Ultrafast photoconductivity dynamics in the lead bromide perovskites studied by time-resolved terahertz spectroscopy

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July 2023

A thesis submitted to McGill University in partial fulfillment of the requirements of the

degree of Master of Science

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Abstract

Metal halide perovskites (MHPs) have been widely explored and promisingly applied in optoelectronics devices because they have tremendous properties, most notably their low recombination rate, general insensitivity to defects, large optical absorption coefficient and great photovoltaic performance. To explain these properties one of the most widely proposed mechanics is large polaron formation.

In this research, we apply ultra-broad band time-resolved teraherz spectroscopy (UBB-TRTS) to study the photoconductivity dynamics of two kinds of lead halide perovskites (LHPs) following non-resonant 400 nm photo-excitation pulses with 3.1eV. We study bulk single crystals of the hybrid organic-inorganic methylammonium lead bromide perovskite CH₃NH₃(MA)PbBr₃ and the all-inorganic cesium lead bromide perovskite CsPbBr₃ at room temperature. Ultrafast dynamic screening of Coulomb interactions are observed, resulting in photocarrier induced shifts in the infrared phonon reflectivity and the formation of new dressed plasmon-longitudinal optical (LO) phonon modes. Fluencesensitive coherent oscillations of the transient reflectivity are observed for THz probe energies near the LO frequency $\left(\frac{\omega_{LO}}{2\pi}\right) \sim 5.32$ THz for MAPbBr₃ and ~4.67 THz for CsPbBr₃ as the fluence increases. The coherent oscillations are strongly anharmonic, possibly indicating that vibrational energy is rapidly dispersed from high energy phonons to low energy phonons via phonon-phonon interactions, which is in agreement with liquid-like lattice excitations mentioned in previous works. We also discuss another possible explanation via the formation of a new plasmon-LO phonon modes leading to the shift

of reststrahlen to higher frequencies as the effect of injecting free carriers on the dielectric function. The rise time of transient reflectivity obtained by numerical Boltzmann fit in CsPbBr₃ is around 2 times larger than that in MAPbBr₃, which is attributed to the slower intervalley scattering process in CsPbBr₃ and relatively faster intervalley scattering process in MAPbBr₃. Physical models are provided to quantify the changing dynamics of transient reflectivity along short and long delay times respectively, quantifying the carrier cooling, the formation of polarons, and the relaxation of transient reflectivity. The photo-excited fluence-dependent complex optical conductivity of the two samples is modelled with a phenomenological Drude-Smith model incorporating coherent back-scattering. With increasing excitation fluence, backscattering becomes less efficient as the initial electronic temperature increases. The Drude-Smith plasma frequency ω_p is found to be saturated gradually due to depletion of the optical joint density of states.

Abrégé

Les pérovskites à halogénure métallique ont été largement explorées et appliquées de manière prometteuse dans les dispositifs d'optoélectronique en raison de leurs propriétés exceptionnelles, notamment leur faible taux de recombinaison, leur insensibilité générale aux défauts, leur grand coefficient d'absorption optique et leurs excellentes performances photovoltaïques. Pour expliquer ces propriétés, l'un des mécanismes les plus couramment proposés est la formation de grands polarons.

Dans le cadre de cette recherche, la spectroscopie térahertz à large bande et à résolution temporelle ultra-rapide est appliquée pour étudier la dynamique de la photoconductivité de deux types de pérovskites à halogénure de plomb suite à des impulsions de photo-excitation non résonnantes de 400 nm avec une énergie de 3,1 eV. Nous étudions des monocristaux en vrac de la pérovskite de bromure de plomb hybride organique-inorganique CH₃NH₃(MA)PbBr₃ et de la pérovskite de bromure de plomb entièrement inorganique CSPbBr₃ à température ambiante. Nous observons l'écrantage dynamique ultra-rapide des interactions coulombiennes, entraînant des décalages induits par les porteurs de charge dans la réflectivité des phonons infrarouges et la formation de nouveaux modes plasmoniques-optiques longitudinaux (LO) phononiques habillés. Des oscillations cohérentes de la réflectivité transitoire sensibles à la fluence sont observées pour des énergies de sonde térahertz proches de la fréquence LO ($\frac{\omega_{LO}}{2\pi}$) ~5,32 THz pour MAPbBr₃ et ~4,67 THz pour CsPbBr₃ à mesure que la fluence augmente. Ces oscillations

cohérentes sont fortement anharmoniques, ce qui pourrait indiquer une dispersion rapide de l'énergie vibratoire des phonons de haute énergie vers les phonons de basse énergie via des interactions phonon-phonon, ce qui est en accord avec les excitations de type maille liquide mentionnées dans des anciens travaux. Une autre explication possible est proposée via la formation de nouveaux modes plasmoniques-LO phononiques conduisant au décalage des reststrahlen vers des fréquences plus élevées, en tant qu'effet de l'injection de porteurs libres sur la fonction diélectrique. Le temps de montée de la réflectivité transitoire obtenu par ajustement numérique de Boltzmann dans CsPbBr₃ est environ deux fois plus long que dans MAPbBr₃, ce qui est attribué au processus de diffusion inter-vallée plus lent dans CsPbBr₃ et au processus de diffusion inter-vallée relativement plus rapide dans MAPbBr₃. Des modèles physiques sont fournis pour quantifier les changements dynamiques de la réflectivité transitoire le long de durées de retard courtes et longues, quantifiant le refroidissement des porteurs, la formation de polarons et la relaxation de la réflectivité transitoire. La conductivité optique complexe dépendante de la fluence photoexcitée des deux échantillons est modélisée par un modèle phénoménologique Drude-Smith incorporant la rétrodiffusion cohérente. Avec l'augmentation de la fluence d'excitation, la rétrodiffusion devient moins efficace à mesure que la température électronique initiale augmente. La fréquence plasma de Drude-Smith est progressivement saturée en raison de l'épuisement de la densité d'états optiques conjoints.

Acknowledgements

First of all, I'd like to express my sincere gratitude to my supervisor Prof. David G. Cooke for his mentorship, patience and encouragement during my master life. I feel lucky to have him as a supervisor who helps me to improve my scientific skills as well as broaden my horizons. I have learnt lots of new academic skills under his guidance.

My special thanks go to the all the group members of the Cooke THz lab, Benjamin Dringoli, Benjamin Colmey, Aidan Schiff-Kearn, Rodrigo Paulino, Monika Azmanska and Yang Lan for their support and kindness all the time. Especially thanks to Benjamin Dringoli for the useful discussion and kind assistance in the lab. Special thanks to Monika Azmanska who helps with the French abstract translation.

Similarly, I'd like to the acknowledge the all the collaborators for their valuable contributions to the work presented in this thesis, especially Dr. Mercouri G. Kanatzidis, Yihui He and their Laboratory, Northwestern University.

Finally, thanks to all my family members for their love and support through my whole life, without their efforts, encouragement, understand and sacrifices I would not be here. Especially thanks to my mom and dad for raising me and accompanying me all the time. Special thanks to all the people and things I have encountered in my life. Without you, I wouldn't be who I am today.

Thesis Contributions

• Huiwen Shen (HS) and supervisor David Cooke (DC) conceptualized the project and set thesis goals.

• HS conducted the literature review and calculated expected responses from previous works.

• HS and Cooke Lab PhD student Yang Lan (YL) designed the TRTS experiments, designed white light reflectance experiments, established the white light reflectance experimental setup, performed alignment, and finished the experiments via UBB-TRTS system as well as white light reflectance experimental setup with guidance from DC.

• HS and YL recorded the datasets.

• HS performed all data analysis procedures of TRTS experiments and white light reflectance experiments with guidance from DC.

• HS wrote all thesis chapters and plotted all the diagrams as well as tables in the thesis with edits from DC.

• The French translation of the abstract was provided by Monika Azmanska from the department of physics and astronomy in McMaster University.

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List of Acronyms

MHPs	Metal Halide Perovskites
LEDs	Light-Emitting Diode
OHPs	Organometal Halide Perovskites
THz	Terahertz
ТА	Transient Absorption
ТАМ	Transient Absorption Microscopy
PL	Photoluminescence
UBB-TRTS	Ultra-Broadband Time-Resolved THz Spectroscopy
LHPs	Lead Halide Perovskites
MAPbBr ₃	CH ₃ NH ₃ PbBr ₃
LO	Longitudinal Optical
ТО	Transverse Optical
HPs	Halide Perovskites
DFT	Density Functional Theory
SOC-DFT	Spin-Orbit Coupling DFT
SR-DFT	Scalar Relativistic DFT
SOC-QSGW	Quasiparticle Self-Consistent GW with SOC corrections
EBIC	Electron Beam Induced Current
SCLC	Space-Charge-Limited Current
IS	Impedance Spectroscopy

JDOS	Joint Density of State
ASE	Amplified Spontaneous Emission
PLQE	Photoluminescence Quantum Efficiencies
NWs	Nanowires
MAPI	Methylammonium Lead Iodide
NCs	Nanocrystals
TR-OKE	Time-Resolved Optical Kerr Effect
TR-2PPE	Femtosecond Time-Resolved Two-photon Photoemission
TR	Transient Reflectance
TR-PL	Time-Resolved Photoluminescence
TR-IR	Time-Resolved Infrared Spectroscopy
LAR	Ligand-Assisted Reprecipitation
ODE	Octadecene
OA	Oleic Acid
OLA	Oleylamine
DMF	Dimethylformamide
AFM	Atomic Force Microscopy
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
CVD	Chemical Vapor Deposition
TSSG	Top-Seeded Solution-Growth
GBL	γ-utyrolactone

DMSO	Dimethyl Sulfoxide
OR	Optical Rectification
FWM	Four Wave Mixing
RD-SOS	Radiation Damaged Silicon on Sapphire
LT-GaAs	Low Temperature Grown GaAs
EO	Electro-Optic
ABCD	Air Biased Coherent Detection
TFISH	Terahertz Field Induced Second Harmonic
THz-TDS	THz Time-Domain Spectroscopy
FWHM	Full Width at Half Maximum
PM	Parabolic Mirrors
BBO	Beta Barium Borate
APD	Avalanche Photodiode
meV	Milli-Electron-Volts
eV	Electron-Volts
ps	Picosecond
fs	Femtosecond
ns	Nanosecond
μs	Microsecond
TAS	Transient Absorption Spectroscopy

List of Symbols

Goldschmidt Tolerance Factor	t_0
More Accurate Goldschmidt Tolerance Factor	$ au_0$
Octahedral Factor	μ_0
Mobility of Carrier	μ
Diffusion Coefficient	D
Diffusion Length	L_D
Binding Energy	E_b
Plasma Frequency	ω_p
Charge Carrier Density	N or n
Complex Conductivity	$ ilde{\sigma}$
Momentum Scattering Time	$ au_s$
Transport Scattering Time	$ au_c$
Effective Mass	m^*
Optical Dielectric Constants	\mathcal{E}_{∞}
Static Dielectric Constants	\mathcal{E}_{S}
Electron-phonon Coupling Constant	α_{e-ph}
Scattering Rate	γ
Longitudinal Optical Phonon Frequency	ω_{LO}
Transverse Optical Phonon Frequency	ω_{TO}
Boltzmann Constant	k _B

Vacuum Permeability	μ_0
Vacuum Impedance	Z_0
Electron Unit Charge	е
Electron Unit Mass	m_0
Planck Constant	h
Reduced Planck Constant	ħ
Speed of Light in Vacuum	С
Electronic Charge	q
Monomolecular Recombination Rate Constant	k_1
Bimolecular Recombination Rate Constant	k ₂
Three-Body Auger Recombination Rate Constant	<i>k</i> ₃
Temperature	Т
Dielectric Constant	ε
Average Dielectric Constant	Ē
Frequency of Light/Photon	Ω
Admittance	Г
Photo-Excited Fluence	F
Backscattering Parameter	c_0 or c or c_n
Radius of Polaron	r_p
Fröhlich Constant	α
Polarization	P
Charge Current	Ĵ

Free Charge Current	J _{cond}
Bound Charge Current	Ĵbound
Thickness	d
Penetration Depth	δ
Index of Refractive	N ₀
Refractive Index	n_0
Concentration of Polarons	N_p
Mean Free Path	λ_s
Frequency	ω
Electron (Hole) Band Mass	m_b
Vacuum Permittivity	ϵ_0
Dielectric Constant	ĩ
Real Part of Dielectric Constant	ε_1
Imaginary Part of Dielectric Constant	\mathcal{E}_2
Transient Reflectivity	$\left \frac{\Delta \tilde{r}}{\tilde{r}_0}\right $
Pump Delay Time	$ au_d$
Complex Refractive Index	ñ
Boltzmann Time Constant	$ au_B$

Physical Constants

Boltzmann Constant	$k_B = 1.380649 \times 10^{-23} \ (m^2 \cdot kg \cdot s^{-2} \cdot K^{-1})$
Vacuum Permittivity	$\epsilon_0 = 8.854187 \times 10^{-12} \ (F/m)$
Vacuum Permeability	$\mu_0 = 1.2566370 \times 10^{-6} (N \cdot A^{-2})$
Vacuum Impedance	$Z_0 = 376.73031 \ (\Omega)$
Electron Unit Charge	$e = 1.60217663 \times 10^{-19} (\mathcal{C})$
Electron Unit Mass	$m_0 = 9.1093835 \times 10^{-31} (kg)$
Planck Constant	$h = 6.62607015 \times 10^{-34} \ (J \cdot s)$
Reduced Planck Constant	$\hbar = 1.05457181 \times 10^{-34} (J \cdot s)$
Speed of Light in Vacuum	$c = 2.9979245 \times 10^8 (m/s)$

Chapter 1

Introduction

Metal halide perovskites (MHPs) have a general ABX₃ stoichiometry where A and B are metal cations arranged with the structure of BX₆ octahedral network and A-site metal cation in 12-fold cuboctahedral coordination. MHPs are well-known for the properties of high photoluminescence quantum efficiencies, relatively high carrier mobility compared with other solution-processed materials, low recombination rate, general insensitivity to defects, large optical absorption coefficient, and tunable bandgaps which provide the possible of application in light-emitting diode (LEDs), injection lasers, electricallypumped lasing [1-5], solar energy supplies with ease of fabrication, relatively low cost, record breaking power conversion efficiencies which have already reach up to ~25.5% achieved for perovskite solar cells [6-10]. Thus, as one kind of MHPs, LHPs has become very promising materials. These properties, however, are counter to what one would expect for a typical direct band gap semiconductor and so their properties must be understood on a basic level. Many studies have been conducted on LHPs through Terahertz (THz) Spectroscopy, Raman Spectroscopy, Ultrafast Kerr Spectroscopy, Transient Absorption (TA) Spectroscopy, Photoluminescence (PL) spectroscopy, as well as X-ray spectroscopy [11-21]. Presenting theories of LHPs explaining these properties include charge carrier-phonon coupling (a kind of dressed quasiparticle named polaron), exciton dissociation, Rashba effects, ferroelectric effects, crystal-liquid duality, etc [17, 22]. Polaronic correlations caused by interactions of charge carriers to phonons in polar media has become the most widely accepted mechanism to explain the mysterious long carrier lifetime and insensitivity to defects. The dynamics of polaron formation time on the order of sub-ps following photon absorption are under scrutiny, with optical pump X-ray probe measurements claiming a more delayed dynamics of 20 ps [21], while other measurements including our own Yang *et al.*' s work claiming much faster dynamics [14]. Current research attempts to reconcile the observed coherent band transport charge with the phonon dynamics of liquids, leading to the classification of lead halide perovskites as so-called phonon glass electron crystals, a concept originally formulated to explain the properties of the most efficient thermo-electrics [17].

In this work, we use time-resolved terahertz spectroscopy (TRTS) to study solutionprocessed grown single crystals of the all-inorganic metal halide perovskite CsPbBr₃ and the organic-inorganic metal halide perovskite MAPbBr₃. At room temperature, where all measurements in this thesis occur, CsPbBr₃ is in orthorhombic phase and MAPbBr₃ is in cubic phase, respectively. Following interband absorption of femtosecond optical pulses, we observe how carriers dynamically interact with polaron phonons on multi-meV energy scales. We apply both one-dimensional (1D) and two-dimensional (2D) ultrabraodband (UBB-TRTS) covering spectra from ~1-20 THz following 400 nm photoexcitation pulses (3.1eV) with varied photo-excited fluences from 23-362 uJ/cm² and ~40 fs temporal resolution. The far infrared reflectivity edge (reststrahlen band) is used as a marker for charge-lattice interactions, monitoring the carrier induced changes to the dielectric function of the polar lattice and is a particularly sensitive probe of polaronic correlations. Following the injection of free carriers, coherent oscillations are observed in the transient reflectivity corresponding to the reststrahlen edge happening around the LO frequency~5.32 THz for MAPbBr₃ and ~4.67 THz for CsPbBr₃. These oscillations are strongly down-chirped, indicating strongly anharmonic phonon landscape whereby vibrational energy is rapidly dispersed from phonons with high energy to phonons with low energy, reflecting the liquid-like lattice excitations of LHPs. These oscillations may also be viewed as the quantum kinetic formation of new coupled plasmon-LO phonon modes, causing the shift of the reststrahlen band. In the dynamic analysis of the transient reflectivity, the photoconductive rise time of CsPbBr₃ is approximately 2 times larger than that of MAPbBr₃, likely due to intervalley scattering processes present in CsPbBr₃ and not in MAPbBr₃. To quantify the transient reflectivity dynamics, we consider the initial relaxation of unscreened hot electrons (carrier cooling process) followed by polaron formation to reach a quasi-equilibrium state within short time in range of ~0-2.25 ps. Following this, relaxation of the transient reflectivity is found to occur over decay times of ~ 300 ps. Finally, we extract the fluence-dependent, transient complex optical conductivity via Fourier analysis, and quantitatively describe the spectra via a phenomenological Drude-Smith model. As the injection carrier density increases, backscattering is found to become less efficient as a consequence of the higher temperature of the initial electron population. The Drude-Smith plasma frequency ω_p reaches saturation gradually as a function of excitation fluence. One possible explanation is the depletion of the density of states, giving rise to a saturation in photon absorption.

Chapter 2

Material-Metal Halide Perovskites(MHPs)

In the last two decades, perovskites have become one of the most promising materials for optoelectronic devices owing to their great properties like strong light absorption [23], direct tunable bandgaps [24], and defect resistance [25]. They are applied in many fields including photovoltaics [26], light-emitting devices [27] and so on. In 1839, Gustav Rose firstly discovered oxide perovskite calcium titanium oxide (CaTiO₃), and named it after the Russian nobleman and mineralogist Count Lev Alekseyevich von Perovski using the term "perovskite" [28]. Then in 1893, inorganic metal halide perovskites with the form CsPbX₃ form where X is Cl, Br, and I were reported. Different from the natural oxide perovskite CaTiO₃, these synthetic perovskites were obtained by the method of solution crystal reaction [29]. Nowadays, a perovskite crystal lattice is defined as a general ABX₃ stoichiometry, where A and B are cations often with different sizes, and X is anion that bonds to both cations. The structure has BX₆ octahedral network and A cation in 12-fold cuboctahedral coordination. There are varied types of perovskites in terms of different methods of classification. For example, with different X, perovskites can be classified into oxide perovskites, halide perovskites (HPs) and so on. And when A and B are different cations (metal ion or organic ion), perovskites can be classified into inorganic metal perovskites, organic inorganic metal perovskites and so on. Combined with the previous two methods of classification, perovskites can be subdivided into inorganic metal halide perovskites and organic-inorganic metal halide perovskites. Materials of the formula ABX₃ consisting of inorganic cations A, metal cations B and halogen anions X are called inorganic metal halide perovskites. In case of organic-inorganic metal halide perovskites, they are materials of the formula ABX₃ where at least one of the A, B, and X sites are organic cations, and the other sites are metal cations, typically A sites are occupied with organic ion while B sites are metal and X sites are halogen anions [30]. Besides, from a dimensional point of view, perovskites can be divided into three-dimensional (3D), two-dimensional (2D), one-dimensional (1D), and zero-dimensional (0D) perovskites [31]. There are also other special types of perovskites, such as double perovskites in which either A or B site can be occupied by two different cations (A'A"B₂X₆ or A₂B'B"X₆) [32], vacant BX₃ perovskites in which A cation site is vacant like AlF₃ [33].

2.1 Properties of Metal Halide Perovskites (MHPs)

2.1.1 Crystal Structure



Figure. 2.1 Diagram of perovskite unit cell composed of A and B cations, and halide X ions.

The stability of 3D perovskite structure can be determined by a semiempirical geometric parameter named Goldschmidt tolerance factor t_0 given by the equation $t_0 = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$ where r_A , r_B , r_X are the ionic radii of A, B and X components respectively [34]. This factor can distinguish between perovskite and non-perovskite and be applied in perovskite discovery. Perovskite is expected when t_0 is in the range of ~0.825-1.059 [35]. However, it is found that the accuracy of Goldschmidt tolerance factor t_0 is often insufficient [35, 36], and a new more accurate tolerance factor is presented with the form of $\tau_0 = \frac{r_X}{r_B}$.

$$n_A\left(n_A - \frac{\frac{r_A}{r_B}}{\ln\left(\frac{r_A}{r_B}\right)}\right)$$
 where n_A is the oxidation state of A, r_A is the ionic radius of ion A, r_B is

the ionic radius of ion B ($r_A > r_B$), and $\tau_0 < ~4.18$ indicates perovskite [35]. The performance of these two tolerance factors in distinguishing perovskites and nonperovskites are compared shown in Ref. [35]. The new tolerance factor increases the accuracy by around 18% for 576 experimentally characterized ABX₃ solids [35]. Another factor named octahedral factor μ_0 given by $\mu_0 = \frac{r_B}{r_X}$ can reflect octahedral stability and present a parameter space for perovskite formability together with Goldschmidt tolerance factor t_0 . Usually μ_0 with the range of ~0.4-0.9 indicates perovskite [37]. Nevertheless, Goldschmidt tolerance factor t_0 and the octahedral factor μ_0 are a necessary but not sufficient conditions.

As the temperature changes, the crystal structure of MHPs undergoes crystal phase transition. Usually there are three common phases which are cubic, tetragonal, and orthorhombic phases. Take MAPbBr₃ as an example, cubic phase transfers to tetragonal phase at ~155K, and tetragonal phase transfers to orthorhombic phase at ~237 K [38]. Not

only temperature can affect the crystal phase, there are also other factors can cause phase transition such as pressure and so on [39, 40].

2.1.2 Electronic Band Structure

Generally, halide perovskites are direct band gap semiconductors leading to strong band edge optical absorption and luminescence, which is highly related to the optoelectronic properties [1]. But there are some special cases such as non-centrosymmetric hybrid compounds induced by Dresselhaus or Rashba splitting as well [41]. And the band gap is usually related to the anion of MHPs. In homologous set of compounds with different anions of Cl, Br, and I, the band gap of compounds with Cl is the biggest while that with Br is the second highest, and that with I is the lowest [42, 43]. Halide substitution can modulate the valence band because of the large *p* contribution of halide. However, anion has little influence on conduction band with nonbonding property [1]. It is found that calculating accurate electronic band structure of inorganic and hybrid MHPs is challenging by using computational methods [1]. As for Density Functional Theory (DFT) method, it has been applied to the MHPs, nevertheless, it is found to obtain lower band gaps compared with real band gaps although it can still provide extensive information on the band dispersion. As for better computational methods with corrections such as spin-orbit coupling DFT (SOC-DFT) and Scalar Relativistic DFT (SR-DFT), these methods cannot calculate accurately for Pb and Sn perovskites [1]. It has been shown that Quasiparticle Self-Consistent GW with SOC corrections (SOC-QSGW) can be used to calculate the band structure correctly in inorganic and hybrid MHPs [43-45]. MHPs' electronic structures are highly affected by the high atomic mass elements. One of the

consequences is MHPs have prevalent SOC arising from the increased atomic mass. Compared with the typical *sp*-hybridized semiconductors such as GaAs where SOC leads to the splitting of the upper valence band because of the anion p character, and SOC leads to spin-orbit splitting of lower conduction band because of large metal pcontribution in MHPs [1].

