



Exciton dynamics in layered semiconductors: interaction effects on formation and relaxation

Valentina Gosetti

Supervisors:

Prof. Dr. Stefania Pagliara

Prof. Dr. Jin Won Maria Seo

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Valentina GOSETTI

Examination committee:

Em. Prof. Dr. Lucie Vandewalle, chair
(KU Leuven)

Prof. Dr. Fausto Borgonovi, chair
(Università Cattolica del Sacro Cuore)

Prof. Dr. Stefania Pagliara, supervisor
(Università Cattolica del Sacro Cuore)

Prof. Dr. Jin Won Maria Seo, supervisor
(KU Leuven)

Prof. Dr. Claudio Giannetti (Università
Cattolica del Sacro Cuore)

Prof. Dr. Lino da Costa Pereira (KU
Leuven)

Prof. Dr. Barbara Ressel
(University of Nova Gorica)

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Uitgegeven in eigen beheer, Valentina Gosetti, Kasteelpark Arenberg 44, B-3001 Leuven (Belgium)

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Penserete che sia tutto qui?

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You might think that's all.

For once, I will try to be wordier. Finding the right words to express myself has never been easy, and often I would have summed it all up with a simple "thank you." But a "thank you" can still be full of meaning and it can be said with passion and sincerity. However, at the end of this journey, I am convinced that a single "thank you" is not enough. I believe it is necessary to try to express as best as I can what I feel.

The journey of the PhD is intense and unique. It is a formative journey, not only professionally but also personally, in which I have probably experienced the entire spectrum of human emotions. Above all, it is the result of countless interactions and shared thoughts with others. For this reason, I want to dedicate more than just a couple of words to thank those who have helped, guided and supported me along the way. Without them, this thesis and this work would not have existed.

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This journey has deeply enriched me, and I am proud of what I have built alongside all the people who have been part of it.

Use of Generative AI

I did not use generative AI assistance tools during the research and writing process of my thesis, except for mere language assistance.

The text and images in this thesis are my own. I have reviewed and edited the content as needed and I take full responsibility for the content of the thesis.

Abstract

Excitons, i.e. electron-hole pairs bound by Coulomb attraction, are fundamental excitations in semiconductors and dominate their non-equilibrium optical response. Understanding how excitons are generated, their subsequent relaxation dynamics, and how they interact with other degrees of freedom of the system is therefore mandatory for both fundamental research and the development of technological applications such as optoelectronics and spintronics.

Recently, the study of exciton physics has focused on low-dimensional materials, which, after the isolation of graphene from graphite in 2004 by Geim's group [124], dominated the research on semiconductor physics. Today, the family of two-dimensional materials encompasses a broad range of compositions that span most elements of the periodic table. This leads to a wide variety of electronic properties, including metals, semimetals, insulators, and semiconductors with direct and indirect band gaps ranging from ultraviolet to infrared, including the visible regime [210]. In low-dimensional semiconductors, the reduction of the screening induced by geometrical confinement, along with strong light-matter interaction, makes excitons a promising platform for studying exciton dynamics and many-body interactions. In these materials, excitons are more stable and less influenced by scattering processes, leading to decoherence times that are longer than those of conventional materials, which are typically on the order of a few tens of femtoseconds. Additionally, the stability of the excitonic resonance, even at room temperature, enables tracking of the exciton dynamics from the early stages up to a timescale of the order of nanoseconds. The study of exciton physics has focused so far on the exciton formation [167, 182, 43], exciton-phonon coupling [183, 157], high-harmonic generation [93], valley-polarized exciton dynamics [112], and the formation of Floquet states by light dressing of excitons [83, 36, 164] in low-dimensional materials with complex electronic structures, characterized by the presence of multiple valleys, such as two-dimensional transition metal dichalcogenides.

The goal of this thesis is to conduct a systematic study of exciton physics in the layered lead-free semiconductor bismuth tri-iodide (BiI_3), with a quasi-direct

gap and a rich excitonic landscape where an isolated bright exciton with a Frenkel-like character dominates the optical response [77, 21]. The peculiar structure of BiI_3 , both in its bulk and in its two-dimensional forms, makes it an ideal material for investigating the role of the environment, such as phonons, defects, and quasi-free carriers, in exciton dynamics, where their presence can be controlled by tuning the experimental conditions. Furthermore, BiI_3 allows us to exploit the advantages of low dimensionality, such as enhanced structural stability and long-lived exciton dynamics, while mitigating some of the associated challenges, including complex experimental conditions.

Since the dynamics in question occur on sub-nanosecond timescales, ultrafast spectroscopies, both in optics and photoemission, have been employed. All-optical transient spectroscopy is typically used to explore photoinduced relaxation pathways and couplings in semiconductors. A pump and probe scheme, where two pulses are generated by a femtosecond-pulsed laser, is used to photoexcite the material and collect snapshots of the system in the non-equilibrium regime after the photoexcitation. This powerful technique allows for the evolution of the transient signal, such as reflectance, transmittance, or absorption, to be resolved in energy and time, but it does not provide access to the momentum domain. However, time- and angle-resolved photoemission spectroscopy is known for its high-momentum resolution and the more straightforward interpretation of the collected signal. By combining these two spectroscopies, a comprehensive characterization of exciton physics has been achieved in this work.

This thesis begins with an overview of exciton physics in layered semiconductors, followed by a description of the methods and materials employed. The results are then presented. In Chapter 4, the formation of excitons from a quasi-free electron population in the conduction band is investigated using time-resolved angle-resolved photoemission during a beam time at the T-Rex Lab of the Elettra Sincrotrone Trieste. The excitonic signal in photoemission is isolated and traced in the time, energy, and momentum domains. In Chapter 5, we explore the manifestation of an excitonic coherent state through transient optical spectroscopy, as well as the transition from the coherent to the incoherent regime. Chapter 6 focuses on many-body interactions between excitons and phonons, as well as between excitons and free carriers. The experimental results are complemented by theoretical predictions, in collaboration with a theoretical group consisting of Jorge Cervantes-Villanueva and Alejandro Molina-Sánchez (University of Valencia), Davide Sangalli (Istituto della Materia-CNR), and Simona Achilli (Università degli studi di Milano). Finally, Chapter 7 presents preliminary results of a powerful experimental technique that combines photoemission with an interferometric approach to directly probe exciton coherence.

Beknopte samenvatting

Excitonen, dat wil zeggen elektron-gaatjesparen gebonden door Coulomb-aantrekkingskracht, zijn fundamentele excitaties in halfgeleiders en domineren hun niet-evenwichtige optische respons. Het begrijpen van hoe excitonen worden gegenereerd, hun daaropvolgende relaxatiedynamica en hoe ze interageren met andere vrijheidsgraden van het systeem is daarom essentieel voor zowel fundamenteel onderzoek als de ontwikkeling van technologische toepassingen zoals opto-elektronica en spintronica. Onlangs heeft de studie van exciton-fysica zich gericht op laag-dimensionale materialen, die, na de isolatie van grafeen uit grafiet in 2004 door de groep van Geim [124], het onderzoek naar halfgeleiderfysica domineerden. Tegenwoordig omvat de familie van tweedimensionale materialen een breed scala aan samenstellingen die de meeste elementen van het periodiek systeem bestrijken. Dit leidt tot een grote verscheidenheid aan elektronische eigenschappen, waaronder metalen, semimetalen, isolatoren en halfgeleiders met directe en indirecte bandgaps variërend van ultraviolet tot infrarood, inclusief het zichtbare spectrum [210]. In laag-dimensionale halfgeleiders maakt de vermindering van de afscherming veroorzaakt door geometrische beperking, samen met sterke licht-materie-interactie, excitonen een veelbelovend platform voor het bestuderen van exciton-dynamica en veel-lichaamsinteracties. In deze materialen zijn excitonen stabiel en minder beïnvloed door verstrooiingsprocessen, wat leidt tot decoherentietijden die langer zijn dan die van conventionele materialen, die typisch van de orde van enkele tientallen femtoseconden zijn. Bovendien maakt de stabiliteit van de exciton-resonantie, zelfs bij kamertemperatuur, het mogelijk om de exciton-dynamica van de vroege stadia tot een tijdschaal van de orde van nanoseconden te volgen. De studie van exciton-fysica heeft zich tot nu toe gericht op de vorming van excitonen [167, 182, 43], exciton-fonon koppeling [183, 157], hoge-harmonische generatie [93], valley-gepolariseerde exciton-dynamica [112], en de vorming van Floquet-staten door lichtverhulling van excitonen [83, 36, 164] in laag-dimensionale materialen met complexe elektronische structuren, gekarakteriseerd door de aanwezigheid van meerdere

valleien, zoals tweedimensionale overgangsmetaal-dichalcogeniden. Het doel van deze thesis is om een systematische studie van de exciton-fysica uit te voeren in de gelaagde loodvrije halfgeleider bismut-tri-jodide (BiI_3), met een quasi-directe bandgap en een rijk exciton-landschap waarin een geïsoleerde heldere exciton met een Frenkel-achtige karakter de optische respons domineert [77, 21]. De bijzondere structuur van BiI_3 , zowel in zijn bulk- als in zijn tweedimensionale vormen, maakt het een ideaal materiaal om de rol van de omgeving, zoals fononen, defecten en quasi-vrije dragers, in exciton-dynamica te onderzoeken, waarbij hun aanwezigheid kan worden gecontroleerd door de experimentele omstandigheden af te stemmen. Bovendien stelt BiI_3 ons in staat om de voordelen van laag-dimensionale structuren te benutten, zoals verbeterde structurele stabiliteit en lang-leven exciton-dynamica, terwijl we sommige van de bijbehorende uitdagingen, waaronder complexe experimentele omstandigheden, kunnen mitigeren. Aangezien de dynamica in kwestie plaatsvinden op subnanoseconde tijdschalen, zijn ultrakorte spectroscopieën, zowel in optiek als in foto-emissie, toegepast. All-optical transient spectroscopy wordt doorgaans gebruikt om foto-geïnduceerde relaxatiewegen en koppelingen in halfgeleiders te verkennen. Een pomp- en probe-schema, waarbij twee pulsen worden gegenereerd door een femtoseconde-puls laser, wordt gebruikt om het materiaal te foto-exciteren en momentopnames van het systeem te verzamelen in het niet-evenwichtige regime na de foto-excitatie. Deze krachtige techniek maakt het mogelijk om de evolutie van het transiënte signaal, zoals reflectantie, transmissie of absorptie, te analyseren in energie en tijd, maar biedt geen toegang tot het momentum-domein. Time- en angle-resolved photoemission spectroscopy is echter bekend om zijn hoge momentum-resolutie en de eenvoudigere interpretatie van het verzamelde signaal. Door deze twee spectroscopieën te combineren, is een uitgebreide karakterisering van de exciton-fysica bereikt in dit werk. Deze thesis begint met een overzicht van de exciton-fysica in gelaagde halfgeleiders, gevolgd door een beschrijving van de gebruikte methoden en materialen. De resultaten worden vervolgens gepresenteerd. In Hoofdstuk 4, wordt de vorming van excitonen uit een quasi-vrije elektronpopulatie in de geleidende band onderzocht met behulp van tijd-resolved angle-resolved photoemission tijdens een beam time in het T-Rex Lab van de Elettra Sincrotrone Trieste. Het exciton-signaal in foto-emissie wordt geïsoleerd en gevolgd in de tijd-, energie- en momentum-domeinen. In Hoofdstuk 5, onderzoeken we de manifestatie van een exciton-coherente toestand door middel van transiënte optische spectroscopie, evenals de overgang van het coherente naar het incoherente regime. Hoofdstuk 6 richt zich op veellichaamsinteracties tussen excitonen en fononen, evenals tussen excitonen en vrije dragers. De experimentele resultaten worden aangevuld met theoretische voorspellingen, in samenwerking met een theoretische groep bestaande uit Jorge Cervantes-Villanueva en Alejandro Molina-Sánchez (Universiteit van Valencia), Davide Sangalli (Istituto della Materia-CNR), en Simona Achilli (Università

degli studi di Milano). Ten slotte presenteert Hoofdstuk 7 voorlopige resultaten van een krachtige experimentele techniek die foto-emissie combineert met een interferometrische benadering om direct de exciton-coherentie te onderzoeken.

