of the original X .

$$RC(i) = [H^{-1}(Y_1), H^{-1}(Y_2), \dots, H^{-1}(Y_L)]$$

eq. 48

$$\sum_{i=1}^L RC(i) \cong X$$

eq. 49

Unfortunately, H^{-1} is the most computationally costing operation of SSA due to the sheer size of $Y(i)$ and the need to iterate over its every element to compute the average. It's recommended to carry out this step with parallelisation.

The only parameter in SSA is the window size, which equals the number of components that the time series is deconstructed into. SSA with large windows size is very computationally costing and choosing the optimal window size is non-trivial and still subjected to debates.^{[221-223](#)} However, the windows size selection primary impact computational costs, instead of data analysis quality as long as the window size is large enough but satisfies $L < \frac{N}{2}$.^{[221](#)} Since our datasets are relatively small, the window size can be generously allocated.

All SSA in the following chapters is done with window length equal to one-third of the total length of the respective time series, unless noted otherwise.

5.7.2 Evaluation of Singular Spectrum Analysis

5.7.2.1 Comparison between SSA and Fourier Analysis

In order to evaluate the effectiveness of SSA analysing time-series in noisy condition, artificial data was created to test BSS ability of SSA. The first test data (Fig. 45 *left*) comprised of a very large exponential decay, one sine wave, and normally distributed noise (SNR=27dB). This test data is designed to simulate simplest scenario of coherent spectrum, where exponential decay of charge carriers is observed along with vibronic beating.

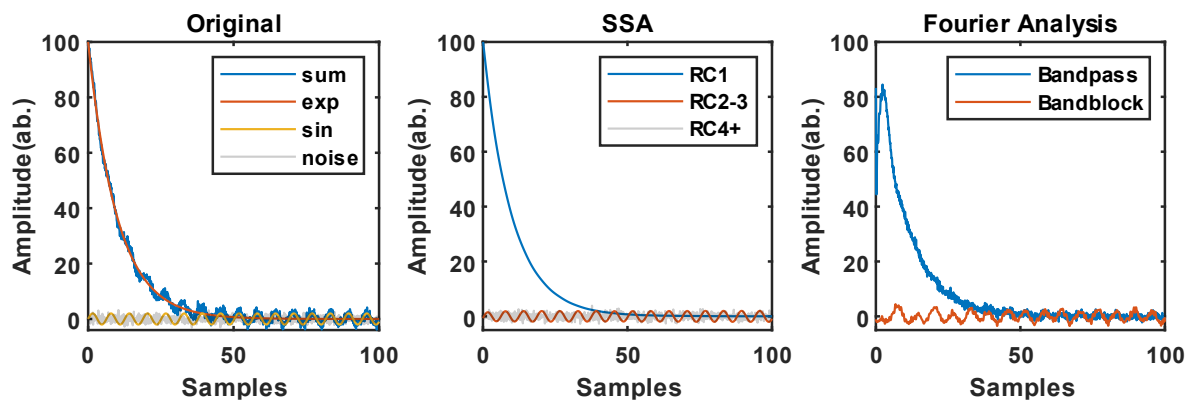


Fig. 45 Time series analysis of mildly noisy data consists of one exponential decay with high amplitude, one sine wave, and noise. (left) test data and its compositions. (middle) Simple SSA of test data without clustering. (right) Fourier analysis of the test data with bandpass filter.

SSA is directly applied to the data with window size one-third of the sample length. The result (reconstructed components) is sorted by amplitude. As illustrated in Fig. 45(*middle*), the separation is nearly perfect and the random noise was cleanly cut out even without the knowledge of sampling frequency.

In contrast, Fourier analysis using bandpass and bandblock filter centred at the sine wave frequency. (Fig. 45 *right*) produced poorly separated exponential and sinusoidal components despite the advantage of knowing the signal frequency. This is expected as the high-amplitude exponential decay is a Lorentzian function in frequency space, which is present at every

frequency cannot be completely blocked by frequency-domain filters. The same goes to the random noise.

5.7.2.2 Signal Recovery from Extreme Noise with SSA

Now that the advantages of SSA over the common Fourier analysis has been demonstrated. More rigours test, such as recovering signals below noise level was also done to demonstrate the BSS capability of SSA.