2.1.3 Carrier Transport

In semiconductors MHPs, charge diffusion happens because of thermal energy k_BT even without electric field. It happens before the recombination, therefore, the diffusion length L_D can be defined as the average distance that each charge distribution is able to move [46]. The diffusion length L_D can be calculated by using $L_D = D\tau$ where D is the diffusion coefficient, and τ is the lifetime of charge carrier. According to the Einstein relation, the mobility μ can be related to field-free diffusion given by the formula $\mu = \frac{Dq}{k_BT}$ where q the electronic charge [1]. There are some models to simplify the process. For example, applying Drude model can obtain the mobility of carrier μ determined by the scattering time τ_s or mean free path λ_s , and effective mass of charge carrier m^* given by the formula $\mu = \frac{q\tau_s}{m^*} = \frac{q\lambda_s}{\sqrt{3kTm^*}}$, indicating that lower scattering and lower effective mass can cause higher mobility [1]. It is noted that in a photo excited system the correct mobility calculated from the diffusion length would be the bipolar mobility, taking into account the fact that one distribution cannot move without dragging the other one. Another model assuming excited charge carriers acting only under the influence of isotropic diffusion is given by the formula $\frac{\partial n}{\partial t} = D\nabla^2 n - k_1 n - k_2 n^2 - k_3 n^3$ where *n* is the density of carriers, *D* is the diffusion coefficient, k_1 is the monomolecular recombination rate constant reflecting excitonic or trap-assisted recombination relying on an individual carrier captured in a trap, k_2 is the bimolecular recombination rate constant indicating intrinsic electron-hole recombination, and k_3 is the three-body Auger recombination rate constant reflecting many-body process involving recombination of an electron, a hole, and the third carrier [47]. Then the total recombination rate is $r(n) = k_1 + k_2 n + k_3 n^2$, and the diffusion length is $L_D(n) = \sqrt{\frac{\mu k_B T}{r(n)e}}$ [48]. As for measurements of diffusion length and carrier mobility, there have been several methods, such as transient absorption microscopy (TAM), TRTS, electron beam induced current (EBIC), Space-charge-limited current (SCLC), impedance spectroscopy (IS), PL and so on For example, the carrier mobility and the diffusion length of MAPbBr₃ single crystal have been measure and have the range of ~10-115 cm²V⁻¹S⁻¹ and ~3-17 μ m by using PL , SCLC and TAM [49].

2.1.4 Optical Absorption and Photoluminescence

As for MHPs' optical absorption, it is determined by the joint density of state (JDOS) as well as transition matrix of states between valence and conduction bands. Based on Fermi's Golden Rule, the absorption coefficient can be given by $W_{\vec{k}} \cong \frac{2\pi}{\hbar} |\langle f | \mathcal{H}' | i \rangle|^2 \delta[E_c(\vec{k}) - E_v(\vec{k}) - \hbar \omega]$ where \mathcal{H}' is the dipole operator, f is the final state, iis the initial state, and $\delta[E_c(\vec{k}) - E_v(\vec{k}) - \hbar \omega]$ is the JDOS [1]. In addition, there is strong optical absorption arising from the transition between halide- p orbitals and metal- porbitals in MHPs since the p orbitals are less dispersive than s orbitals and JDOS close to the fundamental electronic absorption edge is large [50]. As for the photoluminescence, MHPs have already been reported to have amplified spontaneous emission (ASE) and lasing in previous research [3, 4, 51, 52]. For example, in Descher *et al.*'s research, they observed long carrier lifetimes as well as high photoluminescence quantum efficiencies (PLQE) more than 70% in solution-processed mixed halide perovskite CH₃NH₃PbI_{3-x}Cl_x, which shows the potential of MHPs to be used in photovoltaic diode operation [4]. In Zhu *et al.*' s research, they proposed that single crystal lead halide perovskite nanowires (NWs) with long carrier lifetimes and low nonradiative recombination rates can realize wavelength-tunable lasing at room temperature with the lowest lasing thresholds (220 nJ/cm²) and highest Q factors (~ 3600) compared with previously reported NW lasers [3]. Besides, MHPs with relatively high mobilities can realize electrically-pumped lasing as well [5].

2.2 Polaron

2.2.1 Definition of Polaron



Figure. 2.2 Diagram of charge carriers placed in polar lattice. The charge carrier along with self-induced lattice polarization is polaron.

Polaron is a kind of quasiparticle caused by the correlation of charge carriers to virtual phonons in polar media with self-induced polarization proposed by Landau in 1933, and coined by Pekar in 1946 [53, 54]. As the charge carriers move into the lattice, except for

the interaction with the original polar lattice, at the same time, there is a lattice distortion induced by additional carriers to effectively screen the charge of electron as shown in Fig. 2.2. These interactions lead to binding energies that range from 1 – 100 meV and thus they are able to be probed by THz spectroscopic techniques. Polaron interactions naturally lead to modifications in to the band effective mass and scattering rates, and are of importance in the investigation of photoconductivity of materials.

Polarons can be roughly classified as large polarons and small polarons based on the polaron radius compared with the lattice constant [55]. For large polarons also called Fröhlich polarons, they have larger radii than the lattice constant, therefore, lattice can be regarded as a continuous polarization distortion. They are delocalized particles moving coherently under the applied field but with renormalized mass and scattering rate. As for small polarons, also called Holstein polarons, they have smaller polaron radii than the lattice constant, and thermally activated conductivity via hopping through a manifold of localized states [56].

2.2.2 Fröhlich Polaron Coupling Constant

Fröhlich polaron optical phonon interaction, coupling of charge carriers to a single and dispersion-less longitudinal optical (LO) phonon, is a simple theory for large polaron [57]. Fröhlich polaron coupling constant can be used to describe the strength of the coupling between the charge carries and phonon.

$$\Delta \mathbf{x} \approx \frac{\Delta \mathbf{v}}{\omega_{LO}} \tag{2.1}$$

$$\Delta x \Delta p \approx \frac{m}{\omega_{LO} (\Delta \upsilon)^2} \ge \frac{\hbar}{2}$$
(2.2)

$$\Delta \upsilon \ge \sqrt{\frac{\hbar \omega_{LO}}{m}}$$
(2.3)

$$r_p = \Delta \mathbf{x} \ge \sqrt{\frac{\hbar}{2m\omega_{LO}}} \tag{2.4}$$

$$E_b = -\frac{e^2}{r_p \bar{\varepsilon}} = -\frac{e^2}{\bar{\varepsilon}} \sqrt{\frac{2m_b \omega_{LO}}{2\hbar}}$$
(2.5)

$$\frac{1}{\bar{\varepsilon}} = \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_{s}}$$
(2.6)

$$E_b = -\alpha \hbar \omega_{LO} \tag{2.7}$$

$$\alpha = \frac{e^2}{\hbar c} \sqrt{\frac{m_b c^2}{2\hbar\omega_{L0}}} \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_s}\right)$$
(2.8)

If the LO phonon frequency is ω_{LO} , the transport time of the carrier can be given by ω_{LO}^{-1} . Therefore, the distance of carrier traveling Δx that electron can travel is given by Eq. 2.1 where Δv is the electron velocity quadratic mean square deviation. Then according to the uncertainty relation shown in Eq. 2.2, and the range of Δv shown in Eq. 2.3, the radius of polaron r_p is given by Eq. 2.4. The average dielectric constant $\bar{\varepsilon}$ is given by Eq. 2.6 where ε_{∞} is electronic/high frequency dielectric constant, and ε_s is static frequency dielectric constant. Combined with the two formulas of binding energy E_b given by Eq. 2.5 and Eq. 2.7, the Fröhlich electron-phonon coupling constant α can be obtained shown in Eq. 2.8. where m_b is the electron (hole) band mass.

2.2.3 Binding Energy and Effective Mass of Polaron

A weak-coupling theory of the polaron via a perturbation theory was developed by Fröhlich [57]. The results are binding energy $E_b = -\alpha \hbar \omega_{L0}$ and effective mass $m^* = \frac{m_b}{1-\frac{\alpha}{6}}$. Later on, Lee, Low and Pines (LLP) used another method to investigate the properties of a weak-coupling polaron based on canonical transformations inspired by the research on quantum electrodynamics by Tomonaga. The effective mass is now given by $m^* = m_b \left(1 + \frac{\alpha}{6}\right)$ [58]. This kind of LLP approximation is also called intermediate-coupling approximation putting Fröhlich results on a variational basis. As α approach 0, two expressions of effective mass become the same. At present, more general evaluations of binding energy E_b and effective mass m^* of polaron are given by $E_b = -(\alpha + 0.0159196220\alpha^2 + 0.000806070048\alpha^3 + \cdots)\hbar\omega_{L0}$ and $m^* = m_b \left(1 + \frac{\alpha}{6} + 0.02362763\alpha^2 + \cdots\right)$ [59, 60]. For strong-coupling polarons, binding energy E_b and effective mass m^* are $E_b = -(0.108513\alpha^2 + 2.836)\hbar\omega_{L0}$ and $m^* = m_b(1 + 0.0227019\alpha^4)$ [61].

2.2.4 Mobility of Polaron

Mobility is defined as the ratio of the drift velocity to the magnitude of the external field. The mobility of large polarons has been studied by various theoretical approaches, Fröhlich proposed the typical behavior of the large polaron mobility $\mu \propto \exp\left(\frac{\hbar\omega_{LO}}{k_BT}\right)$ in weak-coupling regime where *T* is the temperature, and $k_BT \ll \hbar\omega_{LO}$. The full form of the mobility is $\mu = \frac{e}{2m_b\omega_{LO}\alpha} \exp\left(\frac{\hbar\omega_{LO}}{k_BT}\right)$ [55]. As coupling constant α increases, mobility μ will decrease meaning polaron with the strong coupling prefers to localize in lattice sites. As the temperature *T* increases, the mobility μ will decrease. For small polarons, the mobility is proportional to the phonon density ($\mu \propto \exp(-\hbar\omega_{LO}/k_BT)$) at sufficient low temperature, which is totally different from that of the large polaron [62].

2.2.5 Optical Absorption of Polarons



Figure. 2.3 Diagram of polaron scattering process describing the absorption of an incoming photon and the generation of an outgoing phonon.

The optical absorption is caused by the polaron scattering process in weak-coupling regime and at zero temperature shown in Fig. 2.3. In the weak-coupling limit ($\alpha \ll 1$), the polaron absorption coefficient was obtained by Gurevich, Lang and Firsov for the first time via perturbation theory [63]. The expression of polaron absorption coefficient in the region of comparatively low frequencies ($\frac{\hbar\omega\omega_{LO}}{\xi} - \frac{\hbar\omega_{LO}}{\xi} \ll 1$) is

$$\Gamma(\omega) = \frac{1}{\epsilon_0 n_0 c} \frac{2^{\frac{1}{2}} N_p^{\frac{2}{3}} \alpha}{(3\pi^2)^{\frac{1}{3}}} \frac{e^2}{(\hbar m_b \omega_{LO})^{\frac{1}{2}}} \frac{\omega - 1}{\omega^3} \Theta(\omega - 1)$$
(2.9)

, and the expression of polaron absorption coefficient in the region of comparatively high frequencies $(\hbar\omega\omega_{L0}/\xi - \hbar\omega_{L0}/\xi)$ 1) is

$$\Gamma(\omega) = \frac{1}{\epsilon_0 n_0 c} \frac{2N_p e^2 \alpha}{3m_b \omega_{LO}} \frac{(\omega - 1)^{\frac{1}{2}}}{\omega^3} \Theta(\omega - 1)$$
(2.10)
where ξ is Fermi level for the electrons, ϵ_0 is the dielectric permittivity of the vacuum, n_0 is the refractive index of the medium, N_p is the concentration of polarons, ω is the normalized frequency equaling to frequency of the light divided by ω_{L0} , and $\Theta(\omega - 1)$ is the step function shown in Eq. 2.11 indicating the polaron scattering process happens only when the energy of the incident photon is larger than that of a phonon.

$$\Theta(\omega - 1) = \begin{cases} 1 & if \ \omega > 1 \\ 0 & if \ \omega < 1 \end{cases}$$
(2.11)

When the temperature is not zero, the absorption of a photon can be accompanied by emission and absorption of one or more phonons [63].

In another weak-coupling limit via the canonical-transformation method by Devreese, Huybrechts and Lemmens, the expression of polaron absorption coefficient is

$$\Gamma(\omega) = \frac{N}{2\epsilon_0 n c E^2} \Omega P(\Omega)$$
(2.12)

$$P(\Omega) = 2\pi \sum_{f} \langle \Phi_0 | V | f \rangle \langle f | V | \Phi_0 \rangle \, \delta \big(E_0 + \Omega - E_f \big) \tag{2.13}$$

where $\Omega = \omega \omega_{L0}$ is the frequency of light/photon, $|\Phi_0\rangle$ is the wave function of ground state, $|f\rangle$ is the wave function of final state, E_0 is the energy of ground state, E_f is the energy of final state, $P(\Omega)$ is the probability of the absorption of photon by these polarons in their ground state shown in Eq. 2.13 given by Fermi Golden Rule [64].

$$\Gamma(\omega) = \frac{1}{\epsilon_0 nc} \frac{2N e^2 \alpha}{3m_b \omega^3 \omega_{L0}} \sqrt{\omega - 1} \Theta(\omega - 1)$$
(2.14)

As α almost equals to 0, the absorption coefficient becomes an identical form to the previous polaron absorption coefficient via perturbation theory at relatively high

frequencies shown in Eq. 2.14 [64]. There are also optical absorption by using adiabatic strong-coupling approximation, and arbitrary coupling, which will not be discussed here [63].

2.2.6 Polarons in Metal Halide Perovskites (MHPs)

Here we mainly talk about LHPs, which have been reported to have dielectric responses and phonon dynamics comparable to that of liquids [17]. It has been reported in Wehrenfennig *et al.* that electron-hole recombination rates in LHPs are several orders of magnitude smaller than those of semiconductors obtained from Langevin theory [48]. One of the common explanations is competition between the polaron formation and charge carrier cooling process. The charge carriers coupling with the liquid-like polarizability of lattice forms polaron and polaron's screened Coulomb potential reduces its scattering with defects and other charge carriers leading to the slow rates [17]. Another explanation is that lattice distortion associated with the polaron enlarges the effective mass. Except for reducing its scattering with lattice defects, polaron's screened Coulomb potential can reduce the scattering of charges with defects [12]. Besides, the carrier-carrier scattering of hot carriers can be screened upon polaron formation [65]. There have been many studies focusing on intrinsic carrier cooling as well as polaron formation in general LHPs structure [13, 16, 17, 66, 67].

2.2.6.1 Dominant Phonon Modes in MHPs

In the lead halide perovskites, for example, it has been widely accepted that carrier behavior in polar lattice of lead halide perovskites can be well described by a Fröhlich interaction [68]. The Fröhlich coupling to LO phonons is the dominating charge-carrier

scattering mechanism in hybrid lead halide perovskites at room temperature. As the temperature increases, the impact of the Fröhlich interaction on carrier behavior increases because LO phonons become more thermally available [68, 69]. There are many LO phonon modes, however, only a single LO phonon mode dominates the interaction in the formation of polaron [68]. Which phonon mode, however, has been a subject of debate. The most widely studied LHP, methylammonium lead iodide (MAPI), was found to exhibit coupling between the electronic transition and coherent ~ 0.9 THz optical phonon(s) in MAPI films at room temperature via 2D Electronic Spectroscopy [70]. There is a collection of modes in the frequency range of 0.9–1 THz caused by Pb–I–Pb angular distortions but not coupling to methylammonium cation reorientations (cation rotations), which has already been observed in Raman and THz spectra of orthorhombic and tetragonal phases [71-73]. TRTS, however, is intrinsically sensitive to the internal excitations of the polaron. In our group's previous TRTS work, we studied a bulk single crystal MAPI and observed an intra-band quantum beat superimposed on a slow photoconductive rise time causing by polaron correlations on a sub-picosecond (sub-ps) time scale at room temperature [14]. The quantum beats arose from the dominating LO phonon with $\frac{\omega_{LO}}{2\pi}$ ~3.7 THz coupling to electronic motion combined with Pb-I stretch and translational as well as librational motion of the methylammonium cation.

Take another two types of lead halide perovskites, CsPbBr₃ and MAPbBr₃, as example, Iaru *et al.*'s research found that LO phonon mode at approximately ~4.84 THz (~20meV) acts as a dominant mode responsible for carrier–phonon scattering (Fröhlich interaction) in CsPbBr₃ nanocrystals (NCs) via Raman scattering and THz time-domain spectroscopy [68]. In Miyata *et al.*' s research, they conducted time-resolved optical Kerr effect (TR-OKE) time domain experiments and hybrid DFT calculations on single crystal CsPbBr₃ and MAPbBr₃ to show the coupling of PbBr₃⁻ sublattice motions to across-bandgap electronic transitions (polaron formation), disregarding the cation type [11]. Faster polaron formation of MAPbBr₃ is caused by the coupled motions of the methylammonium cations to the PbBr₃⁻ lattice [11]. They calculated the "killer LO phonon" frequency is ~136 cm⁻¹ (~4.08 THz) and ~194 cm⁻¹ (~5.81 THz) respectively for single crystal CsPbBr₃ and MAPbBr₃ [11]. These previous studies greatly emphasize the significance of considering the dominant LO phonon mode in the formation of polaron, which we will show is in agreement with our UBB-TRTS studies on bulk single crystals as shown in Chapter 4.

2.2.6.2 Formation Time of Polarons in MHPs

There are two important processes for polarons. One is the polaron formation process, the other is polaron decay process. In order to better quantify the polaron dynamics, the time of these two processes, the formation time and lifetime of polarons respectively, leads to extensive research. As for the polaron formation time, in Betz *et al.*' s research of CdTe in 2002, the polaron formation time is approximately at the scale of the reciprocal duration of LO phonon oscillation $\omega_{LO}^{-1} \sim 200$ fs [74]. There are some related researches of MHPs as well. In Bretschneider *et al.*'s research via THz-TDS and a quantifying model considering two distinct, sequential contributions (polaron formation happens after carrier cooling process) to the rise of the photoconductivity, the polaron formation time of FAPbI3 (400 ± 20 fs), MAPbI3 (390 ± 10 fs), and CsPbI₃ (440 ± 10 fs) are similar and

lattice temperature-independent [16]. In Miyata et al.' s research, polarons exist in both single crystal CsPbBr₃ and MAPbBr₃ but the difference is the polaron formation time. For CsPbBr₃ the polaron formation time is 0.6 ± 0.1 ps, and for MAPbBr₃ the polaron formation time is 0.28 ± 0.04 ps at room temperature [11]. Although methylammonium cations in MAPbBr₃ cannot contribute to the polaron formation, their re-orientational motions coupling to Pb-Br-Pb phonon modes can cause faster polaron formation. The different large polaron formation speed/time is arising from the competitiveness between the polaron formation and hot carrier cooling in MAPbBr₃/MAPI not in CsPbBr₃ [11, 12]. In J. S. Evans *et al.*'s research, they found the polaron formation time of CsPbBr₃ is 0.7 ± 0.1 ps and 2.1 ± 0.2 ps at ~300K and ~80 K respectively via femtosecond (fs) timeresolved two-photon photoemission (TR-2PPE) and transient reflectance (TR) spectroscopies [75]. As the temperature increases, the polaron formation rate increases arising from the broadening of phonon resonances, indicating that polaron formation can be facilitated by the phonon disorder. Unlike MAPbBr₃, there's no competition between the polaron formation cooling process of unscreened hot electrons in CsPbBr₃[75].

2.2.6.3 Lifetime of Polarons in MHPs

As for the lifetime, in Miyata *et al.*'s research in 2020, since dielectric screening is significant in exploring polaron dynamics, they conducted research on both single crystal CsPbBr₃ and MAPbBr₃ to explore the reason for the liquid-like dielectric response, and found that the polaron lifetimes of CsPbBr₃ and MAPbBr₃ are approximately ~1.6 μ s and ~ 18 μ s via time-resolved photoluminescence (TR-PL) and time-resolved infrared spectroscopy (TR-IR) [76]. Compared with CsPbBr₃, liquid-like dielectric response in

MAPbBr₃ originates from the liquid-like rotational relaxation of polar methylammonium cation, although liquid-like relaxation has low effects on the formation time of the polarons, the liquid-like polarization can enlarge the lifetime [76]. In He *et al.*'s research, they obtained experimental long lifetime for holes of approximately ~25 μ s in single crystal CsPbBr₃ caused by the polaron formation [77]

While some studies separately consider the polaron lifetime and hot carrier cooling time, some explore polaron lifetime associated with hot carriers. In Niesner *et al.*'s research, they proposed that the lifetime of the initial large polaron formation is 0.25 ± 0.05 ps and the long lifetime with time scale of around ~100 ps is because of the partial preservation of excess electronic energy caused by the fast motion of the methylammonium cation competing with the time scale for LO phonon scattering in MAPbI₃ thin films (reduced scattering with optical phonons) [78]. In Frost *et al.*'s research Kadanoff polaron relaxation time is ~120 fs in MAPbBr₃, ~130 fs in MAPbI₃, and ~80 fs in MAPbCl₃ at ~300K [79].

2.2.6.4 Mobility of Polarons in MHPs

As for the mobility of polarons in MHPs such as lead halide perovskites, there has been many calculations and experiments. By using theoretical calculations, Miyata *et al.* used Feynman- \overline{O} saka formula to obtain the electron and hole polaron mobilities as well as corresponding polaron radii of CsPbBr₃ and MAPbBr₃. For CsPbBr₃, the electron polaron mobility is ~149.8 cm² V⁻¹s⁻¹; the hole polaron mobility is ~79.2 cm² V⁻¹s⁻¹; the Feynman electron polaron radius is ~4.18 nm; the Feynman hole polaron radius is ~3.13 nm [11]. For MAPbBr₃, the electron polaron mobility is ~48.2 cm² V⁻¹s⁻¹; the hole polaron mobility is ~2.67 nm; the Feynman hole

polaron radius is ~2.49 nm [11]. In Frost *et al.*'s research, the electron and hole polaron mobilities in MAPbI₃ are calculated to be ~136 cm² V⁻¹s⁻¹ and ~94 cm² V⁻¹s⁻¹ at room temperature by first-principles calculations [79]. Besides, in Sendner et al.'s research, it is estimated that the average electron/hole polaron mobility of MAPbBr₃ is ~158 cm² V⁻¹s⁻¹ and the corresponding polaron radius is \sim 4.3 nm at room temperature. And the average electron/hole polaron mobility of MAPbI₃ is ~ 197 cm² V⁻¹s⁻¹ and the corresponding polaron radius is ~ 5.1 nm at room temperature. The average electron/hole polaron mobility of MAPbCl₃ is ~58 cm² V⁻¹s⁻¹ and the corresponding polaron radius is ~2.7 nm at room temperature [80]. In Frost *et al.*'s research, predicted Kadanoff mobilities are ~212 cm² V⁻¹s⁻¹ in MAPbBr₃, and ~272 cm² V⁻¹s⁻¹ in MAPbI₃ at 300K. And predicted Hellwarth mobilities are ~157 cm² V⁻¹s⁻¹ in MAPbBr₃, and ~195 cm² V⁻¹s⁻¹ in MAPbI₃ at ~300K [79]. These calculation results are almost in consistent with some experimental results of polaron mobility ~24-164 cm² V⁻¹s⁻¹ for MAPbI₃, ~5-115 cm² V⁻¹s⁻¹ for MAPbBr₃, and ~52 cm² V⁻¹s⁻¹ for CsPbBr₃ at room temperature [77, 81-83]. These are in agreement with the experimental mobilities obtained by our research mentioned in Chapter.4 as well.

In addition, there are some other researches about the temperature-dependence of mobility. In Yi *et al.*'s research of MAPbBr₃ single crystals, they proposed that the intrinsic charge carrier mobility follows an inverse power-law temperature dependence $\mu \propto T^{-\gamma_0}$ via temperature-varied conductivity and Hall effect measurements in single crystals MAPbBr₃ mobility [83]. In the tetragonal phase (under ~235 K but higher than ~155 K), γ_0 equals to 0.5 ± 0.1 while in the cubic phase (higher than 235 K), γ_0 equals to 1.4 ± 0.1, indicating acoustic phonon scattering is dominant rather than impurity scattering [83].

2.3 Synthesis Method of Metal Halide Perovskites (MHPs)

In terms of different dimensions, there are varied types of MHPs, thus the synthesis methods vary in regards of different types. Here mainly discuss several synthesis methods corresponding to zero-dimensional (0D) MHPs nanocrystals, one-dimensional (1D) MHPs nanowires, two-dimensional (2D) MHPs nanoplatelets, and three-dimensional (3D) MHPs single crystals respectively. In our experiments of this research, CsPbBr₃ and MAPbBr₃ single crystals are used as the samples. Their synthesis method will be explicitly discussed later in Chapter. 2.4.4.

2.3.1 Zero-Dimensional (0D) MHPs Nanocrystal



Figure 2.4 Diagram of setup of LAR composed of three-neck flask and injector.