List of Abbreviations

2D Two dimensional. 6, 12, 14, 17, 20, 64, 70, 97, 98, 112

2DES Two dimensional electronic spectroscopy. 17, 19

2PPE two photon photoemission. 121, 122

3D Three dimensional. 6

ARPES angle-resolved photoemission spectroscopy. xxviii, 25–27, 29–35, 57–61, 64, 69–71

BBO Beta barium borate. 79, 96, 135, 143, 153

BF Band filling. 36

BGR Band gap renormalization. 36

BSE Behte Salpeter equation. 10, 18, 64, 65, 71, 72, 75, 88, 102, 104, 110–112

CB Conduction band. 1, 3–7, 9, 15, 34, 38, 96

CC Cross correlation. 62–64, 68

DECP Displacive excitation of coherent phonons. 41

DFT Density functional theory. 2, 9, 44, 45, 59, 64, 71, 72, 75, 109

DOS density of states. 28

EDC energy distribution curve. 62, 63, 68

ESA excites state absorption. 36

- FC** free carriers. 64, 69
- FD** Fermi edge. 135, 136
- FE** free exciton. 8, 10, 64, 66–68, 70, 71
- FT** Fourier Transformation. 70, 71, 84, 85, 100, 101, 103, 114–116
- FTIR** Fourier Transform infrared spectroscopy. 53, 146
- GSB** Ground state bleaching. 36
- HK** Hohenberg-Kohn. 2
- HOMO** highest occupied molecular orbital. 8
- HOPG** Highly oriented pyrolytic graphite. 79, 80, 98, 99
- inter-tr-2PPE** interferometric time-resolved two photon photoemission. 121, 123, 124, 134, 137
- IP** Independent Particle. 112
- IPS** Image potential state. 135–137
- IQP** Independent quasiparticle. 33
- ISRS** Impulsive stimulated Raman scattering. 41
- JDOS** Joint density of states. 4, 6
- KS** Kohn Sham. 110
- LUMO** lowest unoccupied molecular orbital. 8
- MDC** momentum distribution curve. 68
- NOPA** Non-collinear optical parametric amplifier. 78
- OBE** optical Bloch equation. 124–127, 137
- PBE** Perdew-Burke-Ernzerhof. 45, 109, 110
- PE** photoemission/photoemitted. 58–65, 67–70, 123
- PL** Photoluminescence. 7, 66

- SE** Stimulated emission. 36, 37
- SOC** Spin orbit coupling. 45, 46, 110
- SS** Shockley state. 135–138
- STE** Self trapped exciton. 21, 22, 67
- TE** Trapped exciton. 12, 21, 22, 66, 68, 71
- TL** Tauc-Lorentz. 82
- TMD** Transition metal dichalcogenides. 6, 7, 13, 55
- TOF** Time of flight. 135
- TR** Transient reflectance. 25, 84–88, 91, 97, 98, 100, 113–116, 120
- tr-2PPE** time-resolved two photon photoemission. 123
- tr-ARPES** time-resolved angle-resolved photoemission spectroscopy. 27, 30, 31, 57, 59, 60, 64, 65, 71, 72, 74, 75, 121, 139, 143
- VB** valence band. 1, 3, 5–7, 9, 15, 33, 57, 58
- WLG** white light generation. 78, 80
- YAG** Yttrium Aluminium Garnet. 78, 96

List of Symbols

$\langle \hbar\omega \rangle$	Average phonon energy
$\langle \hbar\omega \rangle_X$	Average phonon energy coupled to the exciton with energy E_x
$\langle r_n \rangle$	Exciton Bohr radius
α	Absorption
β_1	First parameter for the Varshni equation
β_2	Second parameter for the Varshni equation
χ	susceptibility
$\Delta\phi$	phase difference
$\Delta\tau$	Delay variation
Δd_B	Thickness variation
δI	Intensity variation
δn	Variation in the electronic population
ΔR_{par}	Parametrized transient reflectance
δ_{eo}	group velocity mismatch
δ_{ij}	Detuning
ϵ	Complex dielectric function
ϵ_0	electric permittivity in vacuum
ϵ_1	Real part of the dielectric function
ϵ_2	Imaginary part of the dielectric function

$\epsilon_{i,L}$	Lorentz imaginary dielectric function
$\epsilon_{i,TL}$	Tauc Lorentz imaginary dielectric function
$\epsilon_{i,T}$	Tauc imaginary dielectric function
$\epsilon_{r,TL}$	Tauc Lorentz real dielectric function
ϵ_{TL}	Tauc Lorentz complex dielectric function
Γ_x	Exciton linewidth
Γ_{xI}	Temperature-independent inhomogeneous broadening
$\hbar$	Reduced Plank constant
$\mathbf{k}_e$	Momentum of the electron
$\mathbf{k}_h$	momentum of the hole
$\mathbf{R}$	Coordinates of the electron-hole centre of mass
$\mathbf{r}_e$	Position of the electron
$\mathbf{r}_h$	Position of the hole
μ	Reduced mass
ν	Frequency
Ω	Phonon Frequency
ω_l	Frequency of the electric field
ω_{CV}	Frequency difference between the valence band and the conduction band.
ϕ	work function
ρ	Density matrix
ρ_{ii}	Population of the j-th state
ρ_{ij}	Coherence between the i-th and the j-th state
σ_l	Width of the electric field
τ	Delay time between the pump and the probe
τ_d	Dumping time
τ_e	Exponential decay time

φ	Azimuthal angle
ϑ	Polar angle
ξ	Penetration depth
A	Optical Absorption
A_l	Amplitude of the electric field
D	Density of states
d_A	Thickness block A
d_B	Thickness block B
d_e	Spot Raman beam
D_J	Joint density of states
d_{ij}	dipole moment
e	electronic charge
$E - E_{VB}$	Intermediate state energy
E_B	Binding energy
E_C	Conduction band energy
E_g	Fundamental band gap
E_K	Kinetic energy
E_n	Energy of the N exciton in the Rydberg series
E_V	Valence band energy
E_X	Exciton energy
E_{CV}	Energy difference between the valence band and the conduction band.
F^*	Threshold luence
F_a	Absorbed fluence
f_{CV}	Oscillator strength
h	Plank constant
I_0	Incident intensity

I_A	Absorbed intensity
I_R	Reflected intensity
I_S	scattered intensity
I_T	Transmitted intensity
I_{Cu}	Light reflected by a sample of Cu
k_B	Boltzmann constant
k_x	x-component of the photoelectron momentum
k_y	y-component of the photoelectron momentum
k_z	z-component of the photoelectron momentum
$k_{ }$	parallel-component of the photoelectron momentum
$k_{\perp}$	perpendicular-component of the photoelectron momentum
m_C	Effective mass of electron in the conduction band
m_e	electronic mass
m_e^*	effective electronic mass
m_h^*	effective hole mass
m_V	Effective mass of electron in the valence band
n	refractive index
n_e	Electronic density
n_c	Electrons in the conduction band
n_{ph}	Photon density
P_{CV}	Dipole matrix element
P_{CV}	Dipole moment between valence and conduction band
Q	Lattice displacement
R	Reflectance
$R_{par,eq}$	Parametrized equilibrium reflectance
$R_{par,neq}$	Parametrized out of equilibrium reflectance

S	Electron-phonon coupling strength
S_K	Constant energy surface
S_X	Exciton-phonon coupling strength
T	Temperature
T	Transmission
T_2^*	Pure dephasing time
T_1^1	Depopulation time of the intermediate state
T_2^{01}	Dephasing time between the initial and intermediate state
T_2^{02}	Dephasing time between the initial and final state
T_2^{12}	Dephasing time between the intermediate and final state
T_1	Depopulation time
T_2	Dephasing time
V_0	Inner potential
v_{ge}	group velocity in the extraordinary medium
v_{go}	group velocity in the ordinary medium
F	Fluence
n	Quantum number

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Chapter 1

Exciton physics in layered semiconductors

In this chapter, we outline the general context of out-of-equilibrium physics in semiconductors, within which the topics of this thesis are framed. In the first part, we describe the equilibrium properties of semiconductors and the quasiparticles involved. In particular, we focus on the impact of the dimensionality on the absorption edge and the excitonic feature. In the second part, we discuss the out-of-equilibrium properties. Specifically, we trace the photoinduced exciton evolution, starting with its formation and following its relaxation pathways and interactions with other degrees of freedom of the system. Furthermore, we provide a detailed focus on the coherent state and its observation. Indeed, a better understanding of the manifestation of coherence in semiconductors is a crucial milestone toward achieving optical control of coherence. We then provide a description of the exciton-phonon coupling. Finally, we offer a brief description of the exciton Mott transition and the localized exciton.

1.1 Onset of the absorption in semiconductors

In this section, we describe the absorption in semiconductors in the absence of excitonic effects with a final remark on the impact of dimensionality on the absorption band edge. Inorganic semiconductors and insulators show a filled band, namely the *valence band* (VB) and an empty band, the *conduction band* (CB), separated by a fundamental band gap (E_g), whose value spans from a few

hundreds of meV to a few eV [96]. In three-dimensional materials, the density of states is $D(E) = \frac{\sqrt{2m_e^3}}{\hbar^3\pi^2} \sqrt{E}$, where m_e is the mass of the electron and $\hbar$ is the reduced Planck constant.

The calculation of the band structure is not trivial since it involves the solution of a many-body Schrödinger equation for a N-particle system described by an eigenvalue E and a eigenfunction $\psi(\mathbf{r}_{e1}, \dots, \mathbf{r}_{eN})$, which is function of $3N$ coordinates. The Hamiltonian describing the system, in the Born-Oppenheimer approximation of fixed nuclei, accounts for the electronic kinetic energy, the interaction among the electrons and the electron-ion interaction. Since the computational complexity increases significantly with the number of elements of the system, to describe complex solid states system some approximations are needed. Plenty of theories have been developed in response to this need and tailored to the physical question.

Density functional theory (DFT) is one of the most widely used theories, and it is the one used to simulate the theoretical predictions that complement our experimental results inserted in this thesis. To give context, we will briefly describe the fundamental concept of *ab initio* simulations. Kohn found that the ground state $\psi(\mathbf{r}_{e1}, \dots, \mathbf{r}_{eN})$ is simplified by writing it as a function of the electronic density $n_e(\mathbf{r})$, reducing the dimensionality from $3N$ to 3 [101, 65]. Moreover, from the first Hohenberg-Khon (HK) theorem, the external potential is a unique function of the density. The second HK theorem dictates that the density that minimizes the energy corresponds to the exact ground state energy. With these concepts, the Schrodinger equation is simplified without using any approximations. However, DFT calculations are usually carried out by defining the density for a non-interacting system (Kohn-Sham system), modelling the electron-electron interaction classically and the electron-ion Coulomb interaction by an external potential. Despite the simplification, spin-orbit coupling and other relativistic effects can be taken into account. The local density functional approximation to the Kohn-Sham potential (describing the non-interacting system) overestimates the fundamental band gap by a factor of 40% [132]. In this framework, the system is non-interacting and does not take into account the change in the screening after the addition or subtraction of an electron from the system. The screening is accounted for the GW approximation, where G refers to the propagation of one particle in an interacting system, described with the Green's functions, and W is the response screened Coulomb interaction [144]. To calculate the band structure, a hybrid GW-DFT approach is used, where the eigenvalue entering in the calculation on the Green's function comes from the GW and the eigenfunctions are calculated from the Kohn-Sham equation [126]. As the last step, observables, such as absorption, can be calculated using as a starting point GW-DFT simulations.

After this brief description of how the electronic structures can be retrieved, we will continue to describe the properties of semiconductors using a simplified

picture where the band structure is composed of two bands: the CB with an upward dispersion and the VB with a downward dispersion separated by an energy gap equal to E_g (Fig. 1.1(a)). In this picture, the electrons are surrounded by other electrons in the conduction or valence band. The electrons are, then, not free to move in the crystal, but they feel a screening, which is included in the effective mass m_V and m_C for electrons in the valence and conduction bands, respectively.

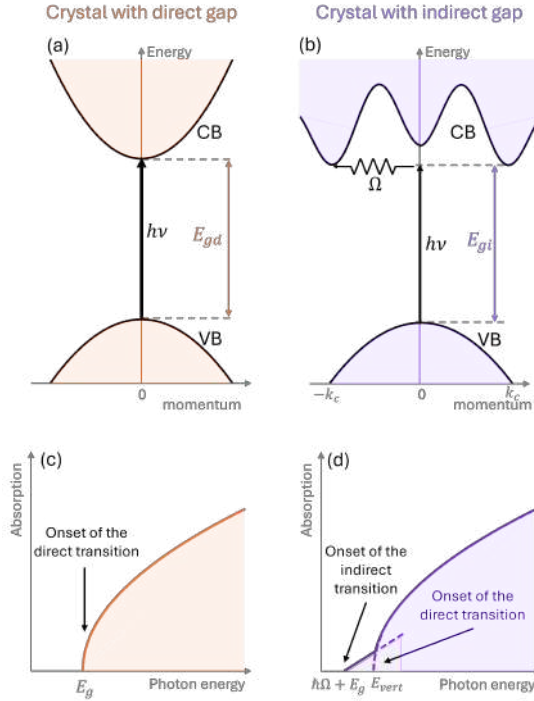


Figure 1.1: (a) Simplified diagram of the band structure of a direct semiconductor. (b) Simplified diagram of the band structure of an indirect semiconductor. (c) Absorption in a direct semiconductor. (d) Absorption in an indirect semiconductor. Adapted from [81].