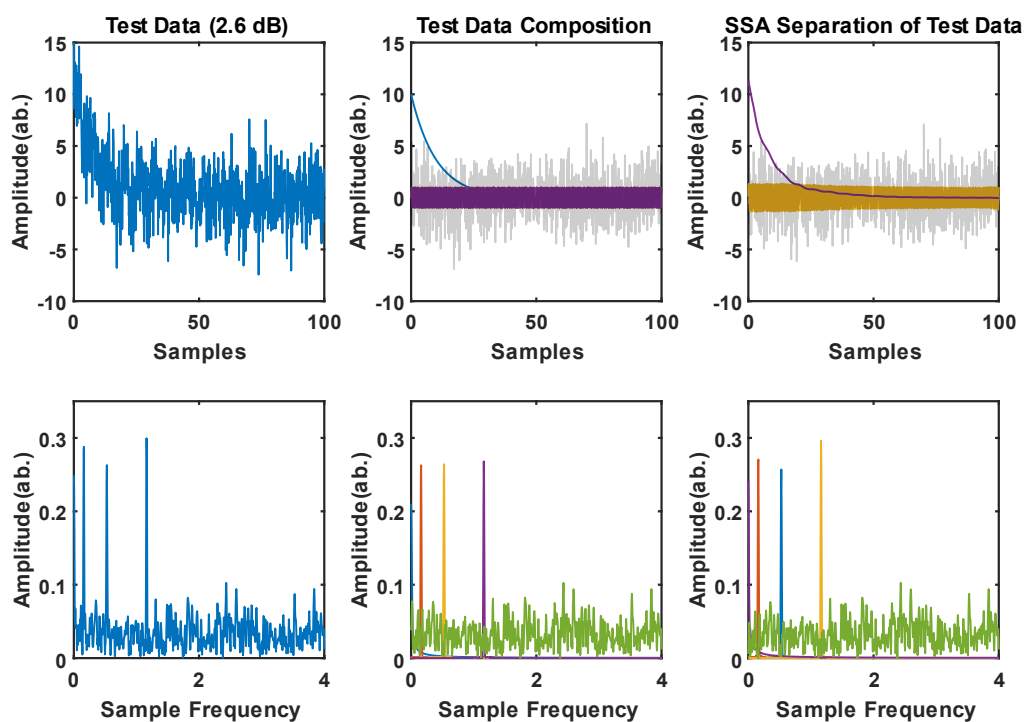


Fig. 46 SSA of extremely noisy data consists of one exponential decay, three sine waves, and extreme noise. (upper row) Time domain; (lower row) Frequency domain; (left) Extremely noisy test data with SNR=2.6dB; (middle) Test data composition; (right) Fourier analysis of the test data with bandpass filter.

SSA was tested on artificial data containing an exponential decay, three sine waves, and extreme noise (Fig. 46 left and middle). The first four components (signals), along with the sum of the rest of the components (noise) of the resultant RC (right) shows excellent reconstruction of the original data (middle) in both time and frequency domain. All three

sinusoidal signals were recovered at accurate frequency and waveform, and the separation only suffered slight amplitude distortion due to the non-ideal orthogonality of the signal components.

5.7.3 Automatic Trend Extraction

Trend extraction is a necessary step for broadband coherent time-resolved spectra analysis, as the exponential components in the time series are substantially more prominent than oscillations in both time and frequency domain. The traditional method for trend extraction is nonlinear fit of the trend with a combination of exponentials and polynomials, which require initial guesses and boundaries. The parameters are different across wavelengths and datasets, making curve-fitting impossible to automate. Instead of assigning this mundane task to unfortunate researchers, who would spend hours if not days trying to find the correct curve-fitting model and parameters.

Trend extraction can be completely automated by SSA and accomplished within one minute in most cases. SSA has been employed for automatic trend extraction on noisy data with success.²²⁴