Actually, 0D MHPs NCs mentioned here are referred to 0D MHPs quantum dots. There have been many methods of synthesis, such as Ligand-Assisted Reprecipitation (LAR) [84], Hot-injection method [85], Template Method, Sonication Method [86] and so on. Take LAR as an example, Hu *et al.* successfully synthesized colloidal CsPbBr₃ NCs by

using this method. They dried octadecene (ODE) and lead bromide (PbBr₂) under vacuum condition at the temperature of ~120 °C for one hour in a three-neck flask shown in Fig. 2.4, then injected dried Oleic acid (OA) and oleylamine (OLA) under N₂ gas, raised the temperature by ~60°C when the mixture became clear, injected Cs-oleate solution, kept the temperature for five seconds, cooled down to room temperature, purified the NCs by centrifugation, and finally dispersed them in toluene to make sure the long-time stability [84].

2.3.2 One-Dimensional (1D) MHPs Nanowire

Many methods have been used to synthesize 1D MHPs nanocrystal, such as the Slip-Coating Method [87], Surface-initiated Solution Growth Method [3], Simple Solution Growth Method [88], and Modified Hot-injection Method [89]. Take as Slip-Coating Method an example, Horváth *et al.* used this method and obtained MAPbI₃ nanowires. They dropped saturated MAPbI₃ solution containing dimethylformamide (DMF) on a glass slide, used another glass slide to squeeze the excess solution relative to the first glass slide, exposed the remaining thin liquid film on the glass slide to the air, waited the thin liquid film to evaporate. Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) measurements can be applied to confirm the formation of nanowires [87].

2.3.3 Two-Dimensional (2D) MHPs Nanoplatelet

As for synthesis of 2D MHPs nanoplatelet defined as thin film with thickness range of several nm to hundreds of nm here, there have been methods such as Chemical Vapor

Deposition (CVD) [90], Solution-Processed Method [91], On-surface Direct Solutionphase Growth [92], and so on.



Figure. 2.5 Diagram of vapor-transport system for MAPbX₃ synthesis refer to [90].

Take CVD as an example, it is a process where some high-quality solid materials (powder, thin films, single crystals) can be deposited successfully from chemical reactions happening in vapor phase under specific conditions of reaction temperature, reaction pressure of gas flows, corresponding sources, substrates/without substrates, and so on [93]. Ha *et al.* have synthesized methylammonium lead halide perovskite (MAPbX₃) nanoplatelets where X can be Cl, Br, and I by using CVD system shown in Fig. 2.5. They used Van der Waals epitaxy to grow lead halide PbX₂ nanoplatelets on freshly-cleaved Muscovite Mica substrate in the quartz tube of CVD system, then put methylammonium halide MAX and PbX₂ nanoplatelets into CVD system accompanying with flow of high pure Ar or N₂ gas. PbX₂ nanoplatelets undergo gas-solid hetero-phase reaction with MAX molecules and change to MAPbX₃ nanoplatelets in the end [90].

2.3.4 Three-Dimensional (3D) MHPs Single Crystal

Many synthesis methods have been developed to obtain 3D MHPs single crystals, such as Top-seeded Solution-growth (TSSG) Method [94], Vapor-diffusion Method [95], Modified Vertical Bridgman Technique [96] and so on.



Figure. 2.6 Diagram of Vapor Diffusion Crystallisation.

In the Vapor-diffusion Method (named Vapor Diffusion Crystallisation as well, a wide vial with volatile solvent is placed into a narrower vial with less volatile solvent. As time goes by, the solvent in the wide vial diffuses into the solvent in the narrower one, then the product of reaction is precipitated and crystallize into single crystals shown in Fig. 2.6 [97]. Semonin *et al.* have used this method to synthesize MAPbI₃ single crystals successfully. They added methylammonium iodide (MAI) as well as lead iodide (PbI) dissolved in hydriodic acid with added hypo-phosphorous acid in the narrower vial, and added nitromethane into the wide vial (container). They kept two vials under an argon environment or air free conditions then obtain ~1–8 mm n-type MAPbI₃ single crystals after several days. Also, they used similar methods to obtain p-type MAPbI₃ single crystals [95].

2.4 Our Samples: CsPbBr₃ and CH₃NH₃(MA)PbBr₃ Bulk Single Crystals

2.4.1 Crystal Structure



Figure. 2.7 Cubic crystal structure (*Pm3m* phase) models of MAPbBr₃ single crystal and orthorhombic crystal structure (*Pnma* phase) models of CsPbBr₃ single crystal viewed along (001) as well as (100) at room temperature(~298K).

CsPbBr₃ and MAPbBr₃ single crystals all exhibit temperature-dependent phase transformations. At room temperature (~298 K) CsPbBr₃ crystallizes into orthorhombic space group (*Pnma*), as the temperature increases, it deforms to tetragonal space group (*l4/mcm*) at ~361K and into cubic space group (*Pm3m*) at ~403K. At room temperature (~298K) MAPbBr₃ crystallizes into cubic structure (*Pm3m*), as the temperature decreases, it goes through a phase transition from cubic space group to tetragonal space group (*l4/mcm* phase) at ~155K, and transforms to orthorhombic space group (*Pnma* phase) at ~237 K [98, 99]. In this research, all the experiments are conducted at room temperature, thus the corresponding phase of CsPbBr₃ and MAPbBr₃ single crystals are orthorhombic structure (*Pnma*) and cubic structure (*Pm3m*) shown in Fig. 2.7. Compared with the orthogonal geometry of the perfect perovskite structure, orthorhombic structure (*Pnma*) at ~ 300K of CsPbBr₃ has a deformed perovskite structure with inclined PbBr₆ octahedrons. Compared with tetragonal structure and disarranged molecules between two

nonequivalent places in the shells, cubic structure (Pm3m) of MAPbBr₃ is more isotropic [38].

2.4.2 Electronic Band Structure



Figure. 2.8 Diagram of the white light optical reflectance experimental setup.

The electronic band structures of MAPbBr₃ and CsPbBr₃ single crystals are mainly referred to Ref. [38]. However, to make sure the accuracy of band gap energy of our samples, white light reflectance experiments are conducted. The diagram of the setup composed of white light source, iris, lenses, parabolic mirror, spectrometer, and a PC with Spectrometer Operating Software is shown in Fig. 2.8. There are three spectra obtained from white light reflectance experiments which are dark spectrum, reference spectrum, and reflectance spectrum obtained in this experiment. A dark spectrum is a spectrum taken with the light path blocked; a reference spectrum is a spectrum taken with the light source on and a blank in the sampling region; a reflectance spectrum is a spectrum taken with the light source on and a sample.



Figure. 2.9 White light optical reflectance spectra of (a) MAPbBr₃ single crystal and (b) CsPbBr₃ single crystal used in our experiments.

After data processing, the results of the white light optical reflectance experiments are shown in Fig. 2.9(a, b). There is a peak at the wavelength of ~545 nm in the reflectance spectrum of MAPbBr₃ and a peak at the wavelength of ~520 nm in the reflectance spectrum of CsPbBr₃. As for MAPbBr₃ single crystal, ~545 nm corresponds to photon energy of approximately ~2.275 eV. Two spectra all have a tiny blip at the wavelength of ~610 nm, which is due to small amount of room lights entering the spectrometer. As for CsPbBr₃ single crystal, 520 nm corresponds to photon energy of approximately ~2.384 eV. These experimental results are almost consistent with the energy gaps ~2.28 eV of MAPbBr₃ and ~2.35 eV of CsPbBr₃ mentioned in Kiyoshi *et al.*'s research as well as energy gaps ~2.28 eV of CsPbBr₃ in He *et al.*'s research [11, 77]. The adjusted electronic band structures of MAPbBr₃ and CsPbBr₃ single crystals based on our measurements as well as Ref. [38] are shown in Fig. 2.10.



Figure. 2.10 Electronic band structure of (a) MAPbBr₃ of cubic structure (*Pm3m*) at room temperature and (b) CsPbBr₃ of orthorhombic structure (*Pnma*) at room temperature. Adjusted based on Ref. [38].

2.4.3 Comparison Between MAPbBr₃ and CsPbBr₃

Both MAPbBr₃ and CsPbBr₃ are semiconductors with direct band gaps and belong to lead bromide halide perovskites. They have many similar properties like the same temperature-dependence phase transformations, polaron formation, low recombination rate, general insensitivity to defects, and large optical absorption coefficient mentioned before. The main difference between them is MAPbBr₃ is a kind of organic-inorganic halide perovskite also called hybrid perovskite with methylammonium cation, while CsPbBr₃ is a kind of all-inorganic halide perovskite with cesium cation. Although they have different cations, they have the same cage-like PbBr₃⁻ sublattice which affects their properties a lot. It has been proposed by some research via dielectric measurements, neutron scattering, and molecular dynamics that there are significant structural fluctuations with time scale of ps in hybrid perovskite crystal without defects mainly arising from the organic methylammonium cation [100-102]. In Yaffe *et al.*'s research they found that anharmonic local polar fluctuations are intrinsic to the lead-halide perovskite structure (octahedral cage-like PbBr₃⁻ sublattice), and not unique to the dipolar organic cation by applying low-frequency Raman scattering as well as first-principles molecular dynamics to MAPbBr₃ and CsPbBr₃ in their cubic and tetragonal phases. The local polar fluctuations in CsPbBr₃ originate from the coupling between head-to-head Cs motion and Br face expansion on few hundred fs time scale [13]. As for the large polaron formation in MAPbBr₃ and CsPbBr₃, according to Miyata et al.'s research, polaron are predominantly caused by the deformation of PbBr3⁻ sublattice like coupled Pb-Br stretching and Pb-Br-Pb bending instead of the cation. Nevertheless, MAPbBr₃ has faster polaron formation than CsPbBr₃ due to the coupled motions of the organic cations to the PbBr₃⁻ sublattice in MAPbBr₃ [11].

2.4.4 Sample Preparation

Two orange single crystals with the diameters of approximately ~5 mm and ~3 mm respectively in Fig. 2.11 are CsPbBr₃ and MAPbBr₃ bulk single crystals provided by Dr. Kanatzidis's Laboratory, Northwestern University, and used for UBB-TRTS measurements. They were grown by the method of solution crystal growth similar to the growth of MAPbI₃ bulk single crystal mentioned in the Ref. [103].



Figure. 2.11 CsPbBr₃ and MAPbBr₃ single crystals used in this research. Provided by Kanatzidis's Laboratory, Northwestern University.

As for the growth of MAPbBr₃ bulk single crystals, the first step was to prepare the precursor solution composed of binary methylammonium bromide (MABr) and lead bromide (PbBr₂) with a stoichiometric ratio of 1:1 in γ-utyrolactone (GBL). Then, filtered the solution, placed the filtered solution in a glass vial, heated it gradually until the nucleation, and kept it at a constant solution temperature ~80 °C to promote single crystal growth of MAPbBr₃ for several hours. The specific time of growth depended on how long it takes to yield single crystal with expected size and flat facets suitable for THz experiments. Finally, in order to obtain single crystal in cubic shape with flat surface, MAPbBr₃ was taken out of the solution and blown dry with nitrogen (N₂) flow [104]. The growing process of CsPbBr₃ bulk single crystals is similar. The precursor solution of CsPbBr₃ single crystals growth was composed of ~0.05 mol cesium bromide (CsBr) and ~0.1 mol lead bromide (PbBr₂) in ~48.5 mL dimethyl sulfoxide (DMSO). After all the materials were dissolved, \sim 4.85 mmol of Tetramethylammonium Bromide (C₄H₁₂BrN) was added into the solution with continuous stirring for one day at ~60 °C. Besides, the solution temperature was increased from~ 60 °C to ~85 °C at a steady rate over one week,

was re-adjusted. In the last step, CsPbBr₃ was taken out from the solution and cleaned with toluene [105]. Except for solution-processed growth method, there is melt growth method for CsPbBr₃ called Bridgman growth used in Dr. Kanatzidis's Laboratory as well [106].

Chapter 3

Methodology

In this thesis, we use time-resolved THz spectroscopy to measure the photoconductivity dynamics of MAPbBr₃ and CsPbBr₃ bulk single crystals with sub-picosecond resolution. In this chapter, we define some important terminology (e.g. THz pulses), outline THz generation and detection methods, the methodology of measuring static and time-resolved THz spectra and related theoretical models of the optical conductivity of materials.

3.1 Terahertz Pulses

3.1.1 Terahertz Radiation



Figure. 3.1 THz radiation region

Generally, THz radiation ranges from the limits of photonics (10Hz) to electronics (100 GHz) in the electromagnetic spectrum show in Fig. 3.1 [107]. As for the energy scale of THz, 1 THz equals to 10¹² Hz. Besides, 1 THz also corresponds to thermal energy available

at around ~48K, a vacuum wavelength of ~300 μ m, and a photon energy of ~4.14 meV. Around thirty years ago, due to the lack of convenient and reliable sources of THz radiation, optical properties of materials corresponding to 0.1 - 20 THz range cannot be probed well. However, in 1989, via the combined usage of ultrafast laser techniques and fast semiconductor, freely propagating as well as extreme far-infrared THz pulse was first generated [108]. Since then, a great diversity of techniques used to generate and detect propagating THz radiation have increasingly developed, promoting the process of various research such as quasiparticle scattering rates in semiconductors [109, 110], exciton transitions [111, 112], superconductivity energy band [113]. Now it is generally accepted that the so-called THz gap is closed.

3.1.2 Terahertz Generation

There have been several commonly used methods of THz pulse generation. Among them, using fast photoconductive switches and applying optical rectification (OR) in a nonlinear optical crystal are two of the most popular methods. Besides these, a newer method called two-color laser plasmas has remarkable advantages in bandwidth as well as pulse intensity.

$$\nabla \times \vec{E} + \frac{\partial \vec{B}}{\partial t} = 0 \tag{3.1}$$

$$\nabla \cdot \vec{B} = 0 \tag{3.2}$$

$$\nabla \times \vec{H} = \frac{\partial \vec{D}}{\partial t} + \vec{J}$$
(3.3)

$$\nabla \cdot \vec{\mathbf{D}} = \rho \tag{3.4}$$

$$\vec{D} = \epsilon \vec{E} \tag{3.5}$$

$$\vec{B} = \mu \vec{H}$$
(3.6)

Through Maxwell Equations, electromagnetic waves can be described greatly. After some transformations, the principle of obtaining THz by the method of nonlinear optical can be clarified clearly.

$$\nabla \times \left(\nabla \times \vec{A}\right) = -\nabla^2 \vec{A} + \nabla \left(\nabla \cdot \vec{A}\right)$$
(3.7)

$$\frac{\partial}{\partial t} \left(\nabla \times \vec{B} \right) = \nabla^2 \vec{E} - \frac{1}{\epsilon} \rho \tag{3.8}$$

$$\nabla^2 \vec{E} - \epsilon \mu \frac{\partial^2 \vec{E}}{\partial t^2} = \mu \frac{\partial \vec{j}}{\partial t}$$
(3.9)

$$\nabla^{2}\vec{E} - \epsilon\mu \frac{\partial^{2}\vec{E}}{\partial t^{2}} = \mu \left(\frac{\partial\vec{j}_{cond}}{\partial t} + \frac{\partial^{2}\vec{P}}{\partial t^{2}}\right)$$
(3.10)

Combination of Eq. 3.1 and Eq. 3.4 can be transformed to Eq. 3.8 by using the vector identity Eq. 3.7. Then apply Eq. 3.3 and condition of no free charge, Eq. 3.8 can be transformed to Eq. 3.9. Since the charges can be divided to free charges current and bound charges current, rewrite charge current \vec{J} as the sum of \vec{J}_{bound} and \vec{J}_{cond} . Additionally, plug $\vec{J}_{bound} = \frac{\partial \vec{P}}{\partial t}$ into Eq. 3.9, obtain Eq. 3.10 where \vec{P} is the polarization and the two terms on second time derivative of the nonlinear polarization right-hand side greatly represent two ways of THz beam generation. One is photoconductive switch generation by first derivative of a conduction current, the other is OR by using the second time derivative of the nonlinear polarization transient.



Figure. 3.2 Diagrams of generating THz pulses by the method of (a) photoconductive switch, (b) optical rectification, and (c) two color laser induced plasma.

3.1.2.1 Photoconductive Switch

The first method introduced detailly here is photoconductive switch generation which is firstly used in 1970s and developed free space THz radiation in 1980s [114, 115]. Fig. 3.2(a) is the diagram of the setup where there are DC voltage bias and direct-gap semiconducting material semi-insulating GaAs wafer. Charge carriers are accelerated in the bias field and emit a THz pulse in the far field, then the THz radiation is proportional the first derivative of a conduction current.

$$P(t) \propto \chi^{(1)} E(t) + \chi^{(2)} E(t)^2 + \chi^{(3)} E(t)^3 + \dots$$
(3.11)

$$E_1(t) = \cos(\omega_1 t) \tag{3.12}$$

$$E_2(t) = \cos(\omega_2 t) \tag{3.13}$$

$$P^{(2)}(t) \propto \chi^{(2)} \cos(\omega_1 t) \cos(\omega_2 t) = \frac{\chi^{(2)} [\cos(\omega_1 + \omega_2) t + \cos(\omega_1 - \omega_2) t]}{2}$$
(3.14)

3.1.2.2 Optical Rectification

The second method introduced in detail here is OR. After applying electric field E(t) to a material, the polarization response P(t) can be written as Eq. 3.11, where different terms can be treated separately and regarded as different contributions of Taylor expansion of the atomic potential (different responses to high field carrier driving). As the anharmonicity in the oscillation of charge within the material, higher order responses become significant only at higher fields attained in fs laser pulses $\sim 10^7 \text{V/cm}$. But secondorder effects, such as sum and difference frequency generation and parametric amplification, can be easily observed in the laboratory. Through second-order nonlinear optical process, THz pulses can be generated successfully. Since the second order polarization corresponds to two photons with frequency ω_1 and ω_2 , $E(t)^2$ can be rewritten as the product of $E_1(t)$ and $E_2(t)$ as shown in Eq. 3.12 and Eq. 3.13. Then one obtains the second order polarization show in Eq. 3.14, leading to the generation of sum and difference frequency. When ω_1 equals to ω_2 , the special case, a quasi-dc polarization (optical rectification), occurs. The THz electric field is proportional to the second time derivative of the nonlinear polarization $(\frac{\partial^2 \vec{P}}{\partial t^2})$. As for $\chi^{(2)}$, it is a tensor related to the crystallographic symmetry of the nonlinear material. Fig. 3.2(b) is the setup of OR, take ZnTe crystal as an example, then detect the parallel component of THz electric field with respect to polarization of generation pulse. If azimuthal angle θ is the angle between [110] axis and the polarization of generation pulse, then electric field of THz pulse is proportional to $\cos(3\theta) - \cos\theta$ [116].

3.1.2.3 Two Color Laser Induced Plasma

$$E_{\text{THz}} \propto \chi^{(3)} E_{\omega} E_{\omega} E_{2\omega} \tag{3.15}$$

The third method and the one primarily used in this thesis to drive the ultrabroadband time-resolved THz spectrometer is a two-color laser induced plasma, which is simple and can emit broad bandwidth and strong THz pulses. THz pulses can be generated by focusing the fundamental frequency ω and second harmonic frequency 2ω as shown in 3.2(c) [117]. The principle under this method can be understood as a four wave mixing (FWM) process with a third order susceptibility in the gas. The THz electric field can be written as Eq. 3.15 in the FWM process where $\chi^{(3)}$ is the third order nonlinear susceptibility, E_{ω} is the electric field of the fundamental, and $E_{2\omega}$ is the electric field of the second harmonic respectively. When using this method, the only the laser pulse duration will limit the bandwidth as phase matching is near perfect across the entire pulse bandwidth. For example, 10 fs laser pulses can generate ultrabroadband pulses up to ~200 THz by air plasma [118]. Besides, longer wavelength can enhance the efficiency of down conversion in the THz region. It should be noted that the FWM approach is only valid in the low plasma density regime, above which one must take into account the complicated dispersion dynamics of the plasma itself.

3.1.3 Terahertz Detection

There have been some methods of THz pulse detection as well. Here mainly discuss three THz detections corresponding to the previous mentioned methods of THz generation, photoconductive switches, OR, and two-color laser plasmas respectively.



Figure. 3.3 Schematic of (a) photocurrent detection, (b) air biased coherent detection (c) free-space electro-optic detection

3.1.3.1 Photocurrent Detection

The first method is photocurrent detection, which is similar to the photoconductive switch as shown in Fig. 3.3(a). Instead of bias voltage source, photocurrent detection uses current amplifiers and connects to a lock-in amplifier. Low temperature grown GaAs (LT-GaAs) and radiation damaged silicon on sapphire (RD-SOS) are two commonly used materials due to their sub-ps recombination time and relatively high carrier mobility [119-121]. After the application of a fs sampling pulse, many free carriers are excited from the semiconductor between the electrodes. When the THz pulse is overlapped with the sampling pulse, a current transient which is directly proportional to the THz electric field can be generated and detected by the amplifier. Therefore, THz electric field as a function

of time can be obtained by scanning the sampling pulse relative to THz pulse. The choice of semiconductor in this case is such that the free carrier lifetime is short, preferably subpicosecond as it is in low-temperature grown GaAs.

3.1.3.2 Free Space Electro-Optic Detection

The second method is free-space electro-optic (EO) detection as shown in Fig. 3.3(c). The principle is making use of the Linear Pockels Effect of EO crystal to detect the quasi-DC electric field of THz radiation with respect to 100 fs sampling pulse [122-124]. There are many kinds of EO crystals, such as ZnTe, GaAs, GaP, GaSe, InP, and DAST [125], though ZnTe is the most common one as it is well phase matched to the 800 nm wavelength from commercial Ti:sapphire lasers. When only a linearly polarized sampling pulse traverses the ZnTe crystal, in the absence of a THz pulse, its polarization is unchanged. It then becomes circular-polarized after going through the quarter-wave plate, after which its polarization components are equally separated by a Wollaston prism and sent to balanced photodiode detector pair producing photovoltages V_A and V_B. Because of the circular polarization of the pulse, photodiodes on detector read the same voltage, leading to a zero reading on lock-in amplifier ($V_A - V_B = 0$). However, when THz pulse and sampling pulse traverse together and overlap in time, sampling pulse's polarization will be affected slightly and tilted by an amount because of Pockels Effect (the tilted polarization is proportional to the electric field). Elliptical polarization is obtained after passing through the quarter-wave plate, then two different voltage signals are obtained after Wollaston prism and detector ($V_A - V_B \neq 0$). By subtraction of two different voltage, lock-in amplifier obtained a signal which is proportional to the electric field of THz

radiation. Therefore, THz electric field can be obtained by scanning the time delay between the sampling pulse and THz pulse. The detection bandwidth is limited by the mismatch between the THz phase velocity and the group velocity of the sampling beam as it propagates through the detection crystal [126, 127]. Reducing the crystal thickness minimizes the influence of phase mismatch, although decreases the interaction length and produces a smaller detector response [128]. Besides the mismatch, take ZnTe as an example, the bandwidth is limited by the absorption phonon at ~1.6 THz, absorption phonon at ~3.7 THz and transverse optical (TO) phonon at ~5.31 THz as well [127].