If the CB minimum and the VB maximum are located in the same position of the Brillouin zone as shown in Fig. 1.1(a), the semiconductor shows a direct band gap, while if they are located at two different points in the Brillouin zone (Fig. 1.1(b)), it shows an indirect band gap. At zero temperature, semiconductors are indistinguishable from insulators. Indeed, at finite temperature, there is a non-zero probability that the electrons can be thermally excited, producing a

population in the CB proportional to the $\exp(-E_g/2k_B T)$, where E_g is the energy band gap and the k_B is the Boltzmann constant. When the temperature is able to excite the electrons in the conduction band, an increase in the conductivity is observed with the increase of the temperature, which is the opposite behaviour of the metals. The presence of defects produces in-gap levels, which are usually located at a few tens of meV near the band edges for shallow defects [5] and affect the conductivity.

The equilibrium optical properties of semiconductors depends on the absorption of light with photon energy $\hbar\nu$. The absorption results from the interband and intraband allowed transition in the energy band of the semiconductor. In direct semiconductors, the threshold for continuous optical absorption is the energy of the band gap, as shown in Fig. 1.1(a). When $\hbar\nu > E_g$, the photon is absorbed with the creation of an electron and a hole. The imaginary part of the dielectric function is described by the following equation:

$$\epsilon_2 = \frac{1}{4\pi\epsilon_0} \left(\frac{2\pi e}{m_e \omega} \right)^2 \sum_{\mathbf{k}} |P_{CV}|^2 \delta(E_C(\mathbf{k}) - E_V(\mathbf{k}) - \hbar\omega) \quad (1.1)$$

where P_{CV} is the dipole matrix element between the valence and the conduction band, E_C is the energy of the conduction band, and E_V is the energy of the valence band. The main contribution is due to the summation of the delta function, which constitutes the joint density of state (JDOS):

$$D_J(E_C - E_V) = \frac{1}{V} \sum_{\mathbf{k}} \delta(E_C(\mathbf{k}) - E_V(\mathbf{k}) - \hbar\omega) \quad (1.2)$$

where V is the volume, E_C is the energy of the conduction band, E_V is the energy of the valence band and ω is the frequency. JDOS gives information on the allowed optical transition between the valence and conduction electronic state at a specific photon energy [18]. To completeness, the real part of the dielectric function is retrieved through the Kramer-Kroenig relations, obtaining the following expression:

$$\epsilon_1 = 1 + \frac{4\pi e^2}{4\pi\epsilon_0 m_e} \left[\sum_{\mathbf{k}} \left(\frac{2}{m_e \hbar \omega_{CV}} \right) \frac{|P_{CV}|^2}{\omega_{CV}^2 - \omega^2} \right] \quad (1.3)$$

where $E_{CV}(\mathbf{k}) = \hbar\omega_{CV} = E_C(\mathbf{k}) - E_V(\mathbf{k})$ is the energy difference between the conduction and valence band energies. This expression resembles the dielectric function for harmonic oscillators in arrangement with the Drude-Lorentz model. The strength of the oscillator f_{CV} is defined as:

$$f_{CV} = \frac{2|P_{CV}|^2}{m_e \hbar \omega_{CV}} \quad (1.4)$$

The joint density of states above the threshold value ($E_{CV} > E_g$) for a three-dimensional material is:

$$D_J = \frac{\sqrt{2\mu^3}}{\pi^2 \hbar^3} \sqrt{E_{CV} - E_g} \quad (1.5)$$

where μ is the reduced mass: $1/\mu = 1/m_V + 1/m_C$. The expression for the JDOS is very similar to the one for the density of states. The absorption α is then: $\alpha(\omega) = \frac{\omega}{cn(\omega)} \epsilon_2(\omega)$ where c is the light velocity and $n(\omega)$ is the frequency-dependent refractive index. The imaginary part of the dielectric function takes the form of:

$$\epsilon_2 = A \sqrt{\hbar\omega - E_g} \quad (1.6)$$

as shown by the Fig. 1.1 (c). The situation in indirect semiconductors is different. Since the CB maximum and the VB minimum are in different positions in the Brillouin zone, to promote an electron in the conduction band also the involvement of phonons is crucial. Phonons are quasiparticles resulting from the quantization of crystal lattice vibration, carrying a momentum $\mathbf{k}_{ph}$ and an energy $\hbar\Omega$, which is generally lower than the band gap, typical values span from 0.01 to 0.03 eV. If the temperature is high enough, phonons can already be thermally excited. Therefore, during the absorption process, the conservation of energy and momentum should be conserved and $\hbar\nu + \hbar\Omega > E_g$. Therefore, the onset of the absorption appears at lower energies than the onset of direct edge as described in Fig. 1.1 (d). After the onset of the direct transition, the calculated absorption is similar to the direct case.

The temperature induces a shift in the onset of direct absorption. The first model introduced to describe the widening of the band gap decreasing the temperature is the Varshni equation [187]:

$$E_g(T) = E_g(0) - \beta_1 \frac{T^2}{T + \beta_2} \quad (1.7)$$

Where β_1 and β_2 are fitting parameters typical for each semiconductor, and the latter is related to the Debye temperature. However, for some specific materials, β_2 is negative [127]. Moreover, at low-temperature, Equation 1.7 does not correctly follow the temperature-induced energy band gap evolution. To overcome this, a new equation that encompasses lattice expansion and the electron-phonon coupling both with optical and acoustic phonons using the average phonon energy is proposed. The interaction is then described through the Bose-Einstein statistical factor, where the exponential term is converted into a hyperbolic cotangent by Euler's formula. In this framework, O'Donnel has proposed a valid substitution for the Varshni equation :

$$E_g(T) = E_g(0) - S < \hbar\omega > [\coth(\frac{< \hbar\omega >}{2k_B T}) - 1] \quad (1.8)$$

where S is a dimensionless electron-phonon coupling constant, $\langle \hbar\omega \rangle$ is the average phonon energy, and k_B is the Boltzmann constant [127].

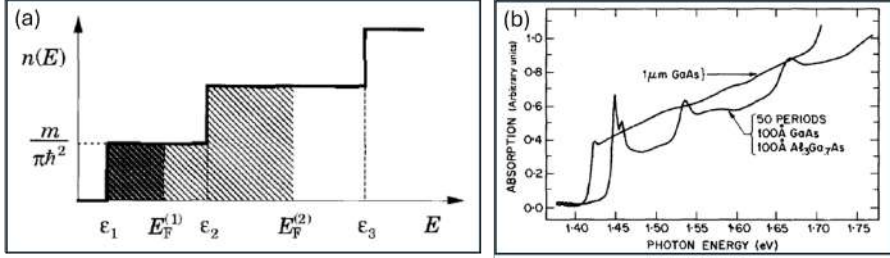


Figure 1.2: (a) Density of state in a 2D semiconductor. (b) Comparison of the absorption in 3D and 2D GaAs. Images from [40]

In low-dimensional materials, the absorption edge changes shape [40]. In particular, in these semiconductors, the density of state ($D(E)$) above the energy gap, shown in Fig. 1.2(a), becomes:

$$D(E) = \frac{m_e}{\pi\hbar} \quad (1.9)$$

where m_e is the electron mass. The density of states for a 2D material is per unit area instead of unit volume, as in the 3D case. By comparison with the 3D case, the JDOS defined in Equation 1.2 has the same form of the density of state:

$$D_J = \frac{\mu}{\pi\hbar^2} \quad (1.10)$$

where μ is the reduced mass. Fig. 1.2 (b) shows a comparison with the absorption of bulk GaAs and low dimensional GaAs, retrieved as heterostructures of GaAs/AlGaAs layers. The bulk GaAs show the absorption that follows Equation 1.6, while, in the low-dimensional case, it shows several squared subbands. It should be noted that the initial increase of all the subbands is due to excitonic effects. Moreover, the active sample is lower in the 2D case than in the 3D case since, in the first case, the active region is an area, while in the second case, it is a volume.

The reduction of dimensionality influences the electronic structure depending on the band character. In transition metal dichalcogenides (TMDs), the exfoliation up to the monolayer produces a change in the position of the CB minimum and VB maximum. This results in a change in the band gap structure from the indirect to direct [100]. Specifically, using MoS₂ as an example [169], decreasing

the dimensionality, the direct band gap at Γ barely changes. Otherwise, the indirect gap one at K increases monotonically. The origin of this different behaviour resides in the character of the bands in the momentum space. Indeed, at K, the conduction band is constituted by d orbitals of Mo, showing a low interlayer interaction, while at Γ , the states are a linear combination between d orbitals of the Mo atoms and the antibonding p_z states of S. In this case, the interlayer interaction becomes non-negligible, and therefore, the energy position of the states depends drastically on the number of layers. In TMDs, the CB and the VB are located in two nonequivalent points in the Brillouin zone; the lack of the inversion symmetry produces a split of the band due to spin-orbit interaction. Moreover, the time-reversal symmetry produces an opposite spin in the bands in the two valleys [100]. In general, the electronic properties of TMDs depend drastically on the number of layers due to the change in the screening environment and a different symmetry [72]. From an experimental point of view, the transition from an indirect band gap to a direct character in TMDs has been observed by photoluminescence (PL) measurement [97]. In indirect semiconductors, the photoluminescence is a photo-assisted phonon process with a low quantum yield. But decreasing the dimensionality there is a monotonically increase of the PL intensity. Moreover, the photoluminescence spectrum shows two structures, one assigned to the direct and the second to the indirect transition. From a bulk state to the monolayer, there is a gradual dominance of the peak associated with the direct transition. However, in absorption, the spectrum does not change the shape but shows only a blueshift of the edge of the absorption, resulting from a change in the screening of the material. An analogous effect is shown in double halide perovskites where the electronic structure is dominated by d electrons [33]. Moreover, Connor et al. state that, in general, the change in the band structure is mainly due to the d band; in fact, in material dominated by sp-bounded structures, the low dimensionality induces different effects to take place. Indeed, other layered materials show no changes in the direct band edge, i.e. in phosphorine the band always remains direct. In this wide panorama, BiI_3 is a quasi-direct semiconductor both in bulk and in monolayer, and reducing the dimensionality, small changes in the electronic structure occur [21].

1.2 Excitons in layered semiconductors

Excitons are quasiparticles that form from the absorption of light in a semiconductor, serving as a prime mechanism in light emission and recombination in low dimensional materials [210, 120]. Also, a simplified description based on the single-particle approximation is shown in Fig. 1.3(a).

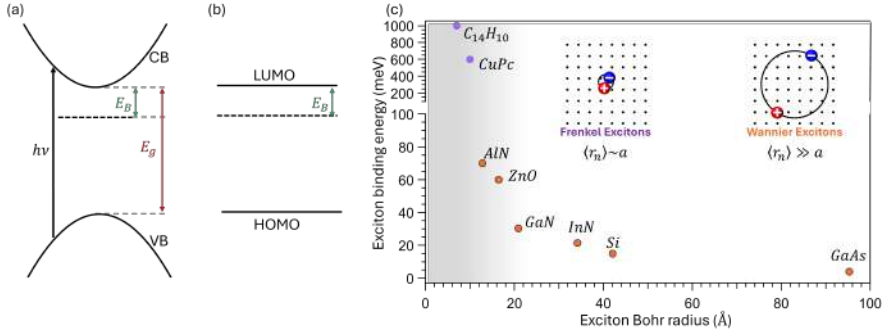


Figure 1.3: (a) Simplified diagram of the band structure of an inorganic semiconductor. (b) Simplified diagram of the band structure of an organic semiconductor. (c) Binding energy vs exciton Bohr radius diagram for exciton in bulk semiconductors. Data digitized from [82, 44].

Under photoexcitation with photon energy that exceeds the fundamental band gap ($h\nu > E_g$), a population of electrons is brought into the conduction band; consequently, a population of holes is left behind in the valence band. When the electronic group velocity and the hole group velocity are the same, a correlated motion is produced by the electrostatic Coulomb attraction between the electron and the hole, creating free excitons (FEs). However, the two group velocities have a similar modulus and the exciton can then be assimilated to the electron-proton bound state of the hydrogen atom. The newly created FEs move freely in the crystal, carrying energy and not charge, being a neutral quasiparticle[81]. The bound electron-hole pairs are characterized by a *binding energy*, which corresponds to the difference between the renormalized free particle band gap energy and the absolute energy of the exciton transition and an *exciton Bohr radius*, which encodes the extension of the exciton wave function in real space. The exciton description also holds for organic material where, by comparison, the valence band and the conduction band are substituted by the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively (see Fig. 1.3(b)).