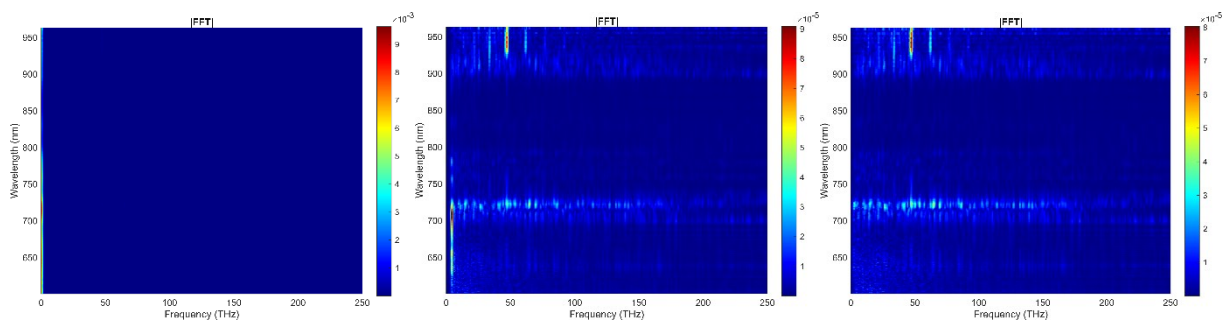


Fig. 47 Detrending application of SSA. (Left) Fourier transform of the raw TA data; (Middle) Automatic detrending using 13th order polynomial; (Right) Automatic detrending with SSA.

The trend extraction capability was tested on a sub-10-fs resolution transient absorption data of polyfluorene (PFO).²²⁵ Detailed instrument configuration and sample preparation method can be found in the cited paper. Fig. 47 (left) shows direct Fourier transform of the TAS data, as expected, the exponentials are transformed into Lorentzian functions so prominent making

everything else invisible. The middle figure is the result of trend extraction by 13th order automatic polynomial fitting, which greatly reduced the amplitude of the Lorentzian functions making peaks visible. However, portions of Lorentzian functions still remain and the user has to choose the correct polynomial order to balance the attenuation on Lorentzian functions and oscillations.

Fig. 47 (right) is the result of automatic detrending by SSA with window size one sixth of the length of the time series, and the first two RCs are removed as trend. The Lorentzian functions are completely extracted leaving a clear picture of what seems to be an impulsive Raman structure. In conclusion, SSA is able to extract trend from time series without curve-fitting and make no assumption other than the trend is highly orthogonal to the rest of the reconstructed components.

5.7.4 Feature Extraction with Hierarchical Agglomerative Clustering

While sorting the reconstructed components in the order of descending eigenvalue amplitude is practical for extracting prominent features from noisy data. Reconstructing complex features in the presence of artifacts and structured noises require most delicate handling of RCs because signal components may have less amplitude than noise even after eigendecomposition. Similar eigenvectors or RCs need to be recognised and classified into the same category. Hierarchical agglomerative clustering (HAC) was chosen as the classification technique due to its flexibility and configurability over other clustering methods such as k-means.

The SSA-HAC is implemented in the SDT with rich GUI allowing users to select clusters to plot either as individual cluster or sum of clusters. The Implementation also includes automatic trend removal with a robust version of Z-score (standardisation) of the time-domain sum. The robust standardisation of data allows the use of a constant threshold for all trend extractions regardless of the data sources.

The robust variant of Z-score is denoted as M-score here. Let i^{th} cluster be a_i and its sum in time-domain be S_i , which is an element of set S that contains the time-domain sum of all clusters:

$$S_i = \sum_t a_i(t) \quad S_i \in S$$

eq. 50

The median absolute deviation of S is defined as:

$$mad(S) \equiv median(|S_i - median(S)|)$$

eq. 51

Finally, the M-score is:

$$M_i \equiv \frac{|S_i - median(S)|}{mad(S)}$$

eq. 52

Since oscillations tend to have smaller S_i as the positive and negative peaks cancel out. The M-score of cluster sums containing exponentials will be much larger than that of oscillations. Applying M-score function on $S(i)$ is the robust analogue to the standardisation of $S(i)$. A constant threshold of $M_i > 0.1$ is used to extract trends.