3.1.3.3 Air Biased Coherent Detection

The third method, and the one used in the ultra-broadband TRTS system, is Air Biased Coherent Detection (ABCD) shown in Fig. 3.3(b). Because dry air is lacking in dispersive excitations, bandwidth limitations happening in electro-optic detection and photoconductive antennas are avoided. In ABCD, the laser pulse duration is the main limitation. The detection of ultrabroadband pulses can be in air and other gases with a third order nonlinearity, which is a four-wave mixing process.

$$E_{2\omega} \propto \chi^{(3)} E_{\text{THz}} E_{\omega} E_{\omega} \tag{3.16}$$

$$I_{2\omega} \propto \left(\chi^{(3)} I_{\omega}\right)^2 I_{\text{THz}} \tag{3.17}$$

THz photon E_{THz} and two laser photons E_{ω} are focused to generate a second harmonic photon $E_{2\omega}$ by third order nonlinear process called terahertz field induced second harmonic (TFISH) as shown in Eq. 3.16. The relation of the intensity of incoherent measured signal and THz pulse is Eq. 3.17 where phase components are lost.

$$E_{2\omega}^{LO} = E_{bias}^{AC} + E_{bias}^{DC}$$
(3.18)

$$I_{2\omega} \propto \langle E_{2\omega}^2 \rangle = \langle (E_{2\omega}^{THz} + E_{2\omega}^{LO})^2 \rangle$$

$$= \langle (E_{2\omega}^{THz} + E_{bias}^{AC} + E_{bias}^{DC})^2 \rangle$$
(3.19)

$$= (E_{2\omega}^{THz})^2 + (E_{2\omega}^{AC})^2 + (E_{2\omega}^{DC})^2$$

$$+ 2\langle E_{2\omega}^{THz} E_{2\omega}^{AC} \rangle + 2\langle E_{2\omega}^{THz} E_{2\omega}^{DC} \rangle + 2\langle E_{2\omega}^{DC} E_{2\omega}^{AC} \rangle$$

$$E_{2\omega}^{THz} \propto \chi^{(3)} I_{\omega} E_{THz}$$

$$E_{2\omega}^{AC} \propto \chi^{(3)} I_{\omega} E_{bias}^{DC}$$
(3.20)

$$E_{2\omega}^{DC} \propto \chi^{(3)} I_{\omega} E_{bias}^{DC}$$

$$I_{2\omega} \propto (\chi^{(3)} I_{\omega})^2 \left[(E_{THz})^2 + (E_{bias}^{AC})^2 + (E_{bias}^{DC})^2 \right]$$

$$\mp 2E_{THz} E_{bias}^{AC} \mp 2E_{THz} E_{bias}^{DC} \mp 2E_{bias}^{AC} E_{bias}^{DC} \qquad (3.21)$$

If one applies a local oscillator (LO) bias field composed of AC and DC components (Eq. 3.18) to the optical focus, a coherent heterodyne measurement can be obtained. The oscillator will mix with the TFISH field, and rewrite the intensity (Eq. 3.19). The field induced second harmonics are shown in Eq. 3.20. Insert them into Eq. 3.19, then Eq. 3.19 becomes Eq. 3.21.

$$I_{2\omega} \propto 4 \left(\chi^{(3)} I_{\omega}\right)^2 E_{\text{THz}} E_{\text{bias}}^{\text{AC}}$$
(3.22)

All DC bias signals can be removed by using lock-in, leading to terms containing AC bias signals to remain only. And by changing the applied DC bias field, the second and sixth terms in Eq. 3.21 can be cancelled, allowing a zero baseline in $I_{2\omega}$. The fourth term in Eq.

3.21 can give the final $I_{2\omega}$, where the intensity is proportional to THz electric field, therefore, the detection can be enhanced by using gases with low THz absorption and high third order nonlinear susceptibility, such as Xenon or alkanes.

3.2 Terahertz Spectroscopy

3.2.1 Terahertz Time-Domain Spectroscopy (THz-TDS)

After applying THz pulse and sampling pulse to substrate, the detection of the response functions such as conductivity from changes in the transmitted/reflected electric field with respect to the reference in time is called THz Time-Domain Spectroscopy (THz-TDS).



Figure. 3.4 Diagram of Transmission and reflection of light at an interface between two different mediums.

$$E_t = E_i + E_r \tag{3.23}$$

$$H_t = H_i + H_r \tag{3.24}$$

$$\mathbf{v}\left|\vec{\mathbf{B}}\right| = \left|\vec{\mathbf{E}}\right| \tag{3.25}$$

$$\mathbf{E}_{t}\mathbf{n}_{t} = \mathbf{E}_{i}\mathbf{n}_{i} + \mathbf{E}_{r}\mathbf{n}_{r} \tag{3.26}$$

$$\tilde{\mathbf{r}} = \frac{\tilde{\mathbf{n}}_i - \tilde{\mathbf{n}}_t}{\tilde{\mathbf{n}}_i + \tilde{\mathbf{n}}_t} \tag{3.27}$$

$$\tilde{\mathbf{t}} = \frac{2\tilde{\mathbf{n}}_{\mathrm{i}}}{\tilde{\mathbf{n}}_{\mathrm{i}} + \tilde{\mathbf{n}}_{\mathrm{t}}} \tag{3.28}$$

Fresnel equations can be used to describe the transmission and reflection of an electromagnetic field at an interface. For example, transmission and reflection of light at an interface between air and a medium are illustrated in Fig. 3.4. When the radiation is normally incident to the medium, the relations of amplitudes of the incident, transmitted and reflected fields are shown in Eq. 3.23 (Eq. 3.24). Because of the relation Eq. 3.25, Eq. 3.24 can be rewritten as Eq. 3.26. The amplitude reflection \tilde{r} and transmission coefficient \tilde{t} can be written as Eq. 3.27 and Eq. 3.28 respectively.



Figure. 3.5 Diagram of incident, transmitted and reflected electric fields in thick slab geometry.

Transmission factor is given in Eq. 3.29, where d is the sample thickness. Consider the simplest condition that the sample is a thick slab with a thickness much larger than the

THz wavelength in the medium. Therefore, etalon effects can be ignored by timewindowing out the reflections of the THz pulse. The diagram with air (sample 1) and medium (sample 2) regions is shown in Fig. 3.5. Complex transmission function from sample 1 to sample 2 then to sample 1 can be written as Eq. 3.30. Later Fourier transform the complex transmission function $\tilde{T}(\omega)$ which can be related to $\tilde{n} = n + i\kappa$ by Eq. 3.31. Since the absorption coefficient α can be written as Eq. 3.32, transmission function can be related α and n.

$$T = e^{i\frac{\omega}{c}\tilde{n}d}$$
(3.29)

$$\widetilde{T}(\omega) = \frac{\widetilde{E}_{SAMPLE}(\omega)}{\widetilde{E}_{REF}} = \frac{t_{12}t_{21}T_2}{T_1}$$
(3.30)

$$\widetilde{T}(\omega) = \frac{4\widetilde{n}}{(1+\widetilde{n})^2} e^{i(\widetilde{n}-1)\frac{\omega}{c}d} = \frac{4\widetilde{n}}{(1+\widetilde{n})^2} e^{-\kappa\frac{\omega}{c}d} e^{i(n-1)\frac{\omega}{c}d} = \frac{4\widetilde{n}}{(1+\widetilde{n})^2} e^{-\frac{\alpha d}{2}} e^{i(n-1)\frac{\omega}{c}d}$$
(3.31)

$$\alpha = \frac{2\kappa\omega}{c} \tag{3.32}$$

Transmission function $\tilde{T}(\omega)$ is a complex value with amplitude $|\tilde{T}(\omega)|$ and phase term $e^{i\phi(\omega)}$ shown in Eq. 3.33, then $|\tilde{T}(\omega)|$ and $\phi(\omega)$ can be obtained shown in Eq. 3.34 and Eq. 3.35. Thus, index of refraction $n(\omega)$ and absorption coefficient $\alpha(\omega)$ are Eq. 3.36 and Eq. 3.37 respectively. After obtaining these parameters, the optical conductivity and dielectric function can be obtained as well through general relations.

$$\widetilde{T}(\omega) = \left| \widetilde{T}(\omega) \right| e^{i\phi(\omega)} \tag{3.33}$$

$$|\tilde{T}(\omega)| = |\frac{4\tilde{n}}{(1+\tilde{n})^2}|e^{-\frac{\alpha d}{2}}$$
 (3.34)

$$\phi(\omega) = (n-1)\frac{\omega}{c}d \qquad (3.35)$$

$$n(\omega) = 1 + \frac{\phi(\omega)c}{\omega d}$$
(3.36)

$$\alpha(\omega) = -\frac{2}{d} \ln\left[\left| \frac{(1+\tilde{n})^2}{4\tilde{n}} \right| |\tilde{T}(\omega)| \right]$$
(3.37)

3.2.2 Time-Resolved Terahertz Spectroscopy (TRTS)



Figure. 3.6 Diagram of (a) TRTS setup of transmission mode and (b) TRTS setup of reflection mode

TRTS is similar to the THz-TDS, adding a pump fs pulse that excites the sample into a non-equilibrium state. Since 1 THz is only ~4.1meV, the low energy of THz pulse can help to probe energy scales spectroscopically well under room temperature. Therefore, the nonequilibrium ps dynamics of systems within bandwidth of the THz pulse (~1 – 100 meV) can be probed by THz pulses, which is named time-resolved terahertz spectroscopy (TRTS). In TRTS experiments, the sample can be excited to a nonequilibrium state after applying fs pump pulse, then the pump induced photoconductivity can be probed by the process of THz radiation traversing through the sample. The change of the induced photoconductivity can be mapped in time because pump probe time delay can be

scanned. The temporal resolution of the technique is determined primarily by the dispersion within the detection medium, which in our case using ABCD where the medium is dispersionless, the resolution is limited solely by the duration of the pump pulse. This is a special property of the coherent detection method, whereby specific choice of sample delay lines can lead to a projection of the dynamic response onto a constant pump-probe time axis. In essence, each measured point of the THz pulse has experienced the exact pump-probe time delay, leading to a simple convolution which can be solved by Fourier transform. TRTS can be used widely, such as bulk material systems, high-Tc superconductors, inorganic and organic semiconductors, insulators, liquids and so on [120, 129-135]. There are two modes of TRTS, one-dimensional (1D) scan whereby only a single point in the THz probe field is measured instead of the entire THz waveform. This ignores the phase information of the electric field and only records an "averaged" response. A two-dimensional (2D) scan, measuring the entire THz waveform for each pump-probe time delay, considers both amplitude and phase of the THz pulse electric field and contains all information about both energetics and dynamics of the interaction. There are also transmission and reflection mode of TRTS, which are shown in Fig. 3.6(ab).

3.2.2.1 One-Dimensional Scan of TRTS

In a 1D scan, the peak of the THz pulse and the sampling beam should arrive at the detection crystal at the same time by adjusting the THz source time delay. Then, lock-ins only monitor the peak of the THz waveform in which all the frequency components of the pulse are in phase. The pump beam which can be moved in time by a delay stage and

modulated by an optical chopper is added to excite the sample. Such a scan only contains useful information in the limit where no transient phase shifts are present in the THz pulse, which would mimic an amplitude shift.

3.2.2.2 Two-Dimensional Scan of TRTS

In a 2D scan, instead of only the peak of the waveform, the full waveform is measured. The pump excitation is moved in time with respect to the THz pulse by delay stage while pump pulse photoexcites the sample. The coherent detection of the amplitude and phase of the THz pulse electric field can be used to obtain complex conductivity on ps time scales without the help of Kramier-Kronig analysis. 1D scans can be derived easily from complete 2D scans. In experiments, the duration of sampling pulse is shorter than THz pulse, therefore, the evolution of THz electric field in time can be resolved. By adding a delay stage used to change the time gap on the fs order between THz radiation and sampling pulse, THz pulse can be sampled can be measured accurately. Small THzinduced change can be measured with the mechanical chopping connected to lock-in amplifier. There are two measurements, one is with sample spectrum where pump-probe delay time is set to a specific positive value, the other is without sample as reference spectrum where pump-probe delay time is negative (THz pulse arrives before the pump pulse). After subsequent Fourier transforming of these two spectrums, frequency domain can be obtained. Then, the complex transmission function obtained from the ratio of the Fourier transforms of these two pulses can be related to the complex conductivity (Eq. 3.51). According to Eq. 3.51, the real and imaginary parts of conductivity can be written

as
$$\sigma_1(\omega) = \frac{N+1}{Z_0 d} \left[\frac{1}{|T(\omega)|} \cos \Phi - 1 \right]$$
 and $\sigma_2(\omega) = -\frac{N+1}{Z_0 d} \left[\frac{1}{|T(\omega)|} \sin \Phi \right]$ in terms of amplitude $|T(\omega)|$ and phase $\Phi(\omega)$.

3.2.2.3 Thin Film Approximation

$$\hat{\mathbf{n}} \times \left(\vec{\mathbf{H}}_1 - \vec{\mathbf{H}}_2\right) = \int_0^\infty \vec{\mathbf{J}} \, d\mathbf{z} = \vec{\mathbf{J}} \, d \tag{3.38}$$

$$\hat{\mathbf{n}} \times \left(\vec{\mathbf{E}}_1 - \vec{\mathbf{E}}_2\right) = 0 \tag{3.39}$$

$$H_i - H_r - H_t = Jd \tag{3.40}$$

$$E_{i} - E_{r} - E_{t} = 0 \tag{3.41}$$

In TRTS experiments, the radiation passes through the thin substrate from the air, therefore, consider the situation of the radiation transmission from media 1 to the media 2, the boundary conditions of electric fields and magnetic fields are given in Eq. 3.38 and Eq. 3.39 where d is the penetration depth. To simplify the situation, consider the normal incidence and obtain the Eq. 3.40 and Eq. 3.41 which are identical to the boundary conditions of Fresnel Transmission derivation.

$$\Gamma = \frac{H}{E}$$
(3.42)

$$E_{t} = \frac{2\Gamma_{1}E_{i} - Jd}{\Gamma_{1} + \Gamma_{2}}$$
(3.43)

$$\Gamma_1 = \frac{H_i + H_r}{E_i + E_r} \tag{3.44}$$

$$\Gamma_2 = \frac{H_t}{E_t} \tag{3.45}$$

Define admittance Γ as shown in Eq. 3.42 and combine Eq. 3.40 as well as Eq. 3.41, transmitted electric field can be obtained (Eq. 3.43) where the Γ_1 and Γ_2 can be expressed by Eq. 3.44 and Eq. 3.45.

$$t = \frac{E_t}{E_i}$$
(3.46)

$$J = \tilde{\sigma} E_t \tag{3.47}$$

$$\tilde{t} = \frac{2\Gamma_1}{\Gamma_1 + \Gamma_2 + \tilde{\sigma}d}$$
(3.48)

$$\Gamma_{a} = \frac{N_{a}}{Z_{0}}$$
(3.49)

$$\tilde{t}_{film} = \frac{2}{N_0 + 1 + Z_0 \tilde{\sigma}(\omega) d} \left(d \ll \frac{\lambda}{n} \right)$$
 (3.50)

Since Eq. 3.46 and Eq. 3.47 where $\tilde{\sigma}$ is the complex photoconductivity, transmitted coefficient \tilde{t} can be obtained shown in Eq. 3.48. Use N_a as the index of refraction of the medium and Z₀ as the impedance of free space, then the admittance can be written as Eq. 3.49. When considering the index of refraction of air is 1 and the index of refraction of substrate is N_0 (roughly real), the final expression of the transmission through a thin conducting film $\left(d \ll \frac{\lambda}{n}\right)$, Tinkham equation, can be obtained (Eq. 3.50) (internal reflections within the photo-excited layer are averaged and neglected) [136].

$$\widetilde{T}(\omega) = \frac{t_{\text{film}}}{t_{\text{subs}}} = \frac{\widetilde{E}_{\text{pump}}(\omega)}{\widetilde{E}_{\text{ref}}(\omega)} = \frac{N_0 + 1}{N_0 + 1 + Z_0 \widetilde{\sigma}(\omega) d}$$
(3.51)

$$\widetilde{T}(\omega) = \frac{t_{\text{film}}}{t_{\text{subs}}} = \frac{\widetilde{E}_{\text{pump}}(\omega)}{\widetilde{E}_{\text{ref}}(\omega)} = \frac{N_0 + 1}{N_0 + 1 + Z_0 \widetilde{\sigma}(\omega) d} e^{-\frac{iN_0 dw}{c}}$$
(3.52)

$$-\frac{\Delta T(t)}{T_0} = \frac{T_0 - T_{pump}}{T_0} = 1 - \frac{N_0 + 1}{N_0 + 1 + Z_0 d\Delta\sigma(t)}$$
(3.53)
$$\Delta\sigma(t) = \frac{N_0 + 1}{Z_0 d} \left(-\frac{\Delta T}{T_0} \right) \left[\frac{1}{1 + \frac{\Delta T(t)}{T_0}} \right]$$
(3.54)

Transmission function $\tilde{T}(\omega)$ from the excited part of substrate to unexcited part is obtained (Eq. 3.51) by using the transmission coefficient of the unexcited substrate $(t_{substrate} = \frac{2}{1+N_0})$. However, for deep penetrating excitation the distance traversing through the substrate differs from the excited substrate, therefore, transmission function changes to Eq. 3.52 by adding a phase factor. When assume the conductivity is real, the differential transmission can be written as the function of pump-induced change in conductivity $\Delta\sigma(t)$ shown in Eq. 3.53, therefore, $\Delta\sigma(t)$ can be written as Eq. 3.54. In experiments, T_0 is the THz transmission at negative pump-probe delay time, and two pump-probe delay scans are needed to obtain the differential transmission ($-\Delta T = T_0 - T_{pump}$) where pump beam is chopped.

3.3 Theoretical Models for Conductivity in Materials

3.3.1 Drude Model

In Drude Model, consider charge carriers as free carriers responding to electric field with a collisional dampening rate of $\frac{1}{\tau_s}$ (τ_s is the scattering time) also called scattering rate γ . In an electric field, the carrier motion can be described by the rate equation Eq. 3.55. The current density is given by Eq. 3.56 where N is the charge carrier density, *e* is the electronic charge and m^* is the effective mass of carrier respectively. Consider the steady state (DC) field, then obtain the relation Eq. 3.57. Combine Eq. 3.55-3.57, σ_{dc} can be obtained shown

in Eq. 3.58 where the plasma frequency ω_p is defined by Eq. 3.59. Besides, mobility μ is defined by Eq. 3.60, then σ_{dc} can be rewrite in another way as Eq. 3.61.

$$m^{*}\frac{d\vec{v}(t)}{dt} = -m^{*}\frac{\vec{v}}{\tau_{s}} - e\vec{E}(t)$$
(3.55)

$$\vec{J} = -\text{Ne}\vec{v} \tag{3.56}$$

$$\frac{\mathrm{d}\vec{v}}{\mathrm{d}t} = 0 \tag{3.57}$$

$$\sigma_{dc} = \frac{\vec{J}}{\vec{E}} = \frac{Ne^2\tau_s}{m^*} = \omega_p^2\epsilon_0\tau_s \tag{3.58}$$

$$\omega_p^2 = \frac{Ne^2}{\epsilon_0 m^*} \tag{3.59}$$

$$\mu = \frac{\vec{v}}{\vec{E}} = \frac{e\tau_s}{m^*} \tag{3.60}$$

$$\sigma_{dc} = \mathrm{Ne}\mu \tag{3.61}$$

The electric field of frequency ω can be written as Eq. 3.62. After substituting this equation into Eq. 3.55, the solution can be obtained (Eq. 3.63), and Eq. 3.55 transforms to $(-i\omega)\vec{v}(\omega) = -\frac{\vec{v}(\omega)}{\tau_s} - e\vec{E}(\omega)$. Since $\tilde{\sigma}(\omega) = \frac{\vec{f}}{\vec{E}}$ and Eq. 3.57, conductivity $\tilde{\sigma}(\omega)$ in Drude model can be written as Eq. 3.64 with real part and imaginary part shown in Eq. 3.65 and Eq. 3.66 respectively where $\sigma_{dc} = \frac{Ne^2\tau_s}{m^*}$, and m^* is effective mass.

$$\vec{E}(t) = Re[\vec{E}(\omega)]e^{-i\omega t}$$
(3.62)

$$\vec{v}(t) = Re[\vec{v}(\omega)] e^{-i\omega t}$$
(3.63)

$$\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = \frac{\sigma_{dc}}{1 - iw\tau_s}$$
(3.64)

$$\sigma_1(\omega) = \frac{1}{1 + (w\tau_s)^2} \sigma_{dc} \text{ or } \frac{Ne^2}{m^*} \frac{\tau_s}{1 + (w\tau_s)^2}$$
(3.65)

$$\sigma_2(\omega) = \frac{w\tau_s}{1 + (w\tau_s)^2} \sigma_{dc} = w\tau_s \sigma_1(\omega) \text{ or } \frac{Ne^2}{m^*} \frac{w\tau_s^2}{1 + (w\tau_s)^2}$$
(3.66)

One example of Drude model is shown below, considering two conditions. The first condition is $\omega \tau \sim 1$ thus $\sigma_1(\omega) \sim \sigma_2(\omega)$ shown in Fig. 3.7(a). The second condition is $\omega \tau \ll 1$ thus $\sigma_1(\omega) \sim \sigma_{dc}$ and $\sigma_2(\omega) \sim \omega \tau_s \sigma_{dc}$ shown in Fig. 3.7(b).



Figure. 3.7 Schematic of conductivity of Drude model in the conditions of (a) $\omega \tau_s \sim 1$ and (b) $\omega \tau_s \ll 1$ (the real and imaginary conductivity corresponds to blue and red curves respectively).

3.3.2 Lorentz Model

In Lorentz Model, light-matter interactions can be described in terms of the electric field inducing oscillations of the atomic dipole by the driving forces acting on the electrons. A single damped harmonic oscillator with force constant k driven by electric field can be described by the equation of motion (Eq. 3.67) where m^* is the effective mass. Substitute the solution form of Eq. 3.68 into Eq. 3.67, then give Eq. 3.69. The resonant frequency of

the oscillator ω_0 has the relation shown in Eq. 3.70, and the dipole moment per unit volume is given by Eq. 3.71 or Eq. 3.72 related to electric susceptibility. Since electric susceptibility can be related to dielectric function (Eq. 3.73), then obtain Eq. 3.74.

$$m^* \frac{d^2 \vec{x}(t)}{dt^2} + \frac{m^*}{\tau_s} \frac{d \vec{x}(t)}{dt} + k \vec{x}(t) = -e \vec{E}(t)$$
(3.67)

$$\vec{x}(t) = \vec{x}(\omega)e^{-i\omega t} \tag{3.68}$$

$$\vec{x}(\omega) = -\frac{e}{m^*} \frac{1}{(\omega_0^2 - \omega^2) - \frac{i\omega}{\tau_s}} \vec{E}(\omega)$$
(3.69)

$$\omega_0^2 = \frac{\mathbf{k}}{m^*} \tag{3.70}$$

$$\vec{P} = -Ne\vec{x} \tag{3.71}$$

$$\vec{P} = \epsilon_0 \chi \vec{E} \tag{3.72}$$

$$\varepsilon = \epsilon_0 (1 + \chi) \tag{3.73}$$

$$\frac{\tilde{\varepsilon}(\omega)}{\epsilon_0} = 1 + \frac{\omega_p^2}{(\omega_0^2 - \omega^2) - \frac{i\omega}{\tau_s}}$$
(3.74)

$$\tilde{\sigma}(\omega) = \frac{\omega_p^2 \epsilon_0 \omega}{i(\omega_0^2 - \omega^2) + \frac{\omega}{\tau_s}}$$
(3.75)

$$\sigma_1(\omega) = \frac{\epsilon_0 \omega_p^2 \omega^2 \left(\frac{1}{\tau_s}\right)}{(\omega_0^2 - \omega^2)^2 + \left(\frac{\omega}{\tau_s}\right)^2} \text{ or } \frac{Ne^2}{m^*} \frac{\omega^2 \left(\frac{1}{\tau_s}\right)}{(\omega_0^2 - \omega^2)^2 + \left(\frac{\omega}{\tau_s}\right)^2}$$
(3.76)

$$\sigma_{2}(\omega) = -\frac{\epsilon_{0}\omega_{p}^{2}\omega(\omega_{0}^{2}-\omega^{2})}{(\omega_{0}^{2}-\omega^{2})^{2} + \left(\frac{\omega}{\tau_{s}}\right)^{2}} \text{ or } -\frac{Ne^{2}}{m^{*}}\frac{\omega(\omega_{0}^{2}-\omega^{2})}{(\omega_{0}^{2}-\omega^{2})^{2} + \left(\frac{\omega}{\tau_{s}}\right)^{2}}$$
(3.77)

Recall that the dielectric function is related to the conductivity by $\tilde{\varepsilon}(\omega) = 1 + \frac{i\tilde{\sigma}(\omega)}{\epsilon_0\omega}$, then Eq. 3.74 can be transformed to the conductivity $\tilde{\sigma}(\omega)$ in Lorentz model shown in Eq. 3.75 with real part and imaginary part shown in Eq. 3.76 and Eq. 3.77 respectively where ω_p is the plasma frequency $(\omega_p^2 = \frac{Ne^2}{\epsilon_0 m^*})$, τ_s is the momentum scattering time (scattering rate $\gamma = \frac{1}{\tau_s}$), and *N* is the charge carrier density.



Figure. 3.8 Schematic of conductivity of Lorentz model example showing the real (blue curve) and imaginary (red curve) parts of the conductivity for $\omega_0 = 6$ THz, $\omega_p = 4 \times 10^{13}$, and $\tau_s = 400$ fs.

An example of Lorentz model with $\omega_0 = 6$ THz, $\omega_p = 4 \times 10^{13}$, and $\tau_s = 400$ fs is plotted shown in Fig. 3.8. The real part of the conductivity $\sigma_1(\omega)$ is the blue curve, and the imaginary part of the conductivity $\sigma_2(\omega)$ is the red curve.