As depicted in Fig. 1.3(c), the FEs can be discerned depending on the localization of their wave function and the binding strength.

In the case of organic semiconductors, the electron and hole are located in the same or nearest neighbouring site, resulting in more bound *Frenkel excitons*. Typical values for exciton binding energies in these materials are on the order of 0.1-1 eV, some examples of exciton binding energies are inserted in Fig. 1.3(c)[101].

In contrast to the previous case, inorganic semiconductors have typically large

dielectric constants, the electrostatic attraction between the electron in the CB and the hole in the VB is then screened by the surrounding electrons in the valence band, resulting in a weakly bounded exciton and the corresponding extension is much larger than the lattice spacing[192, 119]. Since the electron-hole interaction is screened, *Mott-Wannier excitons* are described within the effective mass approximation where the electron and the hole have the effective mass m_e^* and m_h^* of the valence and conduction band respectively[101, 206]. The exciton wave function Ψ results as a combination of Bloch functions for the electron ($\psi_{\mathbf{k}_e}(\mathbf{r}_e)$) and the hole ($\psi_{\mathbf{k}_h}(\mathbf{r}_h)$):

$$\Psi(\mathbf{r}_e, \mathbf{r}_h) = \sum_{\mathbf{k}_e, \mathbf{k}_h} C(\mathbf{k}_e, \mathbf{k}_h) \psi_{\mathbf{k}_e}(\mathbf{r}_e) \psi_{\mathbf{k}_h}(\mathbf{r}_h) \quad (1.11)$$

Considering the interaction of the electron and the hole with the crystal lattice in the hole and electron effective mass, the equation of the electron and the hole:

$$\left[-\frac{\hbar^2}{2m_e^*} \nabla_e^2 - \frac{\hbar^2}{2m_h^*} \nabla_h^2 - \frac{e^2}{\epsilon |\mathbf{r}_e - \mathbf{r}_h|} - \varepsilon \right] \Psi(\mathbf{r}_e, \mathbf{r}_h) = 0 \quad (1.12)$$

which is the same equation that an electron and a proton should fulfil to form a hydrogen atom. The equation can be separated into two parts: one describing the centre-of-mass motion:

$$\left[-\frac{\hbar^2}{2(m_e^* + m_h^*)} \nabla_{\mathbf{R}}^2 - \varepsilon_{\mathbf{R}} \right] \Psi(\mathbf{R}) = 0 \quad (1.13)$$

and the second describes the relative motion of the electron and the hole, which depends on the Coulomb attraction:

$$\left[-\frac{\hbar^2}{2\mu} \nabla_{\mathbf{r}}^2 - \frac{e^2}{\epsilon |\mathbf{r}_e - \mathbf{r}_h|} - \varepsilon_B \right] \Psi(\mathbf{r}) = 0 \quad (1.14)$$

The resolution follows exactly the one for the hydrogen atom. The energy is then

$$En = (-13.6\text{eV}) \frac{\mu}{m_e \epsilon^2 n^2} \quad (1.15)$$

which describes the hydrogen-like excitonic series. Also, the excitonic Bohr radius can be retrieved:

$$\langle r_n \rangle = \frac{m_e \epsilon}{\mu} n^2 a_B \quad (1.16)$$

Therefore, the binding energy is proportional to the inverse of the excitonic Bohr radius $En \propto \frac{1}{\langle r_n \rangle}$ as shown in Fig. 1.3(c). Typical values for binding energies in semiconductors are of the order of 10-30 meV with a spatial extent of tens of lattice constant ($\simeq 100 \text{ \AA}$) [207, 44].

Exciton states are calculated in the framework of the GW-DFT scheme described

in Section 1.8 solving the Bethe Salpeter equation (BSE). In BSE, the exciton polarization is proportional to the product of two one-particle Green's functions, electing BSE as a direct evolution of the GW scheme for a two-particle system. The resulting Hamiltonian has two main contributions: one takes into account the bare Coulomb interaction, while the second represents the screened electron-hole interaction [126].

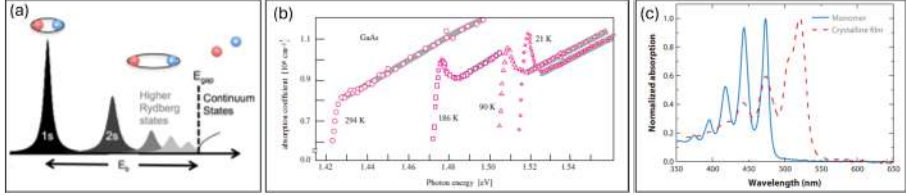


Figure 1.4: (a) Absorption associated to the Hydrogenoid series of excitons. Adapted from [35]. (b) Temperature dependence of bulk GaAs. Image from [206] (c) Absorption spectra for a single molecule and molecular systems. Data taken from [8].

Elliot [46] calculated the imaginary part of the dielectric function for materials dominated by excitons:

$$\epsilon_2(h\nu) = \frac{\mu^3 |P_{CV}|^2}{8\pi^2 \epsilon^6 \omega^2} \sum_1^{+\infty} \frac{1}{n^3} \delta(\omega - \omega_n) \quad (1.17)$$

where μ is the reduced mass, n is the quantum number, ω_n is the frequency related to the n -th exciton level in the Rydberg excitonic series and P_{CV} is the dipole element. Excitons produce in-gap absorption resonances that are neglected otherwise. In-gap absorption of excitons has a Lorentian-like shape (as shown in Fig. 1.4 (a)), where the width accounts for the homogeneous and inhomogeneous broadening. The homogeneous broadening is related to the lifetime of the state, which results from the Heisenberg uncertainty principle. The presence of defects and other centers of scattering in the systems produces an inhomogeneous broadening. Furthermore, when the exciton energy is near the conduction band edge, the exciton series accumulates, becoming a continuum of states. If the continuum is resonant to the conduction band, the absorption also results in an enhancement above the fundamental band gap. Examples of absorption spectra for a bulk GaAs semiconductor are inserted in Fig. 1.4 (b). FEs in GaAs have a binding energy of 5 meV, lower than the energy of 25 meV due to room temperature. Indeed, the exciton does not form or is easily destroyed at room temperature, resulting in the absence of a near-edge excitonic structure. Anyway, the absorption above the onset of the conduction

band still shows an enhancement due to the exciton continuum. Decreasing the temperature, an in-gap excitonic feature appears.

The exciton resonance shows a trend with the temperature, which depends both on the temperature-induced band-gap renormalization and the thermal effect on the exciton binding energies. The shift in energy depends on electron-phonon coupling between the electron and the lattice vibration, and the increase of the phonon availability of the population of phonons under photoexcitation drives the transition between the ground state and the exciton [142]. The formal description is analogous to the one described in Section 1.1, and it is reported here:

$$E_X(T) = E_X(0) - S_X < \hbar\omega >_X [\coth(\frac{< \hbar\omega >_X}{2k_B T}) - 1] \quad (1.18)$$

where $E_X(0)$ is the energy of the exciton at 0 K, S_X is related to the strength of exciton-phonon coupling, and $< \hbar\omega >_X$ is the average energy of the phonon coupled with the exciton. Moreover, the exciton linewidth broads with the increasing of the temperature depending on the scattering processes involved as follows:

$$\Gamma_X = \Gamma_{XI} + \frac{\gamma_{X,ph}}{e^{\frac{< \hbar\omega >_X}{k_B T}} - 1} \quad (1.19)$$

where Γ_{XI} is the inhomogeneous broadening due to temperature-independent scattering with exciton and defects in the system, and the second term is related to the exciton-phonon scattering.

In Frenkel exciton, on the contrary, the large binding energies induce the possibility to observe excited excitonic states [101, 8]. Indeed, the absorption and photoluminescence spectroscopy show resamble to the molecular states with slight differences: a small shift, different linewidths, and a vibronic progression. Fig. 1.4(c) shows an absorption measurement for a single molecule (solid blue line) and a molecular system (dashed red curve). Respect to the single molecule case, the first absorption peak is blue shifted and show a double peak feature resulting from the Davydov splitting. This effect comes from the multiple bands coming from a multiple molecule in the crystal unit cell [8].

We should note that the distinction between Wannier and Frenkel excitons is not sharp, some intermediate cases are registered.

The exciton is a composed quasiparticle that moves freely in the crystal structure. In agreement with the Bloch theorem, the electron-hole bound state is characterized by a momentum $\mathbf{k}$ and a parabolic energy dispersion in momentum if the wavevector is much lower than the lattice constant. After photoexcitation, excitons are bright if the electron and hole are located in the same position in the Brillouin zone and have opposite spin and recombine with the emission of photons. Bright excitons are the only optically active, and a simplified sketch is inserted in Fig. 1.5. In spin-forbidden dark excitons, the electron and the hole have opposite spins, and they cannot recombine via direct

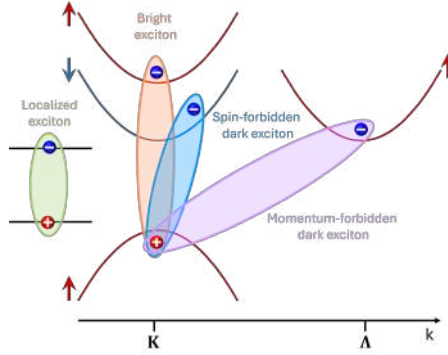


Figure 1.5: Visualization of bright, dark and localized excitons. Adapted from [210].

emission of a photon since the spin conservation is not fulfilled. Moreover, in momentum-forbidden dark exciton, the electron and the hole are located at different points in the Brillouin zone, as in the case of indirect semiconductors or when the absorption process involves phonons, the direct emission is neglected for the conservation law of momentum. In general, the recombination time of dark excitons is much longer than that of the bright ones. Eventually, the electrons and the holes can be allocated in the defect-generated-in-gap levels; the resulting exciton is then trapped in the modification in the crystal lattice, becoming trapped exciton (TE).

In two-dimensional material, the excitonic wave function is spatially confined in the layer for the geometrical change from a three-dimensional layered structure to a bi-dimensional monolayer (as shown Fig. 1.6(a)). This results in a significant reduction in the screening. As a consequence, the dielectric constant $\epsilon > 1$ in bulk materials falls to $\epsilon = 1$ in low-dimensional material. The change in the screening environment results in an increase of the electron-hole Coulomb attraction, in more bound excitons, and in a higher separation from the conduction band as shown in Fig. 1.4(b). In this situation, their binding energy rises to 0.1 - 1 eV, which is usually 30% of the quasiparticle band gap of two-dimensional materials [28, 210]. Specifically in 2D semiconductors, the binding energy shows a linear proportionality to the energy band gap of the material: $E_b \propto E_g/4$ as shown in Fig. 1.6(c).

The enhancement of the binding energy and the oscillator strength of the exciton produces many new effects. Exciton with an enhanced oscillator strength and larger binding energy dominates the optical response of 2D semiconductors and shows its Rydberg series as predicted by the hydrogen atom description of the

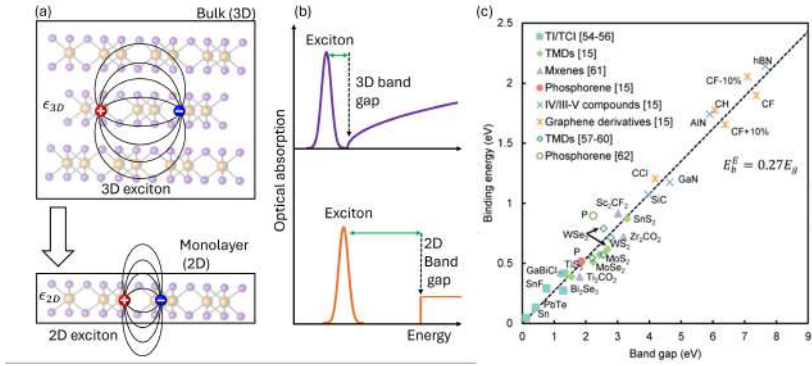


Figure 1.6: (a) Visualization of the geometrical confinement of the excitonic wave function. Adapted from [28] (b) Dimensional-induced change in the absorption spectrum. Adapted from [28] (c) Relation between the binding energy and the band gap in two-dimensional materials. Image from [210].