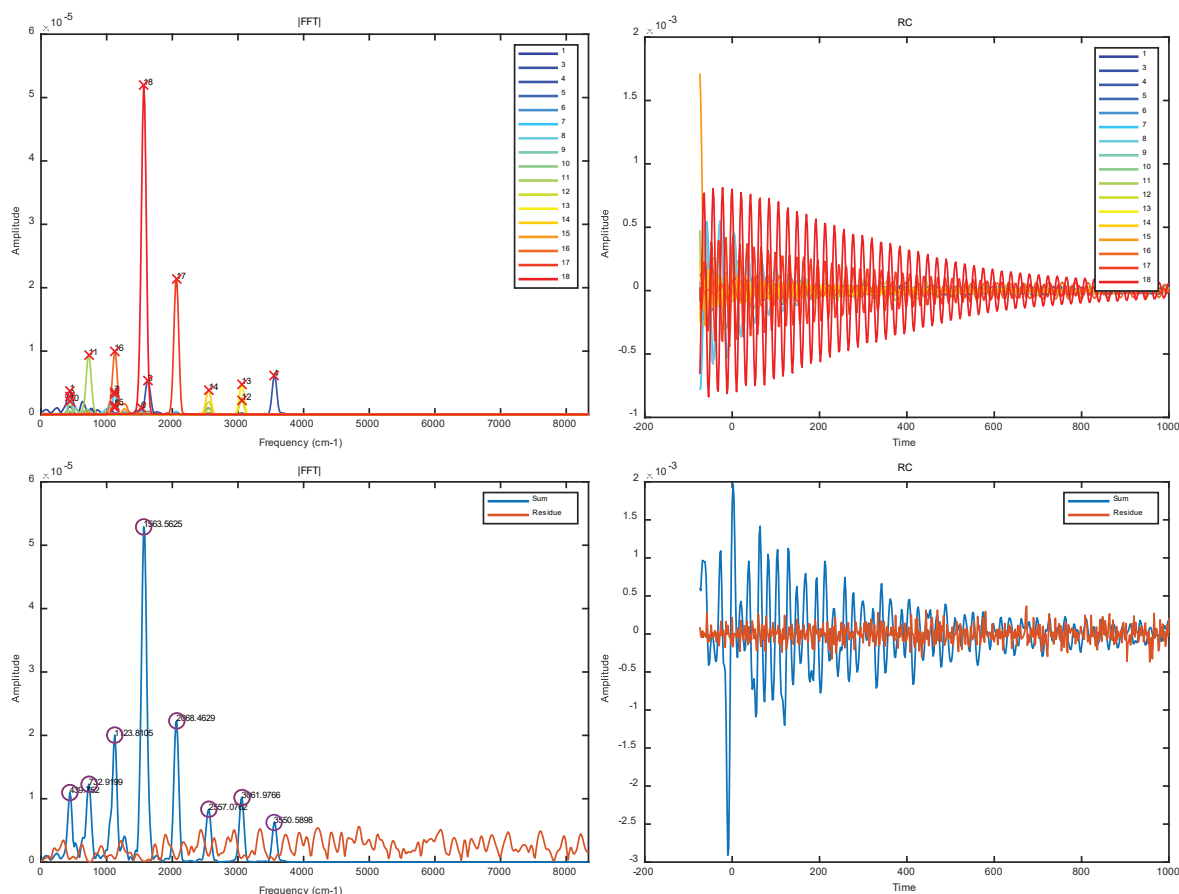


Fig. 48 SSA-HAC of the PFO data, the upper graphs are individual clusters and the lower graphs are the sum of chosen clusters(blue) and excluded clusters(red). The left graphs are plotted in frequency domain and the right graphs are plotted in time domain. (Upper left) Included clusters in frequency domain; (Upper Right) Included clusters in time domain; (Lower left) Sum of included (blue) and excluded (red) clusters in frequency domain; (Lower Right) Sum of included (blue) and excluded (red) clusters in time domain

SSA-HAC was applied to the PFO data²²⁵ around 930 nm to 960 nm where oscillations are prominent (Fig. 47). L1-norm distance metric and complete-linkage clustering method were used for robustness. 20 clusters were produced and one of them is excluded by the automatic detrending function. Another cluster was excluded (Fig. 48 lower, red curves) since it's evident that the cluster represent noises in frequency domain. As illustrated in Fig. 48 left, the impulsive Raman structure was completely extracted as individual peaks.

The principal peaks agrees with literature using traditional Raman spectroscopy²²⁶. Moreover, the impulsive Raman spectrum extracted by SSA-HAC has much greater bandwidth than traditional Raman spectroscopy

6 Conclusion and Outlook

6.1 Conclusion

We proposed and constructed a multi-pulse TRTS system to overcome the limitations of commonly used OPTP when studying hot carrier dynamics. The multi-pulse TRTS utilises optical-pump-infrared-push-terahertz-probe scheme, that excites band-edge carriers to higher vibrational states with infrared pulse, and thus allowing investigation of hot carrier dynamics without the interference from initial carrier excitation and high-order recombination that is present at the initial photoexcitation by the pump pulse.