3.3.3 Drude-Smith Model

Drude model mentioned before is a good model to describe classic ordered systems such as semiconductors. Nevertheless, as for some disordered systems such as quasicrystal, Drude model is not applicable because these systems' real part of the conductivity $\sigma_1(\omega)$ suppresses at low frequency as well as rises to a peak at a non-zero frequency, and imaginary part of the conductivity $\sigma_2(\omega)$ has capacitive response unlike the inductive response in Drude model [107]. A new model named Drude-Smith model based on carrier backscattering proposed by Smith can be greatly helpful for these situations the most of time. Different from the Drude model assuming the elastic isotropic carrier scattering, Drude-Smith model includes of the carrier's previous momentum into the scattering event [137].

$$\frac{\mathbf{j}(\mathbf{t})}{\mathbf{j}(0)} = e^{-\frac{t}{\tau_s}} \left[1 + \sum_{n=1}^{\infty} \frac{c_n \left(\frac{t}{\tau_s}\right)^n}{n!} \right]$$
(3.78)

$$\tilde{\sigma}(\omega) = \frac{\omega_p^2 \epsilon_0 \tau_s}{1 - i\omega \tau_s} \left[1 + \sum_{n=1}^{\infty} \frac{c_n}{(1 - i\omega \tau_s)^n} \right]$$
(3.79)

The Poisson statistics is used to describe current response given by Eq.3.78 where c_n is the fraction of the carrier velocity retained after the nth collision. The complex optical conductivity is obtained by the Fourier transform of the current response based on the impulse response formalism shown in Eq.3.79 [137].

$$\sigma_1(\omega) = \frac{\omega_p^2 \epsilon_0 \tau_s}{[1 + (\omega \tau_s)^2]^2} \left[1 + (\omega \tau_s)^2 + c(1 - \omega^2 \tau_s^2) \right]$$
(3.80)

$$\sigma_2(\omega) = \frac{\omega_p^2 \epsilon_0 \tau_s^2 \omega}{[1 + (\omega \tau_s)^2]^2} \left[1 + (\omega \tau_s)^2 + 2c\right]$$
(3.81)



Figure. 3.9 Diagram of conductivity of Drude-Smith model example showing the real (blue curve) and imaginary (red curve) parts of the conductivity for $\omega_0 = 0$ THz, $\omega_p = 4 \times 10^{14}$, $\tau_s = 10$ fs, and backscattering parameter c_0 (*c*) ranging from 0 to -1.

Here only consider the first order c_n with n = 1, indicating that there's only one scattering event deviating from isotropic Drude scattering with $c_n = 0$. This assumption can be explained that first collision is ballistic and subsequent collisions are diffusive proposed by Mayou *et la.* [138]. It should be noted that this interpretation does not need to be invoked for the Drude-Smith model to be valid. Inspection of Eq. 3.78 reveals that

the Drude response can be modified by any analytic function $g(t/\tau_s)$. The Drude-Smith model simply Taylor expands this unknown function about t = 0 where the c-values are the Taylor coefficients of this function. This explains the versatility of the Drude-Smith model, it can essentially fit any continuously differentiable and well-behaved modification to the Drude exponential decay. The real and imaginary part of conductivity are given in Eq. 3.80 and Eq. 3.81 respectively where c_n is relabeled as backscattering parameter $c_0(c)$ and the values of c ranging from 0 to -1. This generalized Drude formulas have interesting and versatile properties, particularly when c_0 is negative. When c_0 equals 0, the conductivity becomes common Drude conductivity with complete momentum randomization. The dc conductivity is given by $\frac{N^*e^2\tau_s(1+c_0)}{m^*}$ and carrier mobility is given by $\frac{e\tau_s(1+c_0)}{m^*}$ where N^* is adjusted carrier density [137].

The real part of the conductivity $\sigma_1(\omega)$ is the blue curve, and the imaginary part of the conductivity $\sigma_2(\omega)$ is the red curve as plotted in Fig. 3.9 (a-d) for the condition of $\omega_0 = 0$ THz, $\omega_p = 4 \times 10^{14}$, $\tau_s = 10$ fs, and backscattering parameter c_0 in the range from 0 to - 1. In the case of $c_0 = 0$, the curves of conductivity are in agreement with the Drude model. As c_0 decreases ($c_0 < 0$), a dip of conductivity at low frequency and a peak of conductivity at a non-zero frequency appear. When *c* is negative, the backscattering is predominant, and net current j(t) of the electron system reverses its direction before the relaxation to the equilibrium value of 0. For the effect on conductivity $\tilde{\sigma}(\omega)$, the dc conductivity is depressed, and the oscillator strength is shifted to higher frequencies. In the case of $c_0 < -\frac{2}{3}$, conductivity $\tilde{\sigma}(\omega)$ renders a minimum at zero frequency following

a maximum at frequency of $\frac{3c_0+1}{\tau_s^{-2}(c_0-1)}$. In the case of $c_0 = -1$, the dc conductivity is completely suppressed and the maximum happens at frequency of $\frac{1}{\tau_s}$ [137]. In the case of $c_0 < -\frac{1}{2}$, the imaginary part of the conductivity $\sigma_2(\omega)$ is negative at low frequencies in agreement with the capacitive response. As the frequency increases, $\sigma_1(\omega) \sim \frac{1}{(\omega\tau_s)^2}$ and $\sigma_2(\omega) \sim \frac{1}{\omega\tau_s}$ showing Drude behaviour [107].

$$\frac{\mathbf{j}(\mathbf{t})}{\mathbf{j}(0)} = e^{-\frac{t}{\tau_c}} \tag{3.82}$$

$$\tilde{\sigma}(\omega) = \frac{\frac{n^* e^2 \tau_c}{m^*}}{1 - i\omega\tau_c}$$
(3.83)

$$\frac{1}{\tau_c} = \frac{1}{\tau_s} (1 - c_0) \tag{3.84}$$

For simple kinetic models, the assumption is that the duration of a collision is negligible compared with the interval between collisions. Make a further assumption that collisions are independent of each other $c_n = c_0^n$, then obtain Eq. 3.82 and Eq. 3.83 where $1/\tau_c$ is the transport scattering rate given by Eq. 3.84 [137].

3.4 System for Terahertz spectroscopy

3.4.1 Ultrafast Titanium Doped Sapphire Amplifier



Figure. 3.10 Diagram of the Titanium Doped Sapphire Amplifier used in this research. The light source driving the THz spectrometer is significant. An ultrafast Titanium doped sapphire amplifier (Ti: sapphire Amplifier) can generate femtosecond duration pulses which are used in transient multi-THz spectroscopy to study ultrafast dynamics and optical properties of materials. The setup used in this research is shown in Fig. 3.10. First a nJ energy, ~30 fs pulse, centered at ~810 nm with ~400 mW and with a full width at half maximum (FWHM) of ~77 nm, is generated from the mode-locked Ti: sapphire oscillator through Kerr lens induced by Ti: sapphire crystal. Then, the seed fs pulse is directed to a stretcher stage, where the duration of the pulses is enlarged by around three orders of magnitude and the peak power of pulse is decreased below the optical damage threshold of Ti:sapphire gain medium. After that, the pulse goes into regenerative Ti: sapphire amplifier in which Ti: sapphire crystal along with focused 1 kHz frequencydoubled Q-switched Nd: YLF laser to amplify the energy of pulse incrementally as it passes through the crystal for multiple times. Then, the pulse of around ~6 mJ/pulse is

sent to a compressor stage and compressed to pulse of \sim 5 mJ/pulse with FWHM of \sim 40 fs and pulse-center of \sim 800 nm. The ultrashort pulse is obtained and sent to the THz generation via two-color air plasma emission [139].





Figure. 3.11 Diagram of the ultra-broadband TRTS setup used for experiments of this research.

After introducing the light source, the setup used for experiments is introduced here and shown in Fig. 3.11. An ultra-broadband TRTS setup of reflection configuration covering ~1-20 THz range which is mainly composed of delay line, parabolic mirrors (PM) of different sizes, Beta Barium Borate (BBO), high resistivity silicon (Si) wafer, chopper system with controller as well as wheels, beam splitter, ABCD system, 400 nm filter, avalanche photodiode (APD), lock-in amplifiers is used. After the ultrafast pulse is obtained, it is sent to a beam splitter and split into a weak and a strong beam. The strong beam with higher power is sent to the THz spectrometer as the pump pulse, then the

weak beam is sent to another beam splitter and split into two beams (weaker one and stronger one). The weak one is used as sampling pulse later. The stronger one is sent to a delay line firstly, then to a BBO for ~400 nm second harmonic generation by a non-linear process. After the BBO, the ~800 nm fundamental and ~400 nm second harmonic beams of orthogonal polarizations are obtained, then they are focused by a PM to create plasma. Then optical pulses are sent to Si wafer which allows the THz pulse pass through and blocks the ~800 nm fundamental as well as ~400 nm second harmonic beams. After that, the THz beam is focused on the sample by PM, then the response of sample is collimated by PMs and detected by ABCD along with the sampling pulse. The last process is using a 400 nm filter to select the THz-induced second harmonic which can be detected by a APD connected to lock-in amplifiers [139]. No dispersion compensation was utilized to better temporally overlap the two colors in the laser plasma, which limits the peak THz electric field < 20kV/cm such that we remain in the limit of a linear response for typical semiconductors. Two different types of photo-excitation pulses can be provided by the setup. As for the pump pulse, besides 800 nm pump pulse (\sim 1.55 eV), 400 nm (\sim 3.1 eV) pump pulse can be generated by introducing the 800 nm pump pulses into a thin BBO crystal [139].

Chapter 4

Results and Discussion

Electron scattering processes in photo-excited polar semiconductors involve a dynamic screening of the Coulomb interactions, quantified by the dielectric function $\tilde{\varepsilon}$ (Eq. 4.1). The bare Coulomb potential $V_q = \frac{ke^2}{q^2}$ becomes the screened Coulomb interaction $W_q(\omega, \tau_d) = V_q/\tilde{\varepsilon}(\omega, \tau_d)$ which now exhibits dispersion and evolves dynamically following the injection of charge under delay time au_d . In an unexcited polar semiconductor under an externally applied electromagnetic field, the lattice response that is dictated by the steady state dielectric function $\tilde{\varepsilon}(\omega)$ screens the applied field and leads to a strong reflectivity in the far-infrared called the reststrahlen band lying between the LO and TO phonons. For the LHPs there are many phonon modes, N_{atom} atoms in the primitive unit cell (N_{atom}=5 for CsPbBr₃ and N_{atom}=12 for MAPbBr₃) will lead to 3N_{atom} phonon modes (15 for CsPbBr₃ and 36 for MAPbBr₃). Despite this, the optical properties in the THz range are found to be dominated by only a few highly polar TO modes. When carriers are injected via an optical inter-band transition, however, these phonons become dressed by their interactions with plasmon excitations, forming coupled modes which can play an important role in redefining electron-phonon scattering processes. In this chapter, we discuss the role of dynamic screening effects in the LHPs following ultrafast, fs optical injection of charge carriers.

4.1 Lattice Polarization Response



Figure. 4.1 Time domain data of (a) MAPbBr₃ and (b) CsPbBr₃ single crystals respectively at the fluence of 362 uJ/cm² containing reference THz electric field $\tilde{E}_{ref}(t)$ without pump (black curve), and differential THz electric field from normal incidence reflection $\Delta \tilde{E}(t, \tau = 1.25ps) = \tilde{E}_{pump}(t, \tau) - \tilde{E}_{ref}(t)$ (red curve) where choose pump delay time τ at 1.25*ps*, (c, d) Corresponding Fourier amplitudes of the normal incidence reflection without photoexcitation $|\tilde{E}_{ref}(\omega)|$ (black curve), pump induced change of THz electric field $|\Delta \tilde{E}(\omega, \tau = 1.25ps)|$ (red curve), and normal incidence reflectance without photoexcitation $|\tilde{r}_0(\omega)|$ (blue dashed curve) respectively obtained from dielectric parameters of MAPbBr₃ and CsPbBr₃ single crystals given by TABLE. 4.1.

Material	$\frac{\omega_{\rm TO}}{2\pi}$ [THz]	$\frac{\omega_{LO}}{2\pi}$ [THz]	\mathcal{E}_{∞}	Es	γ	m^{*}/m_{0}	α_{e-ph}
MAPbBr ₃	1.85	5.32	9	74.4	0.5	0.15	0.75
CsPbBr ₃	1.79	4.67	4.3	29.3	0.1	0.2	2.3

TABLE. 4.1. Summary of optical and static dielectric constants (ε_{∞} and ε_{s} respectively), angular frequencies [THz] of a characteristic LO phonon mode and TO phonon mode ($\frac{\omega_{LO}}{2\pi}$ and $\frac{\omega_{TO}}{2\pi}$ respectively), scattering rate γ , effective mass of charge carrier m^* , and electron-phonon coupling constant α_{e-ph} used in the data analysis process of MAPbBr₃ and CsPbBr₃.

$$\tilde{\varepsilon}(\omega) = \varepsilon_{\infty} + \frac{(\varepsilon_s - \varepsilon_{\infty})\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega}$$
(4.1)

The background dielectric response for both CsPbBr₃ and MAPbBr₃ in the 1-12 THz region in this work is dominated by a single broadened phonon line at room temperature. The Lydanne-Sachs-Teller relationship defines the relationship between the LO (with frequency of ω_{L0}) and TO (with frequency of ω_{T0}) phonon modes in terms of the static ε_s and high frequency ε_{∞} dielectric constants $\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\varepsilon_s}{\varepsilon_{\infty}}$ [140]. In MAPbBr₃, the optical dielectric constants $\varepsilon_{\infty} = 4.7$, static dielectric constants $\varepsilon_s = 32.3$, and $\frac{\omega_{TO}}{2\pi} = 5.01$ THz as reported by Sendner et al. [80]. We note however that significantly different values of 4.4, 21.36, 5.81 THz (approximately 193.8 cm⁻¹) respectively are reported in Kiyoshi et al. [11, 80]. In CsPbBr₃, the optical dielectric constants ε_{∞} = 4.3, static dielectric constants ε_s = 29.37, and $\frac{\omega_{TO}}{2\pi}$ = 4.07 THz (approximately 135.8 cm⁻¹) in Kiyoshi *et al.* [11]. However, these are all parameters from thin films and nanocrystals, which may differ significantly from their intrinsic values as measured in a single crystal, which can be influenced by crystal orientation when birefringence is present (as it is in the orthorhombic phase). THz pulses are reflected from the MAPbBr₃ and CsPbBr₃ crystal (100) facets as shown in the black traces in Fig. 4.1(a, b), and following Fourier transform we obtain the amplitude spectra in Fig. 4.1(c, d). The sharp reststrahlen features can be seen readily from the amplitude spectra. The reststrahlen band between the TO phonon at $\sim (2\pi)1.85$ THz and a LO phonon at ~ $(2\pi)5.32$ THz is shown, and notably there is a dip centered $\omega \sim (2\pi)5.7$ THz where the lattice is least effective at screening the incident THz pulse field. The parameters found to best fit the measured static THz reflectivity spectra and used our subsequent time-resolved conductivity analysis are shown in TABLE. 4.1 which are relatively in good agreement with the reference THz electric field $E_{ref}(t)$ without pump (black curve) in Fig. 4.1(c, d).



Figure. 4.2 The complex refractive index and static reflectivity of (a) MAPbBr₃ and (b) CsPbBr₃. Complex refractive index n and κ and static reflectivity r₀ are plotted as black, blue and red curves respectively.

Corresponding $\frac{\omega_{LO}}{2\pi}$ modes are calculated using the Lydanne–Sachs–Teller relationship. The complex index of refraction, relevant for extraction of the optical conductivity, is shown in Fig. 4.2. One can divide the spectral regions into two based on these plots. The highly dispersive regime dominated by optical phonons < 7 THz, and the weakly dispersive regime > 7 THz.

As THz is sensitive to the sum of electron and hole conductivities, and these scale inversely to the effective mass, it is appropriate to use an ambipolar effective mass $1/m^* = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ where m_e^* and m_h^* are the electron and hole effective masses, respectively. There have been several reports of the electron-hole(e-h) effective mass has a range of ~0.117-0.19 m_0 in MAPbBr₃ and has a range of ~0.143-0.24 m_0 in CsPbBr₃ here m_0 is bare electron mass [11, 79, 80]. An ambipolar e-h effective mass ~0.15 m_0 in MAPbBr₃ and ~0.2 m_0 in CsPbBr₃ is used. The dimensionless Fröhlich polaron coupling constant α_{e-ph} is also calculated as $\alpha_{e-ph} = \frac{e^2}{\hbar} \frac{1}{4\pi\epsilon_0} \sqrt{\frac{m^*}{2\hbar\omega_{LO}}} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_s}\right)$ where \hbar is the reduced Planck's constant, *e* is the charge of carrier, ϵ_0 is the dielectric constant of vacuum, ω_{L0} is the angular frequency of a characteristic LO phonon mode, ε_{∞} and ε_s are optical and static dielectric constants respectively, and m^* is e-h averaged effective band mass then the electron-phonon coupling constant α_{e-ph} (e-h averaged) is calculated to be 0.75 in MAPbBr₃ and 2.3 in CsPbBr₃. Compared with α_{e-ph} of 2.76 (hole) and 2.64 (electron) in CsPbBr₃ α_{e-ph} of 1.87 (hole) and 1.56 (electron) in MAPbBr₃ according to Miyata *et al.*'s research [11] as well as 1.69 in MAPbBr₃ according to Sendner *et al.*'s research [80]. Our calculated coupling constants are consistent with these values, with the coupling constant for MAPbBr₃ being notably smaller.

4.2 Optical Excitation

To understand the transient THz response following photoexcitation, it is important to understand the initial excitation in view of the electronic band structure. As the optical band gap for both CsPbBr₃ and MAPbB₃ are above the fundamental 1.55 eV photon energy of our Ti:sapphire laser system, we use the second harmonic at 400 nm (3.1 eV) to photoexcite. Important to the quantitative calculation of the photoconductivity, we must

know the pump penetration depth in the sample. Thinning a single crystal down to one hundred nanometers over a size that can be easily characterized by optical excitation (10-100 µm) requires a very difficult to achieve aspect ratio of 100-1000, which is why optical absorption measurements are typically done on deposited polycrystalline thin films on a substrate. Instead, we calculate the optical penetration depth via the dielectric function at room temperature for the relevant structural phases as mentioned in Chapter. 2.4.1. Using literature values of the complex dielectric constant $\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2$ and refractive index $\tilde{n} = n + i\kappa$, the penetration depth δ can be calculated via the formula of $\delta = \frac{\lambda}{4\pi\kappa}$ where $\kappa = \frac{\varepsilon_2}{2n}$, ε_2 is the imaginary part of dielectric constant, *n* is the real index of refractive, and λ is the wavelength of excitation light. Using the complex dielectric constant calculated in Kovalenko et al. at 400 nm (3.1 eV excitation energy) at room temperature, the real and imaginary parts of the dielectric constant in CsPbBr₃ of orthorhombic phase are ~5 and ~0.9 respectively, while those in MAPbBr₃ of cubic phase are ~5.9 and ~1.5 respectively [38]. According to the formulas of $\varepsilon_1 = n^2 - \kappa^2$ and $\varepsilon_2 =$ $2n\kappa$, the calculated n = 2.245 and $\kappa = 0.2$ for CsPbBr₃. For MAPbBr₃, n = 2.448 and $\kappa =$ 0.306. Then calculated penetration depth δ of CsPbBr₃ and MAPbBr₃ are ~159 nm and ~104 nm respectively.

Initial excitation in both samples provides multiple 100's of meV in excess energy to both electrons and holes, much greater than the exciton binding energies. Therefore, excitations are assigned to initially free carrier densities. The maximum carrier density, assuming unity quantum efficiency, injected into the sample is then simplified to $N_{MAX} = \frac{(1-R)F}{\delta h f}$. hf is 3.1eV for this experiments with 400 nm photo-excitation pulses, F is the

incident pump fluence, and R is the pump intensity reflection coefficient [133]. The reflectance for CsPbBr₃ is approximately ~0.03 at 400 nm at room temperature [141] and is 0.1 for MAPbBr₃ [142]. The calculated maximum carrier densities used in these experiments are shown in TABLE. 4.2.

Incident Pump Fluence F	Photo-excited Carrier	Photo-excited Carrier		
	Density in MAPbBr ₃	Density in CsPbBr ₃		
23 uJ/cm ²	$\sim 4.01 \times 10^{24} / m^3$	$\sim 2.82 \times 10^{24} / m^3$		
56 uJ/cm ²	$\sim 9.74 \times 10^{24} / m^3$	$\sim 6.89 \times 10^{24} / m^3$		
110 uJ/cm ²	$\sim 1.92 \times 10^{25} / m^3$	$\sim 1.35 \times 10^{25} / m^3$		
185 uJ/cm ²	$\sim 3.23 \times 10^{25} / m^3$	$\sim 2.27 \times 10^{25}/m^3$		
362 uJ/cm ²	$\sim 6.32 \times 10^{25} / m^3$	$\sim 4.46 \times 10^{25} / m^3$		

TABLE. 4.2. Summary of incident pump fluence $F(uJ/cm^2)$ as well as corresponding photo-excited carrier density ($/m^3$) in MAPbBr₃ and CsPbBr₃ used in 1D TRTS experiments.

The photoexcitation is modelled as a thin conducting film on top of a semi-infinite insulating substrate (unexcited sample). Due to the thickness of the sample and the high dispersion in the vicinity of the phonons, time-frequency artifacts occur when experiments are performed in transmission. As such, all experiments are performed in reflection.

4.3 1D Transient Reflectivity of MAPbBr₃ and CsPbBr₃

The time domain data of reflected THz amplitude spectrum of MAPbBr₃ single crystal is shown in Fig. 4.1(a), where \tilde{E}_{ref} is the THz electric field without photo-excitation and the pump-induced change to the THz electric field is $\Delta \tilde{E} = \tilde{E}_{pump} - \tilde{E}_{ref}$ for a pump-probe delay of 1.25 ps. The corresponding Fourier amplitudes are illustrated in Fig. 4.1(c). The reference THz electric field spectrum reflected from MAPbBr₃ without pump $|\tilde{E}_{ref}(\omega)|$ is show as black curve. Fourier amplitudes of reference sample pulse, differential THz pulse $|\Delta \tilde{E}(\omega, \tau = 1.25ps)|$ and reference reflectivity $|\tilde{r}_0(\omega)|$ calculated using parameters described in Table 4.1 are demonstrated as black, red and blue dashed curves, respectively. For dynamics of the region where the frequency is above ~5.7 THz, the response is dominated by electronic degrees of freedom. Similarly, the reflected THz field spectrum and Fourier amplitudes of CsPbBr₃ single crystals are obtained as well shown in Fig. 4.1(b, d).



Figure. 4.3 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ dynamics evolution of (a) MAPbBr₃ and (b) CsPbBr₃ at longer time scale of around ~300 ps as well as transient reflectivity of (c) MAPbBr₃ and (d) CsPbBr₃ at shorter time scale of the first 2.25 ps under specified pump conditions of different incident pump fluence *F* of 23 uJ/cm², 56 uJ/cm², 110 uJ/cm², 185 uJ/cm², and 362 uJ/cm².

Fig. 4.3(a, c) shows the 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ dynamics of MAPbBr₃ where the THz field is sampled at the point of highest THz electric field when all Fourier components are in phase with one another and add constructively, and the pump-THz probe time delay is scanned. At early delay times as shown in Fig. 4.3(c), $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ exhibits a sub-ps time scale evolution governed by two processes with of different time constants: a faster rise within the first ~200 fs and a second component which takes ~1-2 ps to reach the quasiequilibrium state. This is consistent with photoconductivity/transient reflectance rise dynamics of lead perovskites in previous works. For example, in Bretschneider et al.'s research via TRTS, after photoexcitation the photoconductivity of FAPbI₃, MAPbI₃, and CsPbI₃ increases during the first \sim 1 ps to a steady-state photoconductivity [16]. Additionally, in Miyata et al.'s research, the transient reflectance of CsPbBr3 and MAPbBr3 rises within half ps then reaches a quasi-equilibrium state [11]. This phenomenon is more pronounced at higher photo-excited carrier density as the fluence increases from 23 to 362 uJ/cm^2 . The same measurement of CsPbBr₃ is done as well show in Fig. 4.2(b, d). The results show the same behaviour. Bretschneider et al. and Miyata et al. believed this is due to competition between electron-phonon coupling and carrier cooling as mentioned before in Chapter. 2.2.6. Interestingly, the decaying dynamics within time scale of ~300 ps also exhibits multiple channels regarding to initial relaxation of unscreened hot electrons called carrier cooling [81]. Those processed will be explored more in Chapter. 4.6. It's important to note, however, that such 1D reflection transients are not valid representations of the conductivity, particularly if there is significant imaginary conductivity. In this case, phase changes can be interpreted as amplitude changes, and the dynamics can be misinterpreted. In all previous works, authors have used 1D measurements simply because it allows rapid acquisition of data [16]. A more complete measurement requires a full 2D map, which will be provided in this thesis.