Wannier-Mott excitons with energies:

$$E_n = -13.6 \text{ eV} \frac{\mu}{m_e \epsilon^2 n^2} \quad (1.20)$$

Moreover, the strong absorption ensures a long lifetime of exciton and a visible in-gap absorption also at room temperature, conversely respecting the GaAs example. Eventually, new many-particle phenomena will arise with novel quasiparticle typologies such as trion, biexcitons, and interlayer excitons.

Trions are localized three-particle excitations that are negatively or positively charged, which are basically charged excitons. Positive trions are composed of two holes and an electron, while negative trions are complex of a hole and two electrons. The binding energy of trions is on the order of a few tens of meV for TMD up to a hundred meV in phosphorene [210]. Trions are observed as a resonance just energetically below the exciton through temperature-dependent photoluminescence spectroscopy [172], electrical modulation probed via photoluminescence spectroscopy [202], non-linear optical spectroscopy [204] and until finding excited state by static absorption [4].

Biexcitons are two-exciton complexes, also called molecular excitons, resulting then in a neutral particle. Opposite to the free exciton case where the repulsive Coulomb interaction dominates, biexcitons are created when the attractive Coulomb interaction is dominant. Biexcitons manifest as a peak at lower energy with superlinear behaviour with respect to the intensity of the impinging [205]. Moreover, it is observed in gate photoluminescence spectroscopy where its stability was demonstrated [162].

In addition, low-dimensional material shows an interlayer exciton, which is

an electron-hole-bound state where the electron and the hole are located in two different layers. Under photoexcitation, during the coherent exciton state, the hole can tunnel into another layer assisted by absorption and emission of phonons, forming an incoherent interlayer exciton.

1.3 Out-of-equilibrium properties in semiconductors

After the excitation with ultrashort laser pulses, a semiconductor undergoes several stages of relaxation before returning to the equilibrium. The energy is transferred first to the electrons and then to the lattice. The interaction includes several regimes of carrier excitation and relaxation. We can distinguish the following four regimes: (i) carrier excitation, (ii) thermalization, (iii) carrier removal, and (iv) thermal and structural effects, as shown in Fig. 1.7 [174].

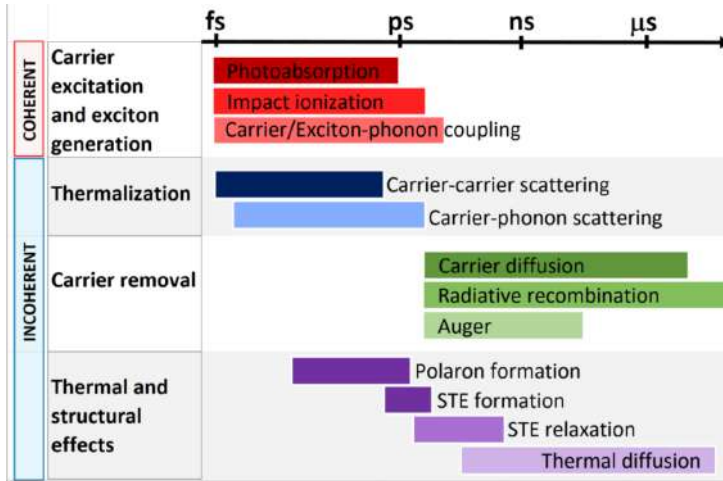


Figure 1.7: Time of the photoinduced processes in semiconductors. Image from [117].

Moreover, impulsive excitation can create coupling among quasiparticles, and also, the relaxation pathways are sensitive to collective modes, such as lattice vibration, charge and spin waves [52]. In layered semiconductors, since the reduction of the dimensionality results in a large oscillator strength, a strong light-matter interaction [191, 169, 90], and a significant many-body coupling, the 2D semiconductor relaxation dynamics are dominated by the photoinduced exciton evolution and interaction with other degrees of freedom. In this section,

we describe the photoinduced dynamics in low dimensional material, focusing on the exciton formation and relaxation dynamics, covering the initial coherent excitonic state, the exciton-phonon coupling, the density-induced exciton Mott transition and the exciton trapping process in lattice deformations.

1.3.1 Exciton formation and relaxation dynamics

Photoexcitation in semiconductors with a pump photon energy that exceeds the optical band gap ($h\nu > E_g$) produces a population of electrons in the CB and a population of holes that remain in the VB. Initially, quasi-free carriers thermalize via scattering processes with the other carriers. Then, the electrons and holes undergo a cooling process toward the bottom of the CB and top of the VB, respectively, losing energy through scattering events with optical and acoustic phonons. Last, the electron-hole recombines through phonon and defect. Simultaneously, when the unbound electron and holes gather in the CB minimum, and VB maximum, a correlated electron-hole pair is created via attractive Coulomb interaction [30]. The exciton formation mechanism is called *bimolecular* since it results from the thermalization of the electron-hole pairs [181]. The exciton relaxation involves scattering events with phonons and free carriers, exciton thermalization, radiative and non-radiative recombination, inter and intervalley scattering, exciton dissociation, and exciton-exciton annihilation [183].

If the photon energy is resonant with the exciton ($h\nu \simeq E_x$), the exciton is created directly by photoexcitation and simultaneous emission of phonons. This requires a strong exciton-phonon interaction, resulting in a formation mechanism called *geminate* [181]. The picture differs slightly with respect to the non-resonant case. The interaction with a photon energy resonant with the excitonic state creates an initial polarization that oscillates between the ground state and the excitonic state, with subsequent emission of an electromagnetic wave at the excitonic frequency [134, 23, 171, 160]. In this initial temporal frame, the system contains virtual or coherent excitons that last only during the action of the pump [134]. The total wave function of the system is a superposition of the ground state $|0\rangle$ and the exciton, $|1\rangle$:

$$\psi = a_0|0\rangle + a_1|1\rangle \quad (1.21)$$

the coefficient is $a_i(t) = c_i(t)\exp(-i\omega_i t)$ with $i=0,1$ and $E_i = \hbar\omega_i$ are the eigenvalues associated to the levels. The density matrix formalism is employed to describe the coherence resulting from the light-matter interaction between an electromagnetic field and a two-level system. The density matrix is defined as:

$$\rho = |\psi\rangle\langle\psi| \quad (1.22)$$

which for a two-level system is:

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} \\ \rho_{10} & \rho_{11} \end{pmatrix} = \begin{pmatrix} |c_0(t)|^2 & c_0(t)c_1^*(t)e^{i\omega_{01}} \\ c_0^*(t)c_1(t)e^{-i\omega_{01}} & |c_1(t)|^2 \end{pmatrix} \quad (1.23)$$

where $\omega_{01} = \frac{E_0 - E_1}{\hbar}$. The diagonal terms represent the populations of the levels $|0\rangle$ and $|1\rangle$, while the out-of-diagonal terms represent the coherence between the states. In an N-element system, the average on the ensemble has to be taken into account ($\langle \rho \rangle_N$). In the coherent interaction regime, the exciton population refrains from scattering events. Moreover, field-induced polarization may enable transient optical responses that are otherwise inaccessible. After the interaction with the laser pulse, many-body scattering processes lead to the dephasing of the field-induced polarization [20] and the decay of the exciton population [165]. The coherent coupling between light and excitonic transitions breaks rapidly within up to a few tens of femtoseconds (fs) due to various dissipative channels such as exciton-exciton collisions, exciton-phonon scattering events [161, 24, 34, 3, 86, 22], and the presence of defects or impurities [148]. Here, due to inelastic scattering events with phonons, the electron-hole liquid containing real or incoherent exciton relaxes to an electron-hole stationary bound state. After the creation of the incoherent exciton population, the relaxation is through scattering events as described in the previous case. The evolution of the coherence and the population is embedded in the Bloch equations:

$$\frac{\partial \rho}{\partial t} = \frac{i}{\hbar} [\rho, H_0 + H_{int}] + D[\rho] \quad (1.24)$$

where H_0 is the Hamiltonian associated with the system, H_{int} is the Hamiltonian associated with the interaction with a pump pulse, and D is a functional that takes into account the scattering processes that produce a depopulation of the diagonal elements and decoherence of the off-diagonal elements. The evolution of the density matrix elements is retrieved by solving four coupled differential equations.

From a theoretical perspective, the use of *ab initio* approaches to study femtosecond exciton dynamics has been eluded due to the computational demand. Recent developments in *ab initio* models permit to investigate the generation of coherent excitons [108, 154, 99, 43, 31], the stability of excitons against non-equilibrium screening [133] and the subsequent exciton coherent dynamics and transport [32].

After having described the photoinduced relaxation pathways and the coherence in layered semiconductors, we want to focus our attention on how the exciton coherence can be observed. The out-of-equilibrium properties and dynamics of photoexcited semiconductors are mostly observed and investigated by means of all-optical transient spectroscopy. Literature reports numerous efforts to address the early-time regime of the excitonic resonance through transient optical

spectroscopy, exploring the sign and energy shifts of the transient signal at the excitonic energy. The observations strongly depend on the investigated system and on the fluence and the photon energy of the pump pulse [185, 29, 141, 7], resulting in difficulty in reaching a consensus on the spectral signature of a coherent excitonic state. Previous work on monolayer MoS₂ [183] has addressed the exciton coherence with a joint experimental and theoretical approach. In monolayer, coherence manifests as an increase of the transient reflectance intensity during the pump-probe cross-correlation. From the energy framework, the pump photon energy is crucial: a pump photon energy much higher than excitonic resonances produces an excess of energy that is transferred to the lattice or to the electronic population, promoting scattering events that break the coherence easily, resulting in the suppression of the initial increase of the intensity. It individuates a fingerprint of the excitonic coherence to be an increase of the initial signal, but it fails to describe how the coherence manifests on the exciton resonance. Nowadays, the measurement of coherent excitonic states by transient optical spectroscopy is still elusive as it demands the careful preparation of these states through a proper choice of the experimental parameters [48]. The coherence can be achieved directly with more complex techniques, i.e. two-dimensional electronic spectroscopy (2DES). 2DES is an optical four-wave mixing spectroscopy that provides an energy resolution in both the probe and the pump. The broad excitation permits simultaneous excitation of multiple levels, whose coupling and transition are shown as peaks in the resulting 2D map. In fact, this broadband excitation permits the preparation of a coherent superposition between the states, that manifests as a periodic modulation in time of the signal. The oscillation has the same frequency as the difference between the two states [20, 88]. Moreover, multi-dimensional spectroscopy allows the discrimination of the dephasing mechanisms by isolating the homogeneous and the inhomogeneous broadening of the exciton linewidth, where the first represents the quantum coherent dynamics and the latter the scattering with defects and impurities [114, 71, 88].

1.3.2 Exciton-phonon coupling

Electron-phonon coupling is among the fundamental interactions in condensed matter which govern the out-of-equilibrium optoelectronic properties of materials by, for instance, guiding the relaxation dynamics of quasiparticles [2, 156, 11, 166] and assisting nonthermally-driven electronic phase transitions [63, 143, 98]. Recently, exciton-phonon coupling has been proposed to impact not only the incoherent carrier-cooling dynamics but also the homogeneous linewidth of the excitonic luminescence and even the diffusion and the coherence length of excitons [113, 24]. The exciton-phonon coupling is a quantum superposition of

electron- and hole- phonon scattering processes, weighted by the exciton wave function of the initial and final state [24], as described in Fig. 1.8.

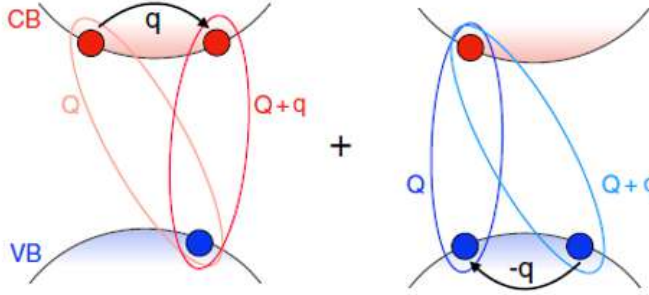


Figure 1.8: Theoretical representation of the exciton phonon coupling. Image from [24]

This is at the forefront of theoretical investigation since, to describe the exciton phonon interactions, the electron-phonon and the electron-hole scattering cannot be calculated separately, but the calculation should account for the electron-hole bound state [24]. In fact, the exciton-phonon coupling mechanism originates from a combined action of the electron-hole and the electron-phonon interactions, both of which can be described from first principles. *Ab initio* calculations of exciton-phonon coupling combine density-functional-perturbation theory for the electron-phonon matrix elements [56], with the Bethe-Salpeter Equation (BSE), which describes the excitonic physics [125]. Such a scheme has been recently developed and applied to two-dimensional materials to compute exciton-phonon lifetimes [34, 24]. An alternative approach computes the excitonic properties by solving the BSE within the GW approximation both at equilibrium and with the atoms displaced along specific phonon modes [183]. This method solves the interacting two-particle problem for an electron and a hole and yields the exciton energies and wave functions, which allow us to predict the optical absorption spectra of materials [3]. This further enables an estimation of atomic displacements with exceptionally high spatial resolution on the sub-picometer scale [79].