The system was based on PCA-generation and EOS-detection for terahertz radiation due to input laser power constrains. The bulk of the laser power was permanently routed to the two OPAs responsible for pump and push pulse generation. PCAs are highly efficient with terahertz emission, but lacks field strength compared with optical rectification sources. As a result, the multi-pulse TRTS system can only measure samples with conductivity down to that of metal-halide perovskites. EOS detection with ZnTe crystal was chosen for its high sensitivity, but ZnTe has strong absorption around 3 THz, which became the hard limit of the spectral bandwidth (0.2-2.5 THz). To compensate the low field strength, the data acquisition of the setup was fully optimised with synchronous-continuous acquisition scheme implemented with a DSP lock-in amplifier.

Then the system was used to study hot carrier dynamics in MAPI. We performed PPP-THz and PPP-IR experiment on solution-processed MAPI sample. The observed carrier dynamics were modelled by a two-step kinetics accounting for strong hot carrier-phonon coupling creating a population of hot polaron-lattice state, and subsequent thermal equilibration to ambient environment. The frequency dependence of photoconductivity exhibits polaronic features and is in good agreement with FHIP quantum treatment of polaron conductivity.

Finally non-parametric model-free data analysis methods including EFA, NMF, ICA and SSA for multivariate high-dimension time-resolved spectroscopy data were introduced and validated against simulated signals and real datasets. All features are implemented in SDT, a GUI software package written and maintained solely by the author.

6.2 Future Work

In order to perform terahertz spectroscopies on less conductive material such as OPVs, the emitted terahertz field strength needs to be significantly increased. The easiest option would be replacing the PCA with one that has larger surface area and high dielectric strength (preferably >1 KV). Alternatively, the terahertz radiation generation method can be switched to optical rectification, which usually require the whole beam of a mode-locked laser. Recent advancement on organic crystal terahertz emitters²²⁷⁻²²⁹ can be exploited instead of relying on traditional EO crystals such as ZnTe and GaP.

The electronic system of the TRTS setup is carefully designed and implemented for compatibility. However, the PCA driver is intended to be used with regeneratively amplified low repetition mode-locked lasers. Should the need of high repetition rates arise, the MCU onboard need to be replaced with newer chips in Arduino nano platform (Samd21, nRF52840, and RP2040 are available at the time of the writing). In addition, hardware timer peripherals need to be configured to keep up with the repetition rate (<10 MHz). For ultra-high repetition rate (<100 MHz), the PCA driver board is no longer suitable and would need to be completely replaced. When using unamplified lasers, the PCA pump should be focused onto the PCA instead of spread out to cover the entire PCA.

While the control software is able to drastically reduce measurement time with synchronous continuous acquisition of time-domain data, it cannot accelerate the measurement of discrete values such as data measured against pump-probe delay. As long as a lock-in amplifier is used, this constraint cannot be circumvented. However, if the main data acquisition hardware is replaced with DAQ modules, data acquisition can be customised so that no frequency-domain filter is used during discrete value acquisition. Alternatively, one could construct a fully customised digitizer hardware with fast high-resolution ADCs followed by real-time DSP implemented on FPGAs for total control of data acquisition.

TRTS has great potential in optoelectronic material study, not only as a conductivity probe, but also as a transient electric or magnetic pump, which may gain insights for spintronics and magnetic material systems. As tabletop coherent single-cycle terahertz radiation sources and detections methods become more stable and accessible, terahertz pulse can be incorporated into various time-resolved spectroscopies, unlocking new schemes and making data interpretation less ambiguous.

Although the SDT software is already quite comprehensive and capable of processing a large variety of time-resolved spectra, none of its functions are phase-aware, i.e., capable of processing complex data without separating its real and imaginary parts. This is unfortunately limited by our current understanding of mathematics. As new algorithms emerge, they will be assessed and integrated into the SDT package. Due to time constraints, some planned features including a multivariate extension of SSA (MSSA), partial least-square regression (PLSR) and cross-validation of NMF were not implemented.

The non-parametric model-free analysis methods implemented in SDT have never been applied to time-resolved spectroscopies before. The BSS approach can greatly simplify physical model fittings with fewer parameters, which would make the results more credible. As time-resolved spectroscopies continue to evolve, more challenging data will be presented to us and the BSS algorithms may become crucial to decipher high-dimension data. While computationally intensive, the use of SSA in coherent spectra analysis has proven to be a huge success, allowing non-parametric extraction of impulsive spectrum with each peak individually resolved.

7 References

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