The fluence-dependence of the maximum value of 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_{0}}\right|$ and fitting curves of MAPbBr₃ and CsPbBr₃ are shown in Fig. 4.4. The fit is based on the material response function

$$\frac{\Delta \tilde{r}}{\tilde{r}_0} = \frac{(1 - n - Z_0 \Delta \sigma d)(1 + n)}{(1 + n + Z_0 \Delta \sigma d)(1 - n)} - 1$$
(4.2)

where *n* is the index of refractive, $Z_0 = 376.7$ is impedance of free space, *d* is penetration depth, and differential conductivity is proportional to the pump fluence *F*. Since the index of refractive complex index of refraction $\tilde{n} = n + i\kappa$ changes as frequency changes as show in Fig. 4.2, used the relatively stable $n\sim2.5$ for MAPbBr₃ and $n\sim1.9$ for CsPbBr₃ after ~7 THz in the fit since refractive index changes a lot before that, however this is only useful for qualitative interpretation. The max $(\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|)$ initially grows linearly with fluence and shows saturation behaviour reflecting the inherently nonlinear relation shown in Eq. 4.2, Besides, the fitting max $(\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|)$ of MAPbBr₃ with larger gradient is plotted as red curve while that of CsPbBr₃ with smaller gradient is plotted as blue curve, which also agree with experimental data.



Figure. 4.4 The maximum 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ of MAPbBr₃ and CsPbBr₃ along fluence of the pump pulse and fit curves.

In Chapter. 3.2.2.3 Thin Film Approximation, it mentioned the calculation of conductivity of the transmission mode. Similarly for reflection mode, use the formula of conductivity $\Delta \sigma = \frac{1}{Z_0 \delta} \frac{(R-1)(n^2-1)}{(R-1)(1-n)+2}$ where $R = \left|\frac{\tilde{E}pump}{\tilde{E}ref}\right|$, and $R - 1 = \left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ is transient reflectivity, therefore, the conductivity $\Delta \sigma$ can be calculated based on the transient reflectivity. The conversion to conductivity from measured differential 1D reflectance $\frac{\Delta \tilde{r}}{\tilde{r}_0}$ is strongly influenced by the background index of refraction of the underlying unexcited crystal. Fig. 4.5 shows how this inversion is influenced by the substrate index, which is strongly dispersive in the THz pulse bandwidth. This is most influenced at early times when the differential reflectance is greater, and eventually becomes independent of *n*. We thus perform time-

intensive 2D maps in the first 2 ps following excitation and rely on 1D scans for long time dynamics.



Figure 4.5. An example of a 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ compared to the extracted differential conductivities for various assumed indices of refraction. The influence of the choice of the index is most apparent for large differential conductivities in the first few picoseconds of the response.

4.4 2D Transient Reflectivity: Early Time Response

The transient 2D reflectivity maps for MAPbBr₃ are shown in Fig. 4.6(a-d), presenting the amplitude of the 2D photo-induced relative transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ dynamics at the early delay time from 0 to 2.25 ps and cuts at three delay time (0.25ps, 0.45ps, and 0.75ps) along ω =1-12 THz. For MAPbBr₃, the strong peaks at approximately 5.9 THz for all the delay times are due to lattice screening by mobile charge carriers at the reflectivity minimum of reststrahlen band high frequency edge where the lattice is least efficient at screening an external field, which agrees well with previous work [14]. The zero crossing of the modulation $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right| \approx 0$ is located at the LO phonon frequency $\frac{\omega_{LO}}{2\pi} = 5.3$ THz,

indicating a restructuring of the reststrahlen reflectivity edge due to the photoexcitation. The dynamics of this restructuring are more ready seen in the constant pump-probe time delay cuts. The modulation is asymmetric favouring the high frequencies, reflecting the fact that injected photocarriers contribute highest to screening the fields just above the reststrahlen band at 5.9 THz. While the dynamics of the screening appears monotonic, we will see later that coherent oscillations appear for frequencies at the reststrahlen edge, where the reflectivity response is most sensitive to external perturbation. Note, however, that the onset of the reflection modulation does not appear simultaneously for all frequencies as the fluence increases. This reflects two processes: 1) carrier cooling due to intial excess energy from the 400 nm ($\hbar \omega = 3.1$ eV) pump pulse, and 2) the dynamics of screening of Coulomb interactions and the formation of new dressed quasiparticles. We will discuss this more in Chapter. 4.5.

Fig. 4.7(a-d) shows the 2D transient reflectivity $\left|\frac{\Delta \vec{r}}{\vec{r}_0}\right|$ maps for the all-inorganic crystal CsPbBr₃. Qualitatively, the differential response is similar to that of MAPbBr₃, however the linewidth of the phonon is less leading to sharper spectral features. This is despite the main IR active phonon corresponding to motion of the orthorhombic Pb-Br cages present in both the hybrid and all-inorganic structure. It might be due to the "dynamic disorder" caused by the rotation of organic methylammonium cation in MAPbBr₃. The strong peaks at approximately ~5.3 THz for all the delay times are due to lattice screening by mobile charge carriers at the reflectivity minimum of reststrahlen band high frequency edge, which agrees well with a previous work [14]. At the frequency approximates ~5 THz, $\left|\frac{\Delta \vec{r}}{\vec{r}_0}\right| \approx 0$, which does not correspond to the LO phonon frequency $\frac{\omega_{LO}}{2\pi} = 4.67$ THz exactly

but this may be because it is within the resolution of the measurement of 0.3 THz. Again, the differential reflectivity spectrum shows an asymmetric bipolar response, although this asymmetry seems to evolve only at higher fluences. Similar to MAPbBr₃, the peaks in the 1D transient reflectivity at frequency of approximately ~5.3 THz corresponding to minimums of the static reflectance r_0 shown in Fig. 4.2(b) where the lattice is least polarizable.



Figure. 4.6 2D amplitude of normalized transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ colourmap for THz frequencies along delay time of MAPbBr₃ and corresponding 1D transient reflectivity cuts at several different delay time 0.25ps, 0.45ps, and 0.75ps with four different incident pump fluences *F* of (a) 23 uJ/cm², (b) 56 uJ/cm², (c) 110 uJ/cm², and (d) 362 uJ/cm².



Figure. 4.7 2D amplitude of normalized transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ colourmap for THz frequencies along delay time of CsPbBr₃ and corresponding 1D transient reflectivity cuts at several different delay time 0.25ps, 0.45ps, and 0.75ps with four different incident pump fluences *F* of (a) 23 uJ/cm², (b) 56 uJ/cm², (c) 110 uJ/cm², and (d) 362 uJ/cm².

After obtaining the amplitude of 2D transient reflectivity and exploring the 1D transient reflectivity along frequencies at a certain delay time, here 1D transient reflectivity corresponding different frequencies along the delay time can be obtained as well. The dynamics are well fit by Boltzmann function $y = \frac{A_1 - A_2}{1 + e^{\frac{x - x_0}{dx}}} + A_2$ where dx is the time constant. The fitting results for both MAPbBr3 and CsPbBr3 are shown in Fig. 4.8(a, c) respectively, where black solid lines are Boltzmann fitting curves. Almost all of the transient reflectivity of all frequencies fit well except the transient reflectivity at the frequency near LO phonon frequency $\omega_{L0}/2\pi$. Below ω_{L0} the lattice is overscreened and above ω_{LO} the lattice is underscreened by the injected photocarriers. Interestingly, there are coherent oscillations along the delay time near reflectivity dynamics near the crossing region ~5.3 THz in MAPbBr3 and ~5 THz in CsPbBr3. At this frequency corresponding to the reststrahlen inflection point, we are most sensitive to charge-induced modifications of the lattice response. We attribute this behaviour to be manifestation of coherent interactions between charge carriers and the ultra-soft polar lattice.

In Fig. 4.8(a, c), for $\omega > \omega_{L0}$, the transient reflectivity is positive as the lattice polarization is underscreened and actually enhanced by the photocarriers. For $\omega < \omega_{L0}$, the transient reflectivity is negative as the lattice is overscreened. This is because when photoexciting, the free carriers are injected in the materials which screens the dipoles in the material and causi the shift of edge of the reststrahlen band to left/right or the increase of the reflectivity of reststrahlen band accompanying with the decrease of left side of minimum reflectivity above 5.7 THz. A similar response is observed for CsPbBr₃. The coherent



response will be discussed later. Firstly we turn to the dynamics of the onset for the screened lattice response.

Figure. 4.8 1D transient reflectivity cuttings at several different frequencies of (a) MAPbBr₃ and (c) CsPbBr₃ from 2D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ colourmap at the incident pump fluence *F* of 362 uJ/cm² where black solid lines are Boltzmann fitting curves. Time constant τ_B of Boltzmann fit at different frequencies for (b) MAPbBr₃ and (d) CsPbBr₃ except the frequencies near coherent oscillations.

After the Boltzmann fit, time constants τ_B corresponding to different frequencies are obtained as plotted in Fig. 4.8(b, d). Ignoring the frequencies in the vicinity fo the coherent oscillation where the Boltzmann fit is poor, we observe that the rise time constants are relatively independent of frequency with $\tau_B \sim 60-80$ fs for MAPbBr₃, and $\tau_B \sim 80-130$ fs for CsPbBr₃. Those time constants can be roughly regarded as the rise time of the transient

reflectivity. However, the rise time varies at different frequencies and there are oscillations which cannot fit to Boltzmann function well. A deeper analysis of the probe frequency dependence of time constants and oscillations should be conducted.



Figure. 4.9 Electronic band structure of (a) MAPbBr₃ and (b) CsPbBr₃ at room temperature. Adjusted based on Ref. [38].

As for the frequency dependence of time constants, for MAPbBr₃, if ignoring the frequencies around the LO frequency, the Boltzmann constants are almost a constant with average of ~0.08 ps. Similarly, the Boltzmann constants of CsPbBr₃ are almost a constant with average of ~0.2 ps. The Boltzmann constants of CsPbBr₃ are more than twice of those of MAPbBr₃. This is because according to the electronic band structures of MAPbBr₃ and CsPbBr₃ at room temperature as show in Fig. 4.9(a, b) where 400 nm long arrow corresponds to the applied 400 nm photo-excitation pulses with ~ 3.1 eV photon energy in the UBB-TRTS experiments as mentioned in Chapter. 2.4.2., when photoexciting the MAPbBr₃, all the electrons and holes stay in the same bands, and so relaxation only

involves intravalley scattering. Therefore, the rise time of transient reflectivity will be fast. However, when photoexciting the CsPbBr₃, intervalley scattering can occur because the possibility of coupling to side valley (X valley). The intervalley scattering process includes the relaxation process in the Γ valley after the photoexcitation down to the X valley then scattering back process to the Γ valley again, which takes time to be realized. The intervalley scattering process in CsPbBr₃ is slower than the intervalley scattering process in MAPbBr₃. The formation of a polaron can only occur after excess electronic energy has dissipated to less than the binding energy of the polaron, estimated to be ~ 42 meV and ~ 39 meV for MAPbBr₃ and CsPbBr₃, respectively [143-146].



Figure. 4.10 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ at frequencies of (a) ~5.625 THz with the incident pump fluence *F* of 23 uJ/cm², (b) ~5.625 THz with the incident pump fluence *F* of 56 uJ/cm², (c) ~5.3125 with the incident pump fluence *F* of 362 uJ/cm² in MAPbBr₃, respectively. 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ at frequencies of ~5 THz with the incident pump fluence *F* of (e) 23 uJ/cm², (f) 56 uJ/cm², (g) 110 uJ/cm², and (h) 362 uJ/cm² in CsPbBr₃, respectively.

To better explore the frequency dependence of oscillations, Fig. 4.10(a-h) plot 1D transient reflectivity of MAPbBr3 and CsPbBr3 near the frequency with coherent oscillations at four incident pump fluence F. For MAPbBr₃, there are oscillations then trending to a stable value near zero at the frequency of \sim 5.625 THz with photo-excited fluences of 56 uJ/cm², while there are similar oscillations at the frequency of ~5.3125 THz with photo-excited fluences F of 110 μ /cm² and 362 μ /cm². And at the photo-excited fluences F of 23 uJ/cm², the oscillations cannot be observed clearly because there is lots of noise. Since the LO frequency $\left(\frac{\omega_{LO}}{2\pi}\right)$ of MAPbBr₃ at ~5.32 THz, indicate that those coherent oscillations happen around the LO frequency. For CsPbBr₃, there are small oscillations then gradually trending to a stable value near zero at the frequency of ~5 THz (near the $\frac{\omega_{LO}}{2\pi}$ ~4.67 THz) with photo-excited fluences F of 110 μ /cm² and 362 μ /cm², while there's almost no oscillation with photo-excited fluences F of 23 uJ/cm^2 and 56 uJ/cm^2 as shown in Fig. 4.10(e-f). As it is known the reststrahlen band is determined by the background parameters including LO phonon frequency. The near-instantaneous photoexcitation depletes bonding states of the Br p-orbital character, modifying the p^{Pb}-p^{Br} interaction according to crystal orbital overlap population calculations [147]. Such an interband transition between bonding and antibonding states can excite coherent phonons. The

relevant phonon modes in this case are fully symmetric A_g modes [148], however, the coherent oscillations don't have complete cycles and cannot be described by a simple harmonic mode. Instead, the oscillations appear negatively chirped whereby initially high frequency oscillations merge with a steady state. Such behaviour may be attributed to the strongly anharmonic, low energy phonons whereby vibrational energy is rapidly dispersed from high energy phonons to low energy phonons. This is consistent with the often described liquid-like lattice excitations of the lead halide perovskites [12, 76].



Shift of Reststrahlen Band

Figure. 4.11 Diagram of Reststrahlen band shifting to left and right.

Another possible mechanism for the coherent oscillations is the formation of the coupled plasmon-LO phonon mode. The effect of injecting free carrier contribution to the dielectric function is to shift the reststrahlen to higher frequencies. This is a consequence of the formation of a new coupled plasmon-LO phonon mode, with coupled modes given by the solution of the quartic equation: $\omega^4 - \omega^2(\omega_{L0}^2 + \omega_p^2 + \omega_q^2) + \omega_{T0}^2(\omega_p^2 + \omega_q^2) = 0$, where the dampening rate has been set to zero. At high densities, q=0 leads to solutions

of $\omega_+ \sim \omega_p$ and $\omega_- \sim \omega_{TO}$. For $\omega_p > \omega_{LO}$, the reflection edge of the reststrahlen band shifts to higher energies. This would lead to a positive differential reflectivity when monitoring the undressed $\omega = \omega_{LO}$, as shown in Fig. 4.11. One can see that this is the asymptotic condition for the highest fluences for both MAPbBr₃ and CsPbBr₃. However, the initial negative differential reflectivity at early times deviates from a simple, static plasmon screening of the LO phonon. Instead, the coherent oscillation indicates a dynamic screening process whereby the inertia of the charge carriers delays the instantaneous screened interaction. The formation of coupled plasmon-phonon modes was studied in InP, a system with well-formed harmonic modes. Here, however, the perovskites seem to show overdamped and even chirped response which is sensitive to the injected carrier density. While the quantum kinetic formation of coupled plasmon-phonon modes was observed and theoretically described in Ref. [112], the expectation for a system with highly anharmonic phonons is unclear. Also of note is the initially negative differential reflectance for the CsPbBr₃ for the lowest fluences. Such a response is anomalous and cannot be described by a simple Drude conductivity for the photo-excited free carriers. One can perhaps understand this behaviour when considering the electron interaction strength with coupled plasmon-phonon modes ω_{-} and ω_{+} , where for intermediate densities ω_{-} can dominate over ω_{+} , but at high fluences the plasmon-like ω_{+} mode dominates and the reststrahlen band shifts upward. Notably, the oscillations appear in both samples at the same fluence of $110 \,\mu\text{J/cm}^2$. This may indicate a crossover where the plasma frequency is greater than the LO phonon frequency.

4.5 Conductivity of MAPbBr₃ and CsPbBr₃

Further analysis by applying Fourier Transformation to 2D data gave access to pumpinduced change to reflectivity, then obtained pump-induced change to the optical conductivity $\Delta \tilde{\sigma}(\omega, \tau)$ by applying the background dielectric function using Eq. 4.1. Fig. 4.12 shows 2D conductivity $\Delta \sigma$ colourmap for THz frequencies along delay time of MAPbBr₃ with four different fluences. It can be observed that there is a large change of the conductivity near the LO frequency forming a "step" due to the sharp change in the background dielectric function. No bi-polar response is present because after applying formula of conductivity $\Delta \sigma = \frac{1}{Z_0 d} \frac{(R-1)(n^2-1)}{(R-1)(1-n)+2'}$ the real part of the conductivity obtained is positive. This must be true for the linear response to be dissipative.



Figure. 4.12 2D conductivity $\Delta\sigma$ colourmap for THz frequencies along delay time of MAPbBr₃ obtained by Fourier analysis corresponding to four different incident pump fluences *F* of a) 23 uJ/cm², (b) 56 uJ/cm², (c) 110 uJ/cm², and (d) 362 uJ/cm².



Figure. 4.13 2D conductivity $\Delta\sigma$ colourmap for THz frequencies along delay time of CsPbBr₃ obtained by Fourier analysis corresponding to four different incident pump fluences *F* of (a) 23 uJ/cm², (b) 56 uJ/cm², (c) 110 uJ/cm², and (d) 362 uJ/cm².

Similar for CsPbBr₃, 2D conductivity $\Delta\sigma$ colourmap for THz frequencies along delay time with four different fluences are obtained shown in Fig. 4.13. It can be observed that there is a large change of the conductivity near the LO frequency (form blue line) as well but
the change in CsPbBr₃ is more pronounced. These 2D conductivity obtained from 2D TRTS scans are much more compete because of considering the frequency-dependence of photoconductivity.



Figure. 4.14 1D conductivity curves cut from the 2D conductivity $\Delta\sigma$ colourmap of (a) MAPbBr₃ at frequency of ~11 THz and (b) CsPbBr₃ at frequency of ~9 THz with four fluences.

As the strong dispersion of the phonon can make inversion of the Tinkham formula to extract the conductivity difficult, we focus on frequencies far away from the LO phonon. Fig. 4.14(a, b) shows the 1D cut conductivity curves from the 2D conductivity $\Delta\sigma$ colourmap of MAPbBr₃ at frequency of ~11 THz and CsPbBr₃ at frequency of ~9 THz with four fluences respectively. Both 1D cut conductivity curves with time range from 0 to 2.25 ps have the similar changing trend (rise then reach equilibrium) to the 1D transient reflectivity from 1D data and the 1D transient reflectivity cut from 2D data at frequency larger than ω_{L0} . And as the fluence increases, the phenomenon becomes more

pronounced. The rising speed of our conductivity measured by 2D TRTS taking the frequency-dependence in account is faster than other research's 1D measurements ignoring the frequency change which is not accurate enough such as Ref.[16, 149]. More analysis will be mentioned later in Chapter. 4.6.



Figure. 4.15 Drude-Smith fit of $\Delta \tilde{\sigma}(\omega, \tau_d = 2 \text{ ps}) = \sigma_1(\omega, \tau_d = 2 \text{ ps}) + i\sigma_2(\omega, \tau_d = 2 \text{ ps})$ of MAPbBr₃ for various incident pump fluences *F* of a) 23 uJ/cm², (b) 56 uJ/cm², (c) 110 uJ/cm², and (d) 362 uJ/cm² as well as of CsPbBr₃ for various incident pump fluences *F* of (e) 23 uJ/cm², (f) 56 uJ/cm², (g) 110 uJ/cm², and (h) 362 uJ/cm² where $\Delta \sigma_1(\omega, 2 \text{ ps})$ is shown as black dot, $\Delta \sigma_2(\omega, 2 \text{ ps})$ is shown as red dot, and corresponding fitting curves are shown as black and red solid lines respectively.

Turning now to the shape of the optical conductivity at a given pump-probe time delay τ_{d} , Fig. 4.15 shows the complex THz differential photoconductivity $\Delta \tilde{\sigma}(\omega, \tau_{d} = 2 \text{ ps}) =$ $\sigma_1(\omega, \tau_d = 2 \text{ ps}) + i\sigma_2(\omega, \tau_d = 2 \text{ ps})$ of MAPbBr₃ and CsPbBr₃ for various incident pump fluences. The spectra are clearly of non-Drude character, with an increasing σ_1 with ω and a negative, capacitive imaginary σ_2 . A phenomenological Drude-Smith model, originally formulated by the late Neville Smith, is used to fit the complex conductivity $\tilde{\sigma}(\omega) = \sigma_1(\omega) + i\sigma_2(\omega) = \frac{\omega_p^2 \epsilon_0 \tau}{1 - i\omega \tau} \left[1 + \frac{c}{1 - i\omega \tau} \right]$. This model has been used previously to describe the influence of the presence of disorder in the conduction process. This model can be shown to essentially describe any small deviation from an exponential current relaxation (Drude) whereby the deviation causes the initial relaxation to be faster than exponential. Such a system can arise through several means, but the most common being the presence of preferential back-scattering (e.g. umklapp scattering). In crystalline materials, such non-isotropic scattering can occur through several means however it is known that the Pb²⁺ ns² lone pairs cause B-site distortions in the perovskite lattice which drive local non-cubic structural fluctuations despite the global structure being cubic on average. Such local structural distortions can cause preferential electronic backscattering, for instance, which is the Drude-Smith model is characterized by the c-parameter approaching -1 (perfect backscattering). The corresponding formulas used in the fitting process are $\sigma_1(\omega) = \frac{\omega_p^2 \epsilon_0 \tau}{[1+\omega^2 \tau^2]^2} [1+\omega^2 \tau^2 + c(1-\omega^2 \tau^2)]$, and $\sigma_2(\omega) = \frac{\omega_p^2 \epsilon_0 \tau^2 \omega}{[1+\omega^2 \tau^2 \tau^2]^2} [1+\omega^2 \tau^2 \tau^2]^2$ $\omega^2 \tau^2 + 2c$] respectively with Drude-Smith scattering time τ , Drude-Smith backscattering parameter *c*, and plasma frequency ω_p . The fitting curves are shown as black and red solid lines in Fig. 4.15(a-d), and well describes the conductivity spectra for all samples, fluences and times. Similar for CsPbBr₃, use the same Drude-Smith model to fit the real part and imaginary part of complex conductivity with unfixed τ , unfixed backscattering parameter *c*, and unfixed ω_p , and the fitting curves are shown as black and red solid lines in Fig. 4.15(e-h). In Burgos-Caminal *et al.*'s research, they also adopted Drude-Smith model on the analysis of conductivity in another kind of LHPs, MAPbI₃ thin films, following 510nm and 740nm photo-excitation pulses with pump fluence of 62 uJ/cm² [66].



Figure. 4.16 Incident pump fluence *F* dependence of the Drude-Smith scattering time of (a) MAPbBr₃ and (b) CsPbBr₃, Drude-Smith backscattering parameter *c* of (c) MAPbBr₃ and (d) CsPbBr₃, calculated carrier mobility $\mu = \frac{(1+c)e\tau}{m^*}$ of (e) MAPbBr₃ and (f) CsPbBr₃,

Drude-Smith plasma frequency ω_p of (g) MAPbBr₃ and (h) CsPbBr₃, Drude-Smith carrier density $N = \frac{\omega_p^2 \epsilon_0 m^*}{e^2}$ of (i) MAPbBr₃ and (j) CsPbBr₃ at delay time of 2 ps.