Experimentally, resonant Raman scattering spectroscopy is among the most common techniques to address exciton-phonon coupling [51, 109]. Here, the effect of the exciton phonon coupling is explored by observing the changes of vibrational mode oscillator strength changing the impinging photon energy as described in Fig. 1.9 (a). Pumping resonant to the exciton, an enhancement

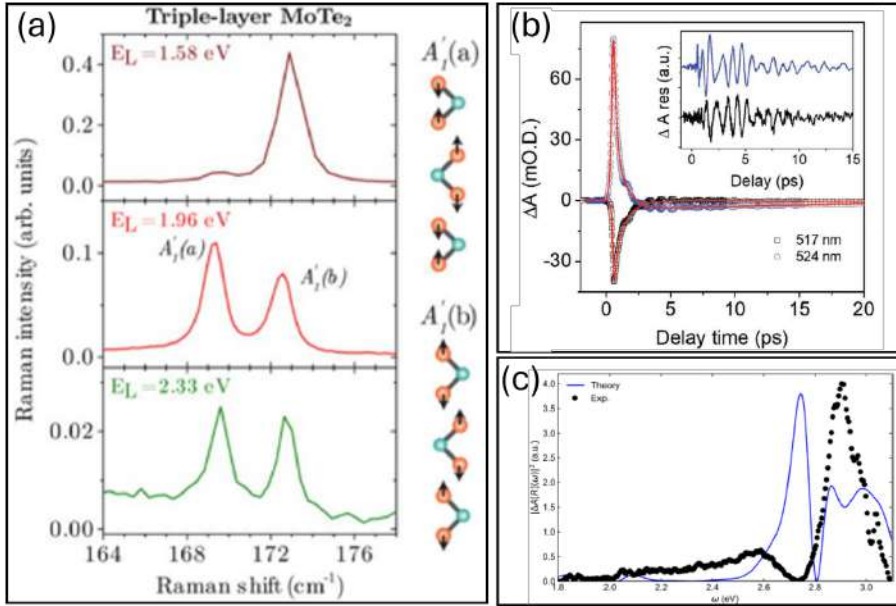


Figure 1.9: (a) Observation of exciton-phonon coupling by means of Raman spectroscopy. Image from [109]. (b) Manifestation of the coherent phonons in transient absorption measurements. Image from [50]. (c) The calculated (blue) and experimental (black) energy-dependent amplitude of the coherent phonons. Image from [183].

of the Raman intensity is observed. However, Raman spectroscopy lacks the energy and temporal resolution, therefore exciton dynamics and spectral changes remain out of reach. Time-resolved optical spectroscopy is the most suitable tool to investigate the interaction between excitons and phonons in the ultrafast time domain [149, 122, 50, 183]. By measuring transient changes in the optical polarization, the technique provides macroscopic snapshots of the nonequilibrium behaviour of the system. Transient optical spectroscopy provides a simultaneous probing of the energetic and the temporal frameworks. From the investigation of the photoinduced changes in the energy spectrum, information on the photoinduced energetic shift of excitons can be retrieved. In the time domain (Fig. 1.9(b)), coherent and incoherent responses of the material are observed. The periodic modulation in the response is assigned to be the generation of coherent optical phonons. Theoretically, the study of the energy-dependent amplitude (blue line in Fig. 1.9) of this oscillation can give information on the exciton phonon coupling [183]. 2DES provides information

that is hardly available with standard optical spectroscopy, such as the exciton phonon coupling strength. This is related to the displacement of the exciton state potential minimum along the phonon coordinates. The exciton phonon strength has been retrieved by comparison of the shape of the excitonic structure in the 2D map with the calculated one [88]. Previous investigations on the exciton-phonon coupling ([24, 183, 129, 88, 109]) have been achieved, but a common description of the effect by both experiment and theory has not been found yet.

1.3.3 Exciton Mott transition

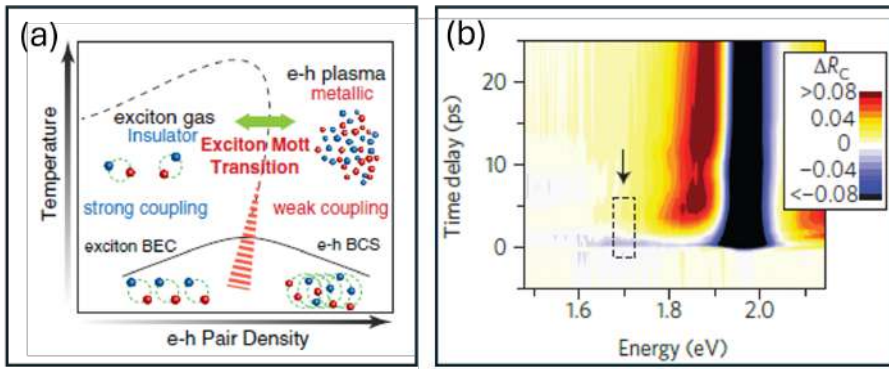


Figure 1.10: (a) Phase diagram for excitons. Image from [159]. (b) Transient reflectance measurement on WS₂. Image from [10].

The insulator-to-metal transition, called the Mott transition, is driven by interparticle Coulomb interactions without a concomitant symmetry breaking [159, 58]. This fundamental phenomenon appears widely in condensed matter systems such as correlated electron materials, doped semiconductors, and ultracold atom gases. A collection of excitons is an ideal model that fits in the theory of the Mott transition due to its electronic nature, the dominant effect of long-distance interaction and the possibility to control the density (n_{ex}) by photoexcitation [159]. Indeed, in exciton Mott transition, if the density surpasses the condensation limit, called Mott density n_{mott} , insulating excitonic gas dissociates into a metallic electron-hole liquid (Fig. 1.10). Increasing the density, there is a concomitant decrease in the interparticle distances; the Mott density is the density where the interatomic distances are comparable with the exciton Bohr radius. The nature of the process is still under investigation since it does not have a univocal manifestation. Mott suggested that the transition

should be of the first order. In the exciton Mott transition, the metallic phase is still elusive. This problem is closely related to the excitonic Bose-Einstein condensation and the electron-hole BCS and the crossover between them (Fig. 1.10(a)). From an experimental point of view, exciton Mott transition is usually studied with optical spectroscopy. Under photoexcitation, the electronic gap shows a redshift due to screening-induced band gap renormalization [35]. Below the Mott density, the exciton shows the same behaviour, i.e. a redshift. Above it, the situation is more shaded since there is no univocal description of the phenomena. In reflectance, WS_2 shows a gradual bleaching build-up at lower energy than the exciton resonance associated with a gradual transition to the electron-hole liquid state (Fig. 1.10(b)). In the time-resolved photoluminescence measure on MoS_2 , the exciton Mott transition is observed as an increase of the intensity just below the exciton position [10].

1.3.4 Localization of excitons

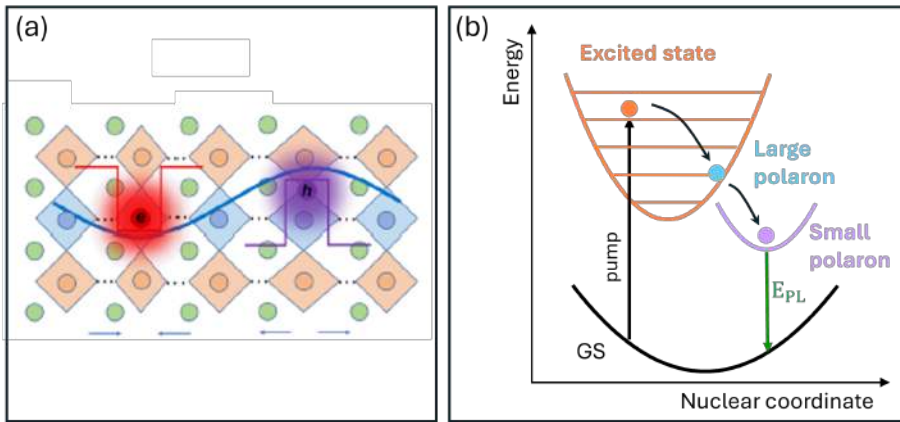


Figure 1.11: (a) Picture of the electron- and hole-polaron. Image from [199]. (b) Energy vs nuclear coordinates diagram for the localization process of excitons. Adapted from [175].

Trapping of initially free excitons can take place due to a potential deformation generated by defects in the crystal structure. These excitonic states are called trapped excitons (TE) and are currently the object of intense study [106, 17, 38, 117]. In the case of soft semiconductors, excitons can also be self-trapped (STE) by the local elastic lattice distortion generated by strong exciton-phonon coupling after photoexcitation [196].

Trapped exciton, as well as self-trapped exciton, are described as a superposition

between an electron-polaron and a hole polaron. A polaron is a collective excitation in which a photoexcited charge induces a lattice deformation that activates specific phonon modes. As a result, the charge localizes in the lattice deformation, and the induced lattice screening affects its recombination [106]. In the case of trapped excitons, the lattice deformation is induced by defects. A polaron can involve both holes and electrons trapped at different sites as described in Fig. 1.11(a). A bound state between a hole-polaron and an electron-polaron by Coulomb attraction is called exciton-polaron. Large exciton polarons, i.e. with a radius much larger than the lattice parameter, are generated by long-range Fröhlich interaction of charges to longitudinal optical phonons. Small exciton-polarons localized on one unit cells are generated by short-range Holstein interaction between charges and acoustic phonons. Small polarons trapped by preexisting defect-induced lattice deformation are referred to as TE. STE and TE are discriminated using temperature- and fluence-dependent photoluminescence measurements. In particular, the fluence-dependent intensity of TE saturates, while the STE intensity exhibits superlinear behaviour. In temperature-dependent photoluminescence measurements, the STE width depends strongly on the coupling with phonons; i.e. if the exciton is coupled with acoustic phonons the width shows a trend linear in temperature, while the width is proportional to the Bose-Einstein phonon occupation when the exciton is coupled with optical phonons. A simplified energy diagram that represents the exciton-polaron formation is inserted in Fig. 1.11(b) [117, 175, 89, 66]. Here, the excited-state potential as a function of the nuclear coordinate describes the continuum of excitations when the lattice is undistorted [49]. The continuum also comprises large exciton polarons, where the lattice distortion is perturbative, and the exciton polaron spreads on in the crystal lattice with a radius larger than the lattice constant. The interaction with the acoustic phonons produces a lattice deformation that results in a continuum of excitation, whose minimum is centred in a new equilibrium position in the nuclear coordinates. Moreover, the minimum is also redshifted with respect to the unperturbed situation. Generally, the trapping process occurs in a few hundred femtoseconds [176] and is usually observed in photoluminescence experiments as a broadband structure below the exciton [199, 201, 38, 37].

1.4 Thesis Outline

Excitons are pivotal in the optical response in layered semiconductors, which are attracting renewed interest in optoelectronic applications. The investigation of how excitons are generated, interact with other degrees of freedom and relax is necessary to acquire a comprehensive understanding of the exciton

physics in low-dimensional semiconductors. The thesis will cover three main topics as shown in Fig. 1.12 that we can summarize into three key-words: formation, coherence and exciton-phonon coupling. In particular, we will focus on the spectroscopic manifestation of these effects and on how the interaction with the other degree of freedom influences the exciton dynamics in layered semiconductors.

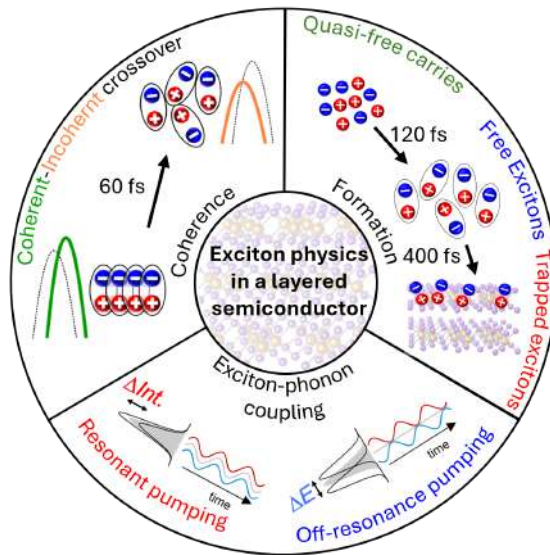


Figure 1.12: Summary of the goal of the thesis.

To pursue our goal, we used two complementary ultrafast spectroscopies: time-resolved angle-resolved photoemission spectroscopy and transient optical spectroscopy. A brief overview of the two methods is reported in *Chapter 2*. A description of the static and out-of-equilibrium properties of BiI_3 is inserted in *Chapter 3*. At the end of the chapter, the temperature-induced effect on the static reflectance acquired by Fourier transform infrared spectroscopy is discussed.

Chapter 4 is focused on the exciton formation of exciton in layered semiconductors by time-resolve photoemission spectroscopy. We are interested in investigating the exciton manifestation in a material that exhibits a rich exciton landscape. Moreover, we provide a description of the exciton formation starting from a population of quasi-free carriers and, pushing a little forward, we arrive to observe an unexpected signal due to trapped excitons.

The exploration of exciton physics in BiI_3 continues in *Chapter 5* with the exciton *coherence*. We initially observe the fingerprints for an excitonic coherent state in transient reflectance spectroscopy. Then, we track the evolution from a coherent to an incoherent state, and we measure the timescale of the decoherence process.

Chapter 6 is devoted to the *exciton-phonon coupling*, exploring its spectroscopic manifestation on the exciton and phonon degrees of freedom of the system after photoexcitation. Moreover, we are interested in the effect of environmental conditions as a first step in the optical manipulation of processes in layered materials. This is achieved by tuning the experimental parameters.

Chapter 7 enters the economy of this thesis as a step forward in the topic of *coherence*, as a possible evolution of Chapter 5, where the coherence is achieved indirectly. Interferometric time-resolved two-photon photoemission is a useful technique that can be employed to achieve excitonic coherence directly. The description of this technique follows two steps: simulation of the photoemitted intensity by solving a set of Bloch equations for a three-level system that interacts with a pair of pulses and preliminary results on a sample of $\text{Cu}(111)$. This dissertation concludes with *Chapter 8*, which summarizes the results and provides future perspectives.

Chapter 2

Methods

The exciton coherence and relaxation pathways in layered semiconductors show time constants ranging from a few femtoseconds to nanoseconds. A sub-ps resolution provided by fs-pulsed lasers is needed to get access to dynamics. Ultrafast lasers are at the core of ultrafast spectroscopies and coupled with the pump and probe scheme, they provide a complete reconstruction of the photoinduced dynamics. The ultrafast laser creates ultrashort coherent pulses with a time duration ranging from a few to several hundreds of femtoseconds. The ultrafast pulses create a non-equilibrium condition in the sample on a time scale faster than the energy exchange with the lattice vibration, magnetic excitation, and other degrees of freedom [52], unveiling relaxation pathways otherwise inaccessible. The pump and probe technique is based on the stroboscopic effect and usually exploits two pulses: the pump and the probe. The more intense pump pulse induces a change in the microscopic properties of the material, while the probe captures snapshots of the systems after the pump arrival. A complete characterization of the temporal evolution of the signal is achieved by changing the delay time between the pump and the probe. In this thesis, we have employed two complementary techniques to observe the temporal evolution of the non-equilibrium properties of BiI_3 : transient optical spectroscopy (TR) and time-resolved angle-resolved photoemission spectroscopy (ARPES). In addition to time-resolved spectroscopies, static spectroscopies have been used to (i) characterize BiI_3 fully, (ii) explore the static properties that are the basis of the analysis of the out-of-equilibrium signal, and (iii) tackle experimental limits.

This chapter focuses mainly on the ultrafast spectroscopies used to probe the exciton formation and relaxation dynamics and couplings. The techniques used to observe the static properties are inserted in Appendix B. The chapter is

arranged as follows. In the first part, we will briefly overview the photoemission spectroscopy. A description of the manifestation of exciton in ARPES is inserted at the end of the section. In the second part, a description of the transient optical spectroscopy is discussed, focusing on the description of the incoherent and coherent optical response under photoexcitation.

2.1 Brief overview of the photoemission spectroscopy

Photoemission spectroscopy is a technique based on the photoelectric effect, firstly observed by *H. Hertz* in 1887 [64], and was then formally described by *A. Einstein* in 1905 [45]. The photoelectric effect states that if the electrons have enough energy to overcome the intrinsic work function ϕ , they can be ejected from the material. The emitted photoelectrons have momentum $\mathbf{k}$ and maximum kinetic energy $E_K = h\nu - \phi$, where ν is the photon frequency and ϕ is the work function. Typical value for ϕ is 2-4 eV. In general, photoemission spectroscopies are used to study the intrinsic dynamics of the valence electrons or to investigate the core levels of the material. The choice of the photon energy dictates the selection of the probed energy region, i. e. to probe the valence band a UV source is exploited while for the core levels, an x-ray source is used. The escape depth depends on the kinetic energy of the photoemitted intensity. The universal curve for the mean free path in solid is inserted in Fig. 2.1 (a). Angle-resolved photoemission spectroscopy (ARPES) is usually employed to have information about the electronic band structure of the solids $E(\mathbf{k})$ from the E_K and the momentum $\mathbf{k}$ of the photoexcited electrons. The complicated data interpretation is simplified by considering the assumption of (i) *independent-particle picture* and (ii) *sudden-approximation*, which neglects the many-body interaction as well as the system relaxation during the photoemission process.

Three-step model (Fig. 2.1 (b)) is used to expedite the photoemission interpretation further and describe well the high kinetic photoelectron and the electronic band structure of solids. This model fails to describe the photoemission process in the *adiabatic limit*, which describes the non-instantaneous escape of low-energy electrons from the solids since they need more than the system response to escape from the solids. In strongly interacting systems, the photoemission process cannot be divided into three independent sub-processes, but a *one-stage process* (Fig. 2.1 (c)) is needed. This treats photoemission as a coherent process that relies on an optical transition between an initial state described by an N-electron eigenfunction for the semi-infinite crystal and a final state characterized by an (N-1)-electron eigenfunction for the semi-infinite crystal, which has to obey specific boundary conditions at the surface of the

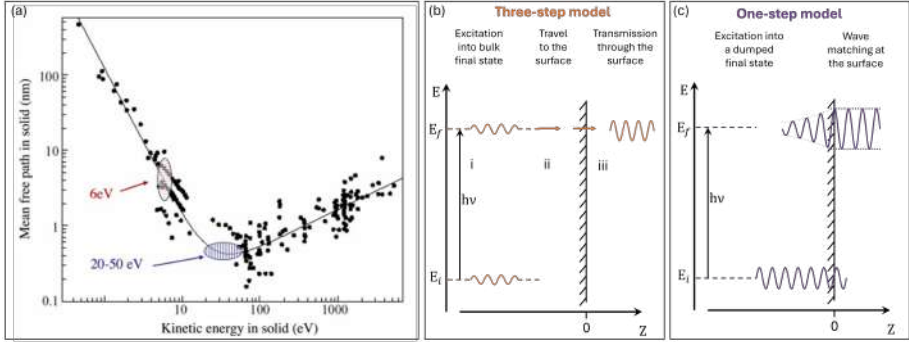


Figure 2.1: (a) Mean free path in solid. Data taken from [85]. Comparison between the *three-stage* (b) and *one-stage* (c) process for photoemission spectroscopy. Adapted from [39].

solids. In this case, an electron is photoemitted if the initial and the final wave functions are overlapped, and the energy and momentum conservation laws are fulfilled. In the following, we will describe the photoemission process more in detail starting from the description of the two models and then extending the description to the time-resolved ARPES (tr-ARPES).

2.1.1 The photoemission process

The aim is to fully characterize the electronic dispersion relation within the solids $E(\mathbf{k})$, i.e. the expression of the binding energy (E_B) in the function of the crystal momentum ($\mathbf{k}$) starting from E_k and $\mathbf{k}$ of the photoelectrons.

The photoemission experiment consists of a beam of monochromatic radiation with an energy of $h\nu$, which impinges on the sample. If $h\nu > \phi$, electrons are emitted in the vacuum along all the directions by the photoelectric process. The photoelectrons are then collected by an analyzer (either a hemispheric or a time of flight one) with an acceptance angle along the emission direction and kinetic energy. Each electronic escape direction is described by the polar angle ϑ and the azimuthal angle φ (Fig. 2.2 (a)). The momentum of the photoelectrons in vacuum is also determined: its modulus is $k = \sqrt{2m_e E_K}/\hbar$, and its parallel $\mathbf{k}_{\parallel} = \mathbf{k}_x + \mathbf{k}_y$ and perpendicular $\mathbf{k}_{\perp} = \mathbf{k}_z$ components are obtained as follow:

$$k_x = \frac{1}{\hbar} \sqrt{2m_e E_K} \sin \vartheta \cos \varphi \quad (2.1)$$

$$k_y = \frac{1}{\hbar} \sqrt{2m_e E_K} \sin \vartheta \sin \varphi \quad (2.2)$$

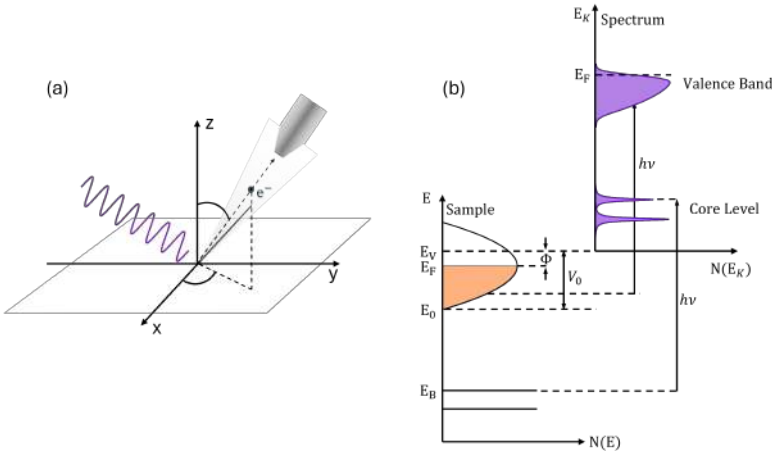


Figure 2.2: Sketch of the photoemitted geometry and the energy diagram for the photoemission process. Adapted from [68].

$$k_z = \frac{1}{\hbar} \sqrt{2m_e E_K} \cos \vartheta \quad (2.3)$$

Since the surface does not change the translational symmetry in the x-y plane, $k_{\parallel} = \frac{1}{\hbar} \sqrt{2m_e E_K} \sin \vartheta$ is conserved in the photoemission process. Conversely, along the z-direction, the potential changes abruptly at the sample surface; therefore, $k_{\perp}$ is not conserved. To reproduce the $k_{\perp}$ of the band structure, the inner potential V_0 has to be considered and then the complete form for the perpendicular component of the momentum is $k_{\perp} = \frac{1}{\hbar} \sqrt{2m_e (E_K \cos^2 \varphi + V_0)}$. The inner potential $V_0 = |E_0| + \phi$ (displayed in Fig. 2.2 (b)) corresponds to the energy of the bottom of the valence band referenced to the vacuum level E_V . The definition of the inner potential holds only for a single band electronic structure and with the quasi-free electron approximation. The most common method is to calculate the inner potential experimentally from the periodicity of $E(\mathbf{k}_{\perp})$ by collecting the photoemitted intensity along the normal of the sample by changing the impinging photon energy. Last, the binding energy is related to the kinetic energy as following $E_K = h\nu - \phi - |E_B|$ for the direct photoemission process, the connection between the energy levels and the density of states (DOS) in solids and the electron energy distribution in the photoemission spectrum is inserted in Fig. 2.2 (b).