After collecting the fitting parameters scattering time τ and backscattering parameter c_0 (c), plot their diagrams along fluences shown in Fig. 4.16(a-d). Firstly the extracted Drude-Smith scattering time τ for MAPbBr₃ in Fig. 4.16(a) shows fluence-dependent transition. τ is relatively constant, varying between ~4.0 ± 1.3 fs to ~6.0 ± 2.5 fs. For CsPbBr₃, the scattering time τ in Fig. 4.16(b) is also relatively fluence-independent as well, varying between $\sim 5.0 \pm 1.4$ fs to $\sim 6.8 \pm 3.5$ fs over the fluence range. Our results are almost consistent with Burgos-Caminal et al.'s work on MAPbI3 thin films, their data fit via Drude-Smith model yields scattering time constant of 2.8 fs and 5 fs for 510nm and 740nm photo-excitation pulses applied, respectively [66]. The scattering time of CsPbBr₃ and MAPbBr₃ single crystals is little bigger than that of MAPbI₃ thin films with 510 nm photo-excitation pulses (near 400 nm of us), which is expected since singe crystals have less disorder while thin films have relatively more grains leading to in plane disorder. Also it may exist grain scattering in thin films. When it comes to the Drude-Smith backscattering parameter c, for MAPbBr₃ the backscattering parameter in Fig. 4.16(c) increases from $\sim -0.7 \pm 0.02$ to $\sim -0.36 \pm 0.12$ along fluence of 23-110 uJ/cm² (photoexcited carrier density of $\sim 4.01 \times 10^{24} - 1.92 \times 10^{25} / m^3$) then reaches relatively stable. For CsPbBr₃, the backscattering parameter c in Fig. 4.16(d) almost keeps increasing from $\sim -0.69 \pm 0.02$ to $\sim -0.37 \pm 0.16$ along the fluence of 23-362 uJ/cm² (photo-excited carrier density of $\sim 2.82 \times 10^{24} - 4.46 \times 10^{25} / m^3$). This implies that the hotter the electron population is the less efficient the backscattering, which is expected. Our results

of $c \sim 0.65 \pm 0.01$ for MAPbBr₃ and $c \sim 0.65 \pm 0.02$ for CsPbBr₃ at fluence of 56 uJ/cm² under 400 nm photo-excitation pulses are roughly comparable to Burgos-Caminal et al.'s Drude-Smith fitting results of backscattering parameters in MAPbI₃ of -0.89 and -0.88 for 510nm and 740nm photo-excitation pulses with fluence of 62 uJ/cm² [66]. As for the carrier mobility μ , it is calculated based on the formula $\mu = \frac{(1+c)e\tau}{m^*}$, and plotted shown in Fig. 4.16(e-f). As the fluence increases, the mobility increases in both MAPbBr₃ and CsPbBr₃ with a range of approximately ~14-45 cm² V⁻¹s⁻¹ for MAPbBr₃ and 13-37 cm² V⁻ ¹s⁻¹ for CsPbBr₃. These mobilities are almost in agreement with some other experimental results of mobility ~5-212 cm² V⁻¹s⁻¹ for MAPbBr₃, and ~52-150 cm² V⁻¹s⁻¹ for CsPbBr₃ at room temperature mentioned in Chapter. 2.2.4.6 as well as Burgos-Caminal et al.'s Drude-Smith fitting mobiliy of ~5.3 cm² V⁻¹s⁻¹ in MAPbI₃ [66]. This is primarily due to the decrease in carrier backscattering as the electronic temperature is increased with fluence. As regards the Drude-Smith plasma frequency ω_p , it is shown in Fig. 4.16(g-h) with the x-axis of different fluences. For MAPbBr₃, as the fluence increases and more carriers are injected into the system, the plasma frequency ω_p reaches saturation gradually at around 110 uJ/cm² (photo-excited carrier density of $\sim 1.92 \times 10^{25}$ /m³). Such a saturation could be explained either by a saturation in photon absorption due to depletion of the density of states. Then with regard to Drude-Smith carrier density, it is calculated by the formula of $N = \frac{\omega_p^2 \epsilon_0 m^*}{e^2}$, and plotted in Fig. 4.16(i-j). For MAPbBr₃, the obtained carrier density grows before the fluence of ~110 μ /cm² (photo-excited carrier density of ~1.92 × 10^{25} /m³) then gradually saturates. For CsPbBr₃, the obtained carrier density keeps



growing along the fluence of 23-362 uJ/cm^2 (photo-excited carrier density of $\sim 2.82 \times 10^{24} - 4.46 \times 10^{25}/m^3$).

Figure. 4.17 Delay time dependence of the Drude-Smith scattering time τ of (a) MAPbBr₃ and (b) CsPbBr₃, Drude-Smith backscattering parameter c of (c) MAPbBr₃ and (d) CsPbBr₃, calculated carrier mobility $\mu = \frac{(1+c)e\tau}{m^*}$ of (e) MAPbBr₃ and (f) CsPbBr₃, Drude-Smith plasma frequency ω_p of (g) MAPbBr₃ and (h) CsPbBr₃, Drude-Smith carrier density $N = \frac{\omega_p^2 \epsilon_0 m^*}{e^2}$ of (i) MAPbBr₃ and (j) CsPbBr₃ with incident pump fluence *F* of 362 uJ/cm².

The time evolution of the Drude-Smith fitting parameters is plotted in Fig. 4.17, applying a similar process for the complex conductivity at the fluence of 362 uJ/cm^2 along different delay times. For both MAPbBr₃ and CsPbBr₃, the Drude-Smith scattering time τ stays relatively constant within fitting error with the average value of approximately ~7.5 fs

for MAPbBr₃ and ~8 fs for CsPbBr₃ along pump delay time when considering the error bar at the same time, indicating that the scattering process of the materials are basically independent of the time as shown in Fig. 4.17(a-b). As for the backscattering parameter c, its absolute value decreases in both material with a range of for from $\sim -0.52 \pm 0.04$ to $\sim-0.36\pm0.12$ for MAPbBr3 and from $\sim-0.49\pm0.07$ to $\sim-0.37\pm0.16$ or CsPbBr3, indicating it becomes more delocalized as time goes as shown in Fig. 4.17(c-d). Besides, carrier mobility μ stays roughly the same with the average value of approximately ~48 cm²V⁻¹s⁻¹ for MAPbBr₃ and ~36.5 cm²V⁻¹s⁻¹ for CsPbBr₃ as delay time increases shown in Fig. 4.17(e-f). For both MAPbBr₃ and CsPbBr₃, the plasma frequency ω_p rises within about half ps then reaches equilibrium since recombination is negligible in such as short delay time window (~2 ps) as shown in Fig. 4.17(g-h). Since the carrier density N is proportional to the square of plasma frequency ω_p , it almost obeys the change rules of plasma frequency, rising within approximately ~0.2-0.5 ps then arriving a relatively equilibrium, which indicate there's no more recombination within the time range of ~ 2 ps as shown in Fig. 4.17(i-j).

4.6 Quantifying Polaron Formation and Charge Carrier Cooling

$$\frac{dN_{hot}}{dt} = -\frac{1}{\tau_{cool}} N_{hot}$$
(4.3)

$$\frac{dN_{cold}(t)}{dt} = \frac{1}{\tau_{cool}} N_{hot}(t) - \frac{1}{\tau_{pol}} N_{cold}(t)$$
(4.4)

$$\frac{dN_{pol}(t)}{dt} = \frac{1}{\tau_{pol}} N_{cold}(t)$$
(4.5)

$$N_{hot}(0) = \mathbf{N} \tag{4.6}$$

$$N_{cold}(0) = N_{pol}(0) = 0 (4.7)$$

To quantify the process of rise dynamics before reaching the equilibrium (then drop down), here provide two models. The first model is proposed by Bretschneider *et al.* for exploring the polaron formation and charge carrier cooling in lead-iodide perovskites [16]. In Bretschneider *et al.*' s work discussed previously, the hot carrier cooling time is from ~40 fs (700 nm pump pulse) to ~275 fs (400 nm pump pulse) for FAPbI₃, ~30 fs (700 nm pump pulse) and ~320 fs (400 nm pump pulse) for MAPbI₃, and ~470 fs for CsPbI₃ with 400 nm pump pulse at ~295 K by using this model.

The first model considers two distinct and sequential contributions to the rise of transient reflectivity (photoconductivity) which are carrier cooling and polaron formation occurring as follows. Then obtain three-level differential equations where three relevant populations are N_{hot} (the number of hot carriers), N_{cold} (the number of cold carriers), and N_{pol} (the number of polarons) as well as two time scales τ_{cool} (relaxation time between hot carriers and cold carriers) and τ_{pol} (polaron formation time) as given by Eq. 4.3-4.5. The initial conditions are that density of hot carriers equals to the number of injected carriers and the density of cold carriers and polarons is assumed to be zero, shown in Eq. 4.6-4.7. The difference between our analysis and Bretschneider *et al.*' s is they consider the dynamics of $\frac{\Delta r}{r_0}$ to be completely described by that of the charge carriers and only dealing

with normalized densities $N_{hot} + N_{cold} + N_{pol} = N = 1$. However, it is the conductivity that is related to the differential reflectivity through a nonlinear relation that is only linear in the small signal limit, and because they work with a normalized signal (albeit in transmission but the argument still applies) it is impossible to verify if they are in this linear regime. In our case, we are clearly outside of this linear regime, as mentioned previously. Still, for comparison to their work we make use of the relation $\frac{\Delta r}{r_0} \propto \Delta \sigma =$ μeN thus $\frac{\Delta r}{r_0} \propto \Delta \sigma = e(\mu_{hot}N_{hot} + \mu_{cold}N_{cold} + \mu_{pol}N_{pol})$. The carrier densities used in the fit are referred to TABLE. 4.1.



Figure. 4.18 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ dynamics evolution obtained from 1D TRTS and fitting curves of (a) MAPbBr₃ and (b) CsPbBr₃ at shorter-time scale of the first 2.25 ps under specified pump conditions of different photo-excited fluences *F* of 23 uJ/cm², 56 uJ/cm², 110 uJ/cm², 185 uJ/cm², and 362 uJ/cm² at~298K.

Fig. 4.18 shows the fitting results of the first model at shorter time scale of the first 2.25 ps at ~298K. The fitting hot carrier cooling time is from around ~130 to ~237 fs for MAPbBr₃ under pump conditions of different photo-excited fluences *F*. Since

Bretschneider et al. do not report their actual carrier density and do not do a fluence dependence, we take our low fluence value (130 fs) for comparison to their work (linear regime), which is faster than the reported cooling times in the iodides in all but the near resonant, band edge excitation conditions. The hot carrier cooling time is from around ~123 to ~172 fs for CsPbBr3 under pump conditions of different photo-excited fluences *F*, which almost agrees the hot electrons cooling time of ≤ 200 fs in J. S. Evans *et al.*'s research of CsPbBr₃ via TR-2PPE and TR spectroscopies [75]. The fitting polaron formation time is from around ~141 to ~243 fs for MAPbBr₃ and from around ~158 to ~290 fs for CsPbBr₃ at varied different photo-excited fluences *F*. These polaron formation time obtained are almost in consistence with those mentioned in Chapter. 2.2.6.2 Formation Time of Polarons in MHPs. Especially in Miyata *et al.*' s research, for CsPbBr₃ the polaron formation time is 0.6 ± 0.1 ps, and for MAPbBr₃ that is 0.28 ± 0.04 ps at room temperature [11]. Additionally in J. S. Evans et al.'s research, they found the polaron formation time of CsPbBr₃ is 0.7 ± 0.1 ps at ~300K which is a little longer than ours [75]. Although the fitting results seem comparable to previous related works, it can be visibly observed the strong deviation of the fitting model showing coherent oscillations. This kind of deviation is observed as well in Bretschneider *et al.*'s research and other research used this model such as Jin et al.'s research [16, 150]. The systematic coherent oscillations need to be better explained outside of this polaron formation and carrier cooling model.

$$\frac{dN_{hot}}{dt} = Gaussian(t) - \frac{1}{\tau_{cool}} N_{hot}$$
(4.8)

$$\frac{dN_{cold}(t)}{dt} = \frac{1}{\tau_{cool}} N_{hot}(t) - \frac{1}{\tau_{pol}} N_{cold}(t)$$
(4.9)

$$\frac{dN_{pol}(t)}{dt} = \frac{1}{\tau_{pol}} N_{cold}(t) - \frac{1}{\tau_{decay}} N_{pol}(t)$$
(4.10)

$$N_{hot}(0) = N_{cold}(0) = N_{pol}(0) = 0$$
(4.11)

Here provides an example of the photo-conductivity from our 2D TRTS measurements: 1D conductivity $\Delta\sigma$ cut of MAPbBr₃ at frequency of ~11 THz and CsPbBr₃ at frequency of ~9 THz respectively shown in Fig. 4.19 where fitting curves obtained via the first model, which avoids the nonlinear relation between transient reflectivity $\frac{\Delta r}{r_0}$ and $\Delta \sigma$. The fitting hot carrier cooling time stays roughly the same with the average value of \sim 45 fs for MAPbBr3 and from ~ 47 fs for CsPbBr3 under pump conditions of different photoexcited fluences F as shown in Fig. 4.19(c-d). These fitting carrier cooling time is smaller than those of 1D measurements mentioned in Bretschneider et al.'s work and our fitting parameters of the transient reflectivity from 1D TRTS data [16]. And the fitting polaron formation time is ~ 330 fs averagely for MAPbBr₃ and ~ 255 fs averagely for CsPbBr₃ at different fluences as shown in Fig. 4.19(e-f). Our fitting polaron formation time for MAPbBr₃ is almost consistent with that of 400 fs and 280± 40 fs for MAPbBr₃ in Burgos-Caminal et al.'s work and Miyata et al.'s research, respectively [11, 81]. Our fitting polaron formation time for CsPbBr₃ is smaller than that of 600 ± 100 fs and 700 ± 100 fs for CsPbBr₃ in Miyata et al.' s and J. S. Evans et al.'s works respectively [11, 75]. And both parameters are in the same time scale of Bretschneider et al. 's work of lead-iodide perovskites mention before but not sure since the samples are different [16]. However, the pronouncedly smaller fitting carrier cooling time in this example greatly shows the limitation of using the relation $\frac{\Delta r}{r_0} \propto \Delta \sigma$ directly without using it in the linear regime.



Figure. 4.19 1D photo-conductivity cut from 2D conductivity and fitting curves of (a) MAPbBr₃ at frequency of ~11 THz and (b) CsPbBr₃ at frequency of ~9 THz within shorter-time scale of the first 2.25 ps under specified pump conditions of different photo-excited fluences *F* of 23 uJ/cm², 56 uJ/cm², 110 uJ/cm², 185 uJ/cm², and 362 uJ/cm² at~298K. Fitting carrier cooling time along fluence of (c) MAPbBr₃ and (d) CsPbBr₃; Fitting polaron formation time along fluence of (e) MAPbBr₃ and (f) CsPbBr₃, respectively.

The second model proposed by us is based on the first model but including the injecting carriers process of gaussian pulse and the decay process of polaron as well. Here are three-level differential equations given by Eq. 4.8-4.10 where three relevant populations are N_{hot} , N_{cold} , and N_{pol} as well as three time scales τ_{cool} , τ_{pol} , and τ_{decay} . The new boundary condition is given by Eq. 4.11. Similarly, the carrier densities used in the fit are referred to TABLE. 4.1.



Figure. 4.20 1D transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$ dynamics evolution obtained from 1D TRTS and fitting curves of (a) MAPbBr₃ and (b) CsPbBr₃ at longer-time scale of around 300 ps under specified pump conditions of different photo-excited fluences *F* of 23 uJ/cm², 56 uJ/cm²,

110 uJ/cm², 185 uJ/cm², and 362 uJ/cm² at ~298K as well as (c-d) diagrams of the first 2.25 ps obtained from (a-b).

Different from the shorter time scale of the first 2.25 ps only considering the rising dynamics until reaching equilibrium, longer time scale of around ~300 ps better describes the rise dynamics as well as decay dynamics. Fig. 4.20(a-b) shows the fitting results of the second model at longer-time scale of around 300 ps at ~298K. If narrow the time to the first 2.25 ps, the fitting curve of rise dynamics before reaching the equilibrium can be obtained as well given by Fig. 4.20(c-d). Under pump conditions of different photoexcited fluences F, the carrier cooling time obtained from the fit is around ~230-307 fs for MAPbBr₃ and ~170-530 fs for CsPbBr₃. The polaron formation time is around ~27-57 ps for MAPbBr₃ and ~49-77 ps for CsPbBr₃ which is much larger than the expected polaron formation. This can be explained that this time constant may cannot represent the polaron formation time well. The decay time τ_{decay} is around ~500-1300 ps for MAPbBr₃ and \sim 800-1900 ps for CsPbBr₃ respectively, which is almost in agreement with the recombination time ~2 ns (2000 ps) obtained in a simple fit model of photo-induced change of electric field considering carriers cool to a lower state (equivalent to the band edge) with high mobility before finally recombining (electron-phonon coupling, phononphonon coupling and the Auger mechanism) of Monti et al.'s research using TAS measurements [151]. Although this model can fit transient reflectivity with the long-time scale of around ~300 ps, however, the coherent oscillation still can be observed and needs to be better explained outside of this model. Besides, the complexity number of fitting parameters of in the differential equations of this model leads to the complexity of significant uncertainty solutions (more parameters). And too many parameters enlarge the fitting difficulty as well as accuracy.

To sum up, two models mentioned above still have limitations, better models should be proposed in the future to quantify carrier cooling, polaron formation, and decay process (recombination process).

Chapter 5

Conclusions and Future Work

In summary, as the injection of charge carriers into the system, the ultrafast screening of Coulomb interactions as well as buildups of new dressed quasiparticles within sub-ps are observed in two kinds of LHPs, MAPbBr3 and CsPbBr3 bulk single crystals, via UBB-TRTS. In the analysis of transient reflectivity $\left|\frac{\Delta \tilde{r}}{\tilde{r}_0}\right|$, the change rule: rising firstly then reaching a quasi-equilibrium state of transient reflectivity in MAPbBr₃ and CsPbBr₃ are in agreement with previous relative works of LHPs or other MHPs, which demonstrates the carrier cooling process caused by the excess energy from 3.1 eV pump pulse and polaron formation[11, 16]. First numerical Boltzmann fits are adopted to analyse the rise of transient reflectivity, the rise time of CsPbBr₃ is near twice larger than that of MAPbBr₃ because the intervalley scattering process in CsPbBr₃ is slower than the intervalley scattering process in MAPbBr₃. Furthermore, two physical models to describe the transient reflectivity dynamics evolution of MAPbBr₃ and CsPbBr₃ are proposed, which greatly quantify the carrier cooling process, carrier-phonon coupling formation, and even recombination process. The carrier cooling time is approximately in the time scale of one or two hundreds fs (~100-200 fs), the polaron formation time is roughly within one or two hundreds fs (~100-200 fs), and the recombination time is around within several ns (~0.5-2 ns). Moreover, the transient reflectivity in both samples has the pattern of fluencesensitive coherent oscillations appearing chirped negatively then merging with a steady

state near $\frac{\omega_{LO}}{2\pi}$ ~5.32 THz for MAPbBr₃ and $\frac{\omega_{LO}}{2\pi}$ ~4.67 THz for CsPbBr₃ when the density of injection charge carriers/photo-excited fluence increases, which can be explained by strongly anharmonic, low energy phonons whereby vibrational energy is quickly dispersed from high energy phonons to low energy phonons called liquid-like lattice excitations of LHPs as well. An alternative possible mechanism for these coherent oscillations is the buildup of coupled plasmon-phonon causing the shift of the reststrahlen to higher frequencies. Then in the fluence-dependence of complex photoconductivity $\Delta \tilde{\sigma}$ analysis with Drude-Smith model, the Drude-Smith backscattering parameter c becomes less negative with the increasing fluence, indicating that the backscattering gets less efficient as the electron population becomes hotter. The Drude-Smith plasma frequency ω_p is also observed to saturate, which may be due to a saturation in photon absorption caused by depletion of the density of states. These research results may shed new light on how carriers evolve and interact with the polar lattice in LHPs.

For future investigations, resonant excitation should be performed by tuning the pump pulse energy to the band gap energy, since the excess kinetic energy of the high energy 400 nm photons used here should strongly interfere with the process and likely mask other coherences. In our group previous work (Yang *et al.*' s research), we applied the pump energy exactly equaling to the band gap energy, and observed a coherent intraband quantum beat reflecting the internal motion of the charge within the polaron potential in MAPI [14]. Therefore, it can be expected to observe the same coherent oscillation if conduct the experiments with pump energy of 2.275 eV for MAPbBr₃ single

crystal and 2.384 eV for CsPbBr₃ single crystal, although this must be verified. In Bretschneider *et al.*' s research they also used the pump energy equaling to the band gap energy and directly assign the rise time to the polaron formation, this may be debatable since only 1D measurements were performed and the conductivity is only linear with the transient reflectivity/transmissivity for low differential responses (< 20%) [16]. We can also do experiments with applied pump energy of band gap energy adding one phonon energy to compare the effect of the resonant and a little bit above bandgap excitation. Two dimensional maps at much lower optical excitation must be performed to better simulate the response experienced by actual photovoltaic cells. Finally, better quantitative models of the transient THz response should be formulated considering not just carrier cooling, polaron formation, and recombination but including intervalley scattering and details of the electronic band structure.

Bibliography

- 1. Manser, J.S., J.A. Christians, and P.V. Kamat, *Intriguing optoelectronic properties of metal halide perovskites*. Chemical reviews, 2016. **116**(21): p. 12956-13008.
- 2. Dubey, A., et al., *A strategic review on processing routes towards highly efficient perovskite solar cells.* Journal of Materials Chemistry A, 2018. **6**(6): p. 2406-2431.
- 3. Zhu, H., et al., *Lead halide perovskite nanowire lasers with low lasing thresholds and high quality factors.* Nature materials, 2015. **14**(6): p. 636-642.
- 4. Deschler, F., et al., *High photoluminescence efficiency and optically pumped lasing in solution-processed mixed halide perovskite semiconductors.* The journal of physical chemistry letters, 2014. 5(8): p. 1421-1426.
- 5. Wehrenfennig, C., et al., *Homogeneous emission line broadening in the organo lead halide perovskite ch3nh3pbi3-x cl x.* The journal of physical chemistry letters, 2014.
 5(8): p. 1300-1306.
- Kojima, A., et al., Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. Journal of the american chemical society, 2009. 131(17): p. 6050-6051.
- 7. Kim, H.-S., et al., *Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding* 9%. Scientific reports, 2012. **2**(1): p. 591.
- Im, J.-H., et al., 6.5% efficient perovskite quantum-dot-sensitized solar cell. Nanoscale, 2011. 3(10): p. 4088-4093.

- 9. Burschka, J., et al., Sequential deposition as a route to high-performance perovskitesensitized solar cells. Nature, 2013. **499**(7458): p. 316-319.
- 10. Min, H., et al., *Perovskite solar cells with atomically coherent interlayers on SnO2 electrodes.* Nature, 2021. **598**(7881): p. 444-450.
- 11. Miyata, K., et al., *Large polarons in lead halide perovskites*. Science advances, 2017.
 3(8): p. e1701217.
- 12. Zhu, H., et al., *Screening in crystalline liquids protects energetic carriers in hybrid perovskites*. Science, 2016. **353**(6306): p. 1409-1413.
- 13. Yaffe, O., et al., *Local polar fluctuations in lead halide perovskite crystals*. Physical review letters, 2017. **118**(13): p. 136001.
- 14. Lan, Y., et al., *Ultrafast correlated charge and lattice motion in a hybrid metal halide perovskite*. Science Advances, 2019. **5**(5): p. eaaw5558.
- 15. Lan, Y., et al., *Coherent charge-phonon correlations and exciton dynamics in orthorhombic CH3NH3PbI3 measured by ultrafast multi-THz spectroscopy*. The Journal of Chemical Physics, 2019. **151**(21): p. 214201.
- 16. Bretschneider, S.A., et al., *Quantifying polaron formation and charge carrier cooling in lead-iodide perovskites.* Advanced Materials, 2018. **30**(29): p. 1707312.
- 17. Miyata, K., T.L. Atallah, and X.-Y. Zhu, *Lead halide perovskites: Crystal-liquid duality, phonon glass electron crystals, and large polaron formation.* Science Advances, 2017.
 3(10): p. e1701469.
- 18. Batignani, G., et al., *Probing femtosecond lattice displacement upon photo-carrier generation in lead halide perovskite.* Nature communications, 2018. **9**(1): p. 1971.

- 19. Price, M.B., et al., *Hot-carrier cooling and photoinduced refractive index changes in organic–inorganic lead halide perovskites*. Nature communications, 2015. **6**(1): p. 8420.
- Yamada, Y., et al., *Photocarrier recombination dynamics in perovskite CH3NH3PbI3 for* solar cell applications. Journal of the American Chemical Society, 2014. **136**(33): p. 11610-11613.
- 21. Guzelturk, B., et al., *Visualization of dynamic polaronic strain fields in hybrid lead halide perovskites.* Nature materials, 2021. **20**(5): p. 618-623.
- 22. Miyata, K. and X.-Y. Zhu, *Ferroelectric large polarons*. Nature materials, 2018. 17(5): p. 379-381.
- 23. Cao, D.H., et al., 2*D* homologous perovskites as light-absorbing materials for solar cell applications. Journal of the American Chemical Society, 2015. **137**(24): p. 7843-7850.
- Zhou, T., et al., *Two-dimensional lead-free hybrid halide perovskite using superatom anions with tunable electronic properties*. Solar Energy Materials and Solar Cells, 2019.
 191: p. 33-38.
- 25. Huang, H., et al., *Lead halide perovskite nanocrystals in the research spotlight: stability and defect tolerance.* ACS energy letters, 2017. **2**(9): p. 2071-2083.
- 26. Jena, A.K., A. Kulkarni, and T. Miyasaka, *Halide perovskite photovoltaics: background, status, and future prospects.* Chemical reviews, 2019. **119**(5): p. 3036-3103.
- 27. Lu, M., et al., *Metal halide perovskite light-emitting devices: promising technology for next-generation displays.* Advanced Functional Materials, 2019. **29**(30): p. 1902008.
- 28. Rose, G., De novis quibusdam fossilibus quae in montibus Uraliis inveniuntur. 1839: typis AG Schadii.

- 29. Wells, H.L., *Über die cäsium-und kalium-bleihalogenide*. Zeitschrift für anorganische Chemie, 1893. **3**(1): p. 195-210.
- 30. Saparov, B. and D.B. Mitzi, *Organic–inorganic perovskites: structural versatility for functional materials design.* Chemical reviews, 2016. **116**(7): p. 4558-4596.
- Lin, H., et al., Low-dimensional organometal halide perovskites. ACS Energy Letters, 2017. 3(1): p. 54-62.
- Anderson, M.T., et al., *B-cation arrangements in double perovskites*. Progress in solid state chemistry, 1993. 22(3): p. 197-233.
- 33. Akkerman, Q.A. and L. Manna, *What defines a halide perovskite?* ACS energy letters,
 2020. 5(2): p. 604-610.
- 34. Goldschmidt, V.M., Die gesetze der krystallochemie. Naturwissenschaften, 1926.
 14(21): p. 477-485.
- 35. Bartel, C.J., et al., *New tolerance factor to predict the stability of perovskite oxides and halides.* Science advances, 2019. **5**(2): p. eaav0693.
- 36. Li, W., et al., *Chemically diverse and multifunctional hybrid organic–inorganic perovskites*. Nature Reviews Materials, 2017. **2**(3): p. 1-18.
- 37. Li, C., et al., *Formability of abx3* (*x*= *f*, *cl*, *br*, *i*) *halide perovskites*. Acta Crystallographica Section B: Structural Science, 2008. **64**(6): p. 702-707.
- 38. Kovalenko, M., et al. *Structural, Electronic and Optical Properties of CsPbBr 3 and CH* 3 NH 3 PbBr 3: First-Principles Modeling. in 2021 IEEE 12th International Conference on Electronics and Information Technologies (ELIT). 2021. IEEE.

- 39. Matsuishi, K., et al., *Optical properties and structural phase transitions of lead-halide based inorganic–organic 3D and 2D perovskite semiconductors under high pressure.* physica status solidi (b), 2004. **241**(14): p. 3328-3333.
- 40. Dobrovolsky, A., et al., *Defect-induced local variation of crystal phase transition temperature in metal-halide perovskites.* Nature communications, 2017. **8**(1): p. 34.
- 41. Kepenekian, M., et al., *Rashba and Dresselhaus effects in hybrid organic–inorganic perovskites: from basics to devices.* ACS nano, 2015. **9**(12): p. 11557-11567.
- 42. Papavassiliou, G.C., G.A. Mousdis, and I. Koutselas, *Structural, Optical, and Related Properties of Some Perovskites Based on Lead and Tin Halides: The Effects on Going from Bulk to Small Particles.* Halide Perovskites: Photovoltaics, Light Emitting Devices, and Beyond, 2018: p. 1-24.
- Huang, L.-y. and W.R. Lambrecht, *Electronic band structure, phonons, and exciton binding energies of halide perovskites CsSnCl 3, CsSnBr 3, and CsSnI 3.* Physical Review B, 2013. 88(16): p. 165203.
- 44. Umari, P., E. Mosconi, and F. De Angelis, *Relativistic GW calculations on CH3NH3PbI3 and CH3NH3SnI3 perovskites for solar cell applications*. Scientific reports, 2014. **4**(1): p. 4467.
- 45. Chiarella, F., et al., *Combined experimental and theoretical investigation of optical, structural, and electronic properties of C H 3 N H 3 Sn X 3 thin films (X= Cl, Br).* Physical Review B, 2008. 77(4): p. 045129.

- 46. Bisquert, J. and I. Mora-Seró, *Simulation of steady-state characteristics of dye-sensitized solar cells and the interpretation of the diffusion length.* The Journal of Physical Chemistry Letters, 2010. **1**(1): p. 450-456.
- 47. Herz, L.M., *Charge-carrier dynamics in organic-inorganic metal halide perovskites*. Annual review of physical chemistry, 2016. **67**: p. 65-89.
- 48. Wehrenfennig, C., et al., *Charge-carrier dynamics in vapour-deposited films of the organolead halide perovskite CH 3 NH 3 PbI 3– x Cl x.* Energy & Environmental Science, 2014. **7**(7): p. 2269-2275.
- 49. Shi, D., et al., *Low trap-state density and long carrier diffusion in organolead trihalide perovskite single crystals.* Science, 2015. **347**(6221): p. 519-522.
- 50. Yin, W.J., T. Shi, and Y. Yan, *Unique properties of halide perovskites as possible origins of the superior solar cell performance*. Advanced materials, 2014. **26**(27): p. 4653-4658.
- 51. Xing, G., et al., *Low-temperature solution-processed wavelength-tunable perovskites for lasing*. Nature materials, 2014. **13**(5): p. 476-480.
- 52. Sutherland, B.R., et al., *Conformal organohalide perovskites enable lasing on spherical resonators*. ACS nano, 2014. **8**(10): p. 10947-10952.
- 53. Landau, L.D., *On the motion of electrons in a crystal lattice*. Phys. Z. Sowjetunion, 1933. **3**: p. 664.
- 54. Landau, L. and S. Pekar, *Effective mass of a polaron*. Zh. Eksp. Teor. Fiz, 1948. 18(5):p. 419-423.
- 55. Devreese, J. *Polarons*. in *AIP Conference Proceedings*. 2003. American Institute of Physics.

- 56. Wellein, G., H. Röder, and H. Fehske, *Polarons and bipolarons in strongly interacting electron-phonon systems*. Physical Review B, 1996. **53**(15): p. 9666.
- 57. Fröhlich, H., *Electrons in lattice fields*. Advances in Physics, 1954. **3**(11): p. 325-361.
- 58. Lee, T., F. Low, and D. Pines, *The motion of slow electrons in a polar crystal*. Physical Review, 1953. **90**(2): p. 297.
- 59. Röseler, J., *A new variational ansatz in the polaron theory*. Physica status solidi (b), 1968. **25**(1): p. 311-316.
- 60. Selyugin, O. and M. Smondyrev, *Phase transition and Padé approximants for Fröhlich polarons.* physica status solidi (b), 1989. **155**(1): p. 155-167.
- 61. Miyake, S.J., *Strong-coupling limit of the polaron ground state*. Journal of the Physical Society of Japan, 1975. **38**(1): p. 181-182.
- 62. Devreese, J., *Polarons*. arXiv preprint cond-mat/0004497, 2000.
- Gurevich, V., I. Lang, and Y.A. Firsov, On the part played by optical phonons in infrared absorption by free carriers in semiconductors. Soviet Physics-Solid State, 1962.
 4(5): p. 918-925.
- 64. Devreese, J., W. Huybrechts, and L. Lemmeks, *On the optical absorption of free polarons at weak coupling*. physica status solidi (b), 1971. **48**(1): p. 77-86.
- 65. Joshi, P.P., S.F. Maehrlein, and X. Zhu, *Dynamic screening and slow cooling of hot carriers in lead halide perovskites*. Advanced Materials, 2019. **31**(47): p. 1803054.
- 66. Burgos-Caminal, A., et al., *Hot carrier mobility dynamics unravel competing sub-ps cooling processes in Lead Halide perovskites.* arXiv preprint arXiv:1909.04589, 2019.

- 67. Zhu, X.-Y. and V. Podzorov, *Charge carriers in hybrid organic–inorganic lead halide perovskites might be protected as large polarons.* 2015, ACS Publications. p. 4758-4761.
- 68. Iaru, C.M., et al., *Fröhlich interaction dominated by a single phonon mode in CsPbBr3*.
 Nature communications, 2021. 12(1): p. 1-8.
- 69. Wright, A.D., et al., *Electron–phonon coupling in hybrid lead halide perovskites*. Nature communications, 2016. **7**(1): p. 11755.
- 70. Monahan, D.M., et al., *Room-temperature coherent optical phonon in 2D electronic spectra of CH3NH3PbI3 perovskite as a possible cooling bottleneck*. The journal of physical chemistry letters, 2017. **8**(14): p. 3211-3215.
- 71. Leguy, A.M., et al., *Dynamic disorder, phonon lifetimes, and the assignment of modes to the vibrational spectra of methylammonium lead halide perovskites.* Physical Chemistry Chemical Physics, 2016. **18**(39): p. 27051-27066.
- 72. Brivio, F., et al., *Lattice dynamics and vibrational spectra of the orthorhombic, tetragonal, and cubic phases of methylammonium lead iodide.* Physical Review B, 2015. **92**(14): p. 144308.
- 73. La-o-Vorakiat, C., et al., *Phonon mode transformation across the orthohombic–tetragonal phase transition in a lead iodide perovskite CH3NH3PbI3: a terahertz time-domain spectroscopy approach.* The journal of physical chemistry letters, 2016. **7**(1): p. 1-6.
- 74. Betz, M., et al., Virtual carrier–LO phonon interaction in the intermediate coupling region: the quantum dynamical formation of polarons. Physica B: Condensed Matter, 2002. 314(1-4): p. 76-80.

- 75. Evans, T.J., et al., *Competition between hot-electron cooling and large polaron screening in CsPbBr3 perovskite single crystals*. The Journal of Physical Chemistry C, 2018.
 122(25): p. 13724-13730.
- 76. Miyata, K., et al., Liquid-like dielectric response is an origin of long polaron lifetime exceeding 10 μ s in lead bromide perovskites. The Journal of Chemical Physics, 2020.
 152(8): p. 084704.
- 77. He, Y., et al., *High spectral resolution of gamma-rays at room temperature by perovskite CsPbBr3 single crystals.* Nature communications, 2018. **9**(1): p. 1609.
- 78. Niesner, D., et al., *Persistent energetic electrons in methylammonium lead iodide perovskite thin films*. Journal of the American Chemical Society, 2016. **138**(48): p. 15717-15726.
- Frost, J.M., *Calculating polaron mobility in halide perovskites*. Physical Review B, 2017.
 96(19): p. 195202.
- 80. Sendner, M., et al., *Optical phonons in methylammonium lead halide perovskites and implications for charge transport.* Materials Horizons, 2016. **3**(6): p. 613-620.
- Burgos-Caminal, A., et al., *Hot carrier mobility dynamics unravel competing subpicosecond processes in lead halide perovskites*. The Journal of Physical Chemistry C, 2020. 125(1): p. 98-106.
- 82. Saidaminov, M.I., et al., *High-quality bulk hybrid perovskite single crystals within minutes by inverse temperature crystallization*. Nature communications, 2015. 6(1): p. 7586.

- 83. Yi, H.T., et al., *Intrinsic charge transport across phase transitions in hybrid organoinorganic perovskites*. Advanced Materials, 2016. **28**(30): p. 6509-6514.
- 84. Hu, F., et al., *Superior optical properties of perovskite nanocrystals as single photon emitters*. ACS nano, 2015. **9**(12): p. 12410-12416.
- 85. Protesescu, L., et al., Nanocrystals of cesium lead halide perovskites (CsPbX3, X= Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut. Nano letters, 2015. 15(6): p. 3692-3696.
- Huang, H., et al., Top-Down Fabrication of Stable Methylammonium Lead Halide Perovskite Nanocrystals by Employing a Mixture of Ligands as Coordinating Solvents. Angewandte Chemie, 2017. 129(32): p. 9699-9704.
- 87. Horváth, E., et al., Nanowires of methylammonium lead iodide (CH3NH3PbI3) prepared by low temperature solution-mediated crystallization. Nano letters, 2014. 14(12): p. 6761-6766.
- Fu, Y., et al., Broad wavelength tunable robust lasing from single-crystal nanowires of cesium lead halide perovskites (CsPbX3, X= Cl, Br, I). ACS nano, 2016. 10(8): p. 7963-7972.
- 89. Amgar, D., et al., *Tunable length and optical properties of CsPbX3* (X= Cl, Br, I) *nanowires with a few unit cells.* Nano letters, 2017. **17**(2): p. 1007-1013.
- 90. Ha, S.T., et al., *Synthesis of organic-inorganic lead halide perovskite nanoplatelets: towards high-performance perovskite solar cells and optoelectronic devices.* 2014.

- 91. Huo, C., et al., *Field-effect transistors based on van-der-Waals-grown and dry-transferred all-inorganic perovskite ultrathin platelets*. The Journal of Physical Chemistry Letters, 2017. 8(19): p. 4785-4792.
- 92. Dou, L., et al., *Atomically thin two-dimensional organic-inorganic hybrid perovskites*.
 Science, 2015. **349**(6255): p. 1518-1521.
- 93. Carlsson, J.-O. and P.M. Martin, *Chemical vapor deposition*, in *Handbook of Deposition Technologies for films and coatings*. 2010, Elsevier. p. 314-363.
- 94. Dong, Q., et al., *Electron-hole diffusion lengths>* 175 μm in solution-grown *CH3NH3PbI3 single crystals.* Science, 2015. **347**(6225): p. 967-970.
- 95. Semonin, O.E., et al., *Limits of carrier diffusion in n-type and p-type CH3NH3PbI3 perovskite single crystals.* The journal of physical chemistry letters, 2016. 7(17): p. 3510-3518.
- 96. Liu, X., et al., *Metal Halide Perovskites: Synthesis, Ion Migration, and Application in Field-Effect Transistors.* Small, 2018. **14**(36): p. 1801460.
- 97. Millar, S., *Tips and Tricks for the Lab: Growing Crystals Part* 3. 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- 98. Stoumpos, C.C., et al., *Crystal growth of the perovskite semiconductor CsPbBr3: a new material for high-energy radiation detection.* Crystal growth & design, 2013. **13**(7): p. 2722-2727.
- 99. Onoda-Yamamuro, N., T. Matsuo, and H. Suga, Calorimetric and IR spectroscopic studies of phase transitions in methylammonium trihalogenoplumbates (II). Journal of Physics and Chemistry of Solids, 1990. 51(12): p. 1383-1395.

- Bakulin, A.A., et al., *Real-time observation of organic cation reorientation in methylammonium lead iodide perovskites*. The journal of physical chemistry letters, 2015. 6(18): p. 3663-3669.
- 101. Mattoni, A., et al., Methylammonium rotational dynamics in lead halide perovskite by classical molecular dynamics: the role of temperature. The Journal of Physical Chemistry C, 2015. 119(30): p. 17421-17428.
- 102. Mattoni, A., et al., *Temperature evolution of methylammonium trihalide vibrations at the atomic scale*. The Journal of Physical Chemistry Letters, 2016. **7**(3): p. 529-535.
- He, Y., et al., *Resolving the energy of γ-ray photons with MAPbI3 single crystals*. Acs
 Photonics, 2018. 5(10): p. 4132-4138.
- 104. Guo, P., et al., *Polar fluctuations in metal halide perovskites uncovered by acoustic phonon anomalies*. ACS Energy Letters, 2017. **2**(10): p. 2463-2469.
- Pan, L., et al., Ultra-High Flux X-Ray Detection by Solution-Grown Perovskite CsPbBr3
 Single Crystal Semiconductor Detector. Advanced Materials, 2023: p. 2211840.
- He, Y., et al., *CsPbBr3 perovskite detectors with* 1.4% *energy resolution for high-energy γ-rays.* Nature Photonics, 2021. 15(1): p. 36-42.
- 107. Cooke, D.G., *Time-resolved terahertz spectroscopy of bulk and nanoscale semiconductors*.2007.
- 108. Fattinger, C. and D. Grischkowsky, *Terahertz beams*. Applied Physics Letters, 1989.
 54(6): p. 490-492.
- 109. Huber, R., et al., *How many-particle interactions develop after ultrafast excitation of an electron–hole plasma*. Nature, 2001. **414**(6861): p. 286-289.

- Beard, M.C., G.M. Turner, and C.A. Schmuttenmaer, *Transient photoconductivity in GaAs as measured by time-resolved terahertz spectroscopy*. Physical Review B, 2000.
 62(23): p. 15764.
- 111. Kaindl, R.A., et al., *Ultrafast terahertz probes of transient conducting and insulating phases in an electron–hole gas.* Nature, 2003. **423**(6941): p. 734-738.
- Huber, R., et al., Broadband terahertz study of excitonic resonances in the high-density regime in GaAs/ Al x Ga 1- x As quantum wells. Physical Review B, 2005. 72(16): p. 161314.
- 113. Nuss, M.C., et al., *Terahertz time-domain measurement of the conductivity and superconducting band gap in niobium*. Journal of Applied Physics, 1991. **70**(4): p. 2238-2241.
- 114. Auston, D.H., *Picosecond optoelectronic switching and gating in silicon*. Applied Physics Letters, 1975. 26(3): p. 101-103.
- Auston, D.H., K.P. Cheung, and P.R. Smith, *Picosecond photoconducting Hertzian dipoles*. Applied physics letters, 1984. 45(3): p. 284-286.
- 116. Rice, A., et al., *Terahertz optical rectification from*< 110> *zinc-blende crystals*. Applied physics letters, 1994. 64(11): p. 1324-1326.
- 117. Cook, D. and R. Hochstrasser, *Intense terahertz pulses by four-wave rectification in air*.Optics letters, 2000. 25(16): p. 1210-1212.
- 118. Matsubara, E., M. Nagai, and M. Ashida, *Ultrabroadband coherent electric field from far infrared to 200 THz using air plasma induced by 10 fs pulses*. Applied Physics Letters, 2012. **101**(1): p. 011105.

- 119. Doany, F., D. Grischkowsky, and C.C. Chi, *Carrier lifetime versus ion-implantation dose in silicon on sapphire*. Applied Physics Letters, 1987. **50**(8): p. 460-462.
- Lui, K. and F. Hegmann, Ultrafast carrier relaxation in radiation-damaged silicon on sapphire studied by optical-pump-terahertz-probe experiments. Applied Physics Letters, 2001. 78(22): p. 3478-3480.
- Beard, M.C., G.M. Turner, and C.A. Schmuttenmaer, Subpicosecond carrier dynamics in low-temperature grown GaAs as measured by time-resolved terahertz spectroscopy. Journal of Applied Physics, 2001. 90(12): p. 5915-5923.
- 122. Jepsen, P.U., et al., *Detection of THz pulses by phase retardation in lithium tantalate*.Physical Review E, 1996. 53(4): p. R3052.
- 123. Nahata, A., et al., *Coherent detection of freely propagating terahertz radiation by electrooptic sampling*. Applied physics letters, 1996. **68**(2): p. 150-152.
- 124. Wu, Q., T. Hewitt, and X.C. Zhang, *Two-dimensional electro-optic imaging of THz beams*. Applied Physics Letters, 1996. **69**(8): p. 1026-1028.
- 125. Nazarov, M., et al., On the choice of nonlinear optical and semiconductor converters of femtosecond laser pulses into terahertz range. Radiophysics and Quantum Electronics, 2009. 52: p. 536-545.
- 126. Wu, Q. and X.-C. Zhang, *Free-space electro-optics sampling of mid-infrared pulses*. Applied physics letters, 1997. **71**(10): p. 1285-1286.
- 127. Gallot, G., et al., *Measurements of the THz absorption and dispersion of ZnTe and their relevance to the electro-optic detection of THz radiation*. Applied Physics Letters, 1999.
 74(23): p. 3450-3452.

- Kübler, C., R. Huber, and A. Leitenstorfer, *Ultrabroadband terahertz pulses: generation and field-resolved detection*. Semiconductor science and technology, 2005.
 20(7): p. S128.
- 129. Federici, J.F., et al., *Direct picosecond measurement of photoinduced Cooper-pair breaking in lead.* Physical Review B, 1992. **46**(17): p. 11153.
- 130. Averitt, R.D., et al., *Conductivity artifacts in optical-pump THz-probe measurements of YBa 2 Cu 3 O 7.* JOSA B, 2000. **17**(2): p. 327-331.
- 131. Kaindl, R.A., et al., *Dynamics of Cooper pair formation in Bi 2 Sr 2 Ca Cu 2 O 8+ δ*.
 Physical Review B, 2005. **72**(6): p. 060510.
- 132. Schall, M. and P.U. Jepsen, *Photoexcited GaAs surfaces studied by transient terahertz time-domain spectroscopy*. Optics letters, 2000. **25**(1): p. 13-15.
- 133. Hegmann, F., et al., *Picosecond transient photoconductivity in functionalized pentacene molecular crystals probed by terahertz pulse spectroscopy*. Physical review letters, 2002.
 89(22): p. 227403.
- 134. Ostroverkhova, O., et al., Bandlike transport in pentacene and functionalized pentacene thin films revealed by subpicosecond transient photoconductivity measurements. Physical Review B, 2005. 71(3): p. 035204.
- 135. Shan, J., et al., *Measurement of the frequency-dependent conductivity in sapphire*. Physical review letters, 2003. **90**(24): p. 247401.
- 136. Glover III, R. and M. Tinkham, *Conductivity of Superconducting Films for Photon Energies between 0.3 and 4 0 k T c.* Physical Review, 1957. **108**(2): p. 243.

- 137. Smith, N., Classical generalization of the Drude formula for the optical conductivity. Physical Review B, 2001. 64(15): p. 155106.
- 138. Mayou, D., *Generalized Drude formula for the optical conductivity of quasicrystals*.Physical Review Letters, 2000. 85(6): p. 1290.
- 139. Chávez, D.A.V., Transient Multi-THz Spectroscopy of Hybrid Organometallic Perovskites. 2017, McGill University, Montreal.
- 140. Chaves, A. and S. Porto, *Generalized lyddane-sachs-teller relation*. Solid State Communications, 1973. **13**(7): p. 865-868.
- 141. Chen, X., et al., *Temperature dependent reflectance and ellipsometry studies on a CsPbBr3 single crystal*. The Journal of Physical Chemistry C, 2019. 123(16): p. 10564-10570.
- 142. Zhang, Y., et al., Direct Growth of Pyramid-Textured Perovskite Single Crystals: A New Strategy for Enhanced Optoelectronic Performance. Advanced Functional Materials, 2020. 30(34): p. 2002742.
- 143. Dendebera, M., et al., *Time resolved luminescence spectroscopy of CsPbBr3 single crystal*.Journal of Luminescence, 2020. 225: p. 117346.
- 144. Yuan, Y., et al., *Exciton recombination mechanisms in solution grown single crystalline CsPbBr3 perovskite*. Journal of Luminescence, 2020. **226**: p. 117471.
- 145. Yang, Y., et al., *Low surface recombination velocity in solution-grown CH3NH3PbBr3 perovskite single crystal.* Nature communications, 2015. **6**(1): p. 7961.
- 146. Ramade, J., et al., *Fine structure of excitons and electron-hole exchange energy in polymorphic CsPbBr 3 single nanocrystals.* Nanoscale, 2018. **10**(14): p. 6393-6401.

- 147. Goesten, M.G. and R. Hoffmann, *Mirrors of bonding in metal halide perovskites*.Journal of the American Chemical Society, 2018. **140**(40): p. 12996-13010.
- 148. Kutt, W.A., W. Albrecht, and H. Kurz, *Generation of coherent phonons in condensed media*. IEEE journal of quantum electronics, 1992. **28**(10): p. 2434-2444.
- 149. Okochi, H., et al., *Photon energy-dependent ultrafast photoinduced terahertz response in a microcrystalline film of CH3NH3PbBr3*. The Journal of Physical Chemistry Letters, 2020. 11(15): p. 6068-6076.
- 150. Jin, Z., et al., *Photoinduced large polaron transport and dynamics in organic-inorganic hybrid lead halide perovskite with terahertz probes*. Light: Science & Applications, 2022.
 11(1): p. 209.
- 151. Monti, M., et al., Hot carriers in mixed Pb-Sn halide perovskite semiconductors cool slowly while retaining their electrical mobility. Physical Review B, 2020. 102(24): p. 245204.