2.1.2 Three-step model

The *three-step model* is a phenomenological model that splits the photoemission process into three independent sequential processes: (i) optical excitation of the electrons between an initial and a final state in bulk, (ii) travel of the photoexcited electron to the surface and (iii) escape of the photoelectron into the vacuum. In this model, the total photoemitted intensity results from three independent terms related to each of the previously mentioned steps. In particular, the first term is related to the total probability for an electron to undergo a photoinduced transition between the initial and final states, and it contains all the information about the intrinsic electronic structure of the material. The second one includes the probability that the travelling electrons arrive at the surface, described by an effective mean free path, which is proportional to the probability for the electron to reach the surface without scattering events. Eventually, the third term is the transmission probability through the surface potential barrier, this depends on the energy of the excited electrons and the material work function ϕ . The probability of excitation from an initial state Ψ_i^N to a final state Ψ_f^N is dictated by the Fermi golden rule $w_{f,i}$. Under the *sudden approximation* assumption, the final state can be factorized as follows:

$$\Psi_f^N = \mathcal{A} \phi_f^k \Psi_f^{N-1} \quad (2.4)$$

where $\mathcal{A}$ is an antisymmetric operator to satisfy the Pauli principle. This simplification describes a photoelectron with a wave function of ϕ_f^k and the final state wave function that describes the system left behind Ψ_f^{N-1} . This can be defined as an excited state with an eigenvalue E_m^{N-1} and eigenfunction Ψ_m^{N-1} . For the initial state, the Ψ_i^N can be described with a one electron orbital and an (N-1) particle term:

$$\Psi_i^N = \mathcal{A} \phi_i^k \Psi_i^{N-1} \quad (2.5)$$

The Ψ_i^{N-1} is not an eigenstate of the (N-1) particle Hamiltonian but only what remains from the exit of the electron. Considering these states, the total photoemission intensity $I(E_k, \mathbf{k}) = \sum_{f,i} w_{f,i}$ is proportional to

$$\sum_{f,i} |M_{f,i}^k|^2 \sum_m |c_{m,i}|^2 \delta(E_K + E_m^{N-1} - E_i^N - h\nu) \quad (2.6)$$

where $M_{f,i}^k = \langle \phi_f^k | H_{int} | \phi_i^k \rangle$ is the one-electron dipole matrix element, $|c_{m,i}|^2 = | \langle \Psi_m^{N-1} | \Psi_i^{N-1} \rangle |^2$ is the probability that the removal of an electron from the i state will leave the (n-1)- particle system in the excited state m . For a single particle system, only one $|c_{m,i}|^2$ is different from zero, and the ARPES signal is constituted by a delta located at the excited energy otherwise in a strongly correlated system of the dipole matrix elements are finite resulting in a structured ARPES signal.

2.1.3 Single-step model

The most common way to treat the *single-step* model is to use Green's function formalism, which describes the probability that the system evolves toward another state after the addition or removal of an electron. The ARPES signal is related to the Green function $G(\mathbf{k}, \omega)$. Using the same assumption introduced earlier, the photoemitted intensity is described by the Fermi golden rule and it is described as follows:

$$I(\mathbf{k}, \omega) = A(\mathbf{k}, \omega) |M(\mathbf{k}, \omega)|^2 f(\omega) \quad (2.7)$$

where $A(\mathbf{k}, \omega) = -\frac{1}{\pi} \text{Im} G(\mathbf{k}, \omega)$ is the one particle spectral function that accounts for the single particle band structure and of the correlation effect through the *self energy* $\Sigma(\mathbf{k}, \omega)$, $|M(\mathbf{k}, \omega)|^2$ is the photoemission matrix elements that take into account of the electron momentum, the polarization of the incoming wave and the initial and final states and $f(\omega) = (e^{\omega/k_b T} + 1)^{-1}$ is the Fermi-Dirac function that makes sure of the probing only the occupied states. The self-energy is a complex quantity $\Sigma(\mathbf{k}, \omega) = \Sigma'(\mathbf{k}, \omega) + i\Sigma''(\mathbf{k}, \omega)$ where the real part $\Sigma'(\mathbf{k}, \omega)$ is connected to the renormalization energy associated with quasiparticle, i.e. an electron dressed by the screening while the imaginary part $\Sigma''(\mathbf{k}, \omega)$ is related to the changes in the quasiparticle lifetime.

2.1.4 Time-resolved ARPES

The tr-ARPES is spectroscopy based on the pump and probe technique depicted in Fig. 2.3. The pump pulse produces a change in band occupation, generates collective excitation and leads to the emergence of new non-equilibrium or metastable phases. The probe, arriving after a time delay τ , is used to take a snapshot of the system in the non-equilibrium state, allowing the following the transient evolution of the electronic band structure and its occupation.

In the extension to the non-equilibrium investigation, the intensity of the tr-ARPES is implemented as follows:

$$I(\mathbf{k}, \omega, \tau) \simeq A(\mathbf{k}, \omega, \tau) |M(\mathbf{k}, \omega, \tau)|^2 f(\mathbf{k}, \omega, \tau) \quad (2.8)$$

where $f(\mathbf{k}, \omega, \tau)$ is the electronic distribution, $|M(\mathbf{k}, \omega, \tau)|^2$ is the photoemission matrix element and $A(\mathbf{k}, \omega, \tau)$ is the spectral function. The first term is related to the transient occupation of the band structures, usually opposite from the equilibrium in this case the distribution is highly anisotropic and therefore the dependence of momentum is necessary in the short time delay. After the thermalization, this can be approximated by the momentum-independent

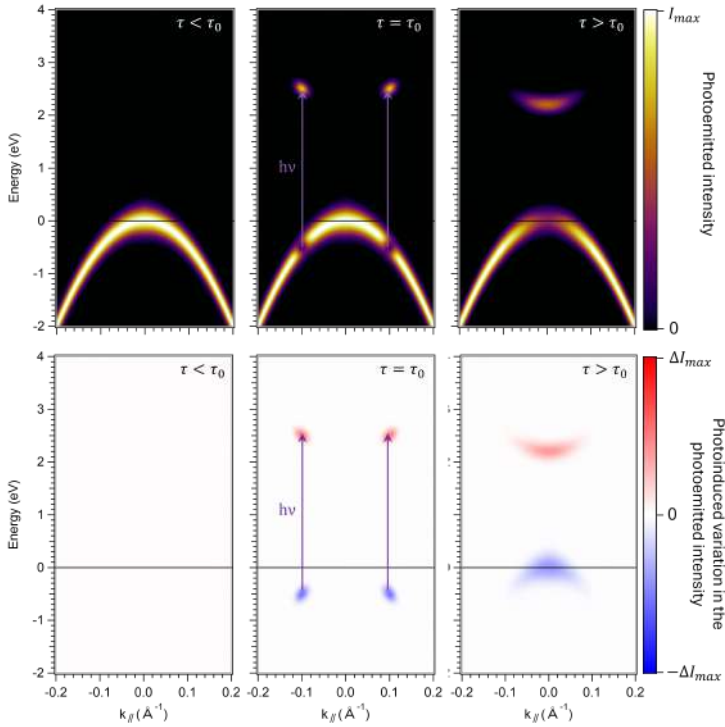


Figure 2.3: (a-c) description of the tr-ARPES experiment, (d-f) are simulations of the ARPES intensity at several time frames and (g-i) are the differential intensity at several time frames. Adapted from [39]

Fermi-Dirac distribution with a time-dependent electronic temperature. The photoemission matrix elements are calculated under the *sudden approximation*, and this encodes the dependence from the polarization, the photon energy and also the geometry of the experiment. The transient modification of the matrix element is usually neglected. The last term, the spectral function takes into account the transient change in the band structure, the density of states and also the many-body interactions. This description holds only within the limits of the quasi-equilibrium ($\tau \gg 0$), but this is not true during the pump and probe cross-correlation. Here, the intensity is related to the Fourier transformation of the Lesser Green function.

2.1.5 Excitons in ARPES

As reported in the previous sections, ARPES is usually used to describe single-particle electronic structures. Only in recent years, ARPES has been used to address a system formed by two-fermion quasiparticles. This has required a formal theoretical description and a detailed experimental investigation of the exciton signature in ARPES.

From a theoretical point of view, the pioneering work of *Elliot et al.*[46] has set the first milestone for the computation of the ARPES signal. Their work formally describes the optical transition under photoexcitation in the presence of exciton, which is the first step toward the complete modelling of the ARPES signal.

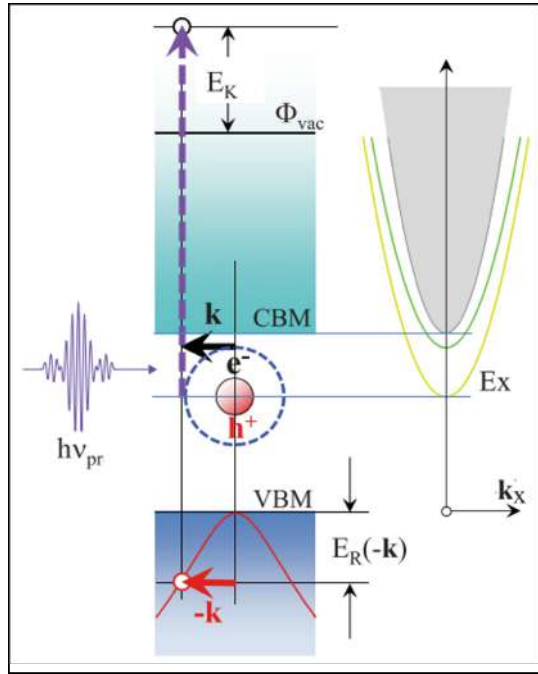


Figure 2.4: Description of the photoemission from an excitonic level. Adapted from [178].

The description starts from the definition of the excitonic state $|n, \mathbf{k}_X\rangle$, characterized by the index n , which denotes the internal structure and the center-of-mass momentum wave vector $\mathbf{k}_X$ [178]. $\mathbf{k}_X$ is the sum of the electron

and hole wavevector: $\mathbf{k}_X = \mathbf{k}_e + \mathbf{k}_h$. The excitonic state can be expanded in terms of independent quasiparticle (IQP) Bloch functions, where $f_{\mathbf{k}_X^n}(\mathbf{k}_e, \mathbf{k}_h)$ is the amplitude of the constituent IQP band states:

$$|n, \mathbf{k}_X \rangle = \sum_{\mathbf{k}_e, \mathbf{k}_h} f_{\mathbf{k}_X^n}(\mathbf{k}_e, \mathbf{k}_h) a_{\mathbf{k}_e}^+ b_{\mathbf{k}_h}^+ |0 \rangle \quad (2.9)$$

where $a_{\mathbf{k}_e}^+$ is the creator operator for an electron at the momentum $\mathbf{k}_e$ in the conduction band and $b_{\mathbf{k}_h}^+$ is the creator operator for an hole at the momentum $\mathbf{k}_h$ in the valence band. When the electron is photoemitted from the excitonic state, the holes must return to their ‘original’ VB states. This results in a *recoil effect* on the photoemitted electrons. In the picture, the center-of-mass momentum is zero. Under momentum and energy conservation for the recoil energy $E_r(-\mathbf{k}_e)$ of the hole with momentum $-\hbar\mathbf{k}_e$, the photoemitted electron from the excitonic state has momentum $\hbar\mathbf{k}_e$ and the kinetic energy is given by:

$$E_K = \hbar\nu_{pr} + E_X^n(0) - E_I - E_r(-\mathbf{k}_e) \quad (2.10)$$

where ν_{pr} is the frequency of the probe, $E_X^n(0)$ is the energy of the n-th excitonic state, E_I is the ionization energy and E_r is the recoil energy. The recoil E_r is strictly related to the momentum distribution of the valence band. Consequently, the momentum dispersion of the exciton resembles the hole-like dispersion of the valence band. The intensity of photoemission is proportional to $|f_{\mathbf{k}_{ex}}^n(\mathbf{k}_e, \mathbf{k}_h)|^2$ so that ARPES directly measures the amplitudes of momentum- and energy-resolved IQP Bloch functions of which excitonic states are composed. The work of *Perfetto et al.* [134] provided a first proposal for an accurate diagrammatic approximation to calculate the time-resolved angle-resolved photoemission spectrum for insulator or semiconductor material showing a low-energy spectrum dominated by excitons. This calculation is done with the lesser Green function formalism. The ARPES signal has been modeled for indirect gap semiconductors by solving the Behte-Salpeter equation in the green function formalism [150]. The photoinduced transitions involve phonon since the valence band maximum and the valence band minimum are not located at the same position in the Brillouin zone. This work provides a description of how excitonic resonance manifests in ARPES measurement both for direct and indirect semiconductors. First of all, in the photoemission spectrum, the exciton is located in the gap below the conduction band. The difference between the conduction band and the excitonic resonance is exactly the binding energy of the exciton. Secondly, the shape of the ARPES signal depends on the exciton distribution. If the exciton distribution is narrow, the ARPES signature exhibits a downward concavity that resembles the VB dispersion under the single-band approximation. Conversely, if the distribution

is broader, an additional contribution that mirrors the CB distribution is observed. Moreover, the photoemitted intensity accounts for both the zero and finite momentum excitons, thereby enabling a complete characterization of the signal [150, 170, 151, 30, 154]. Nowadays, the modelization of ARPES signal has also been proposed for excitons in a more complicated system, such as heterostructures. Here, there is the rising of the hetero-excitons where the hole and the electron are located in layers of different materials [107]. The evolution of excitons has been calculated by Brem et al. [15] by proposing a cascade process. The pump excites near the quasiparticle conduction band minimum creating an electron-hole pair. These hot excitons dissipate the excess energy via the emission of phonons, performing a cascade-like relaxation through energetically lower-lying exciton orbitals. The population cools down to the 1s excitonic level, through also different excitonic series located in different positions in the k framework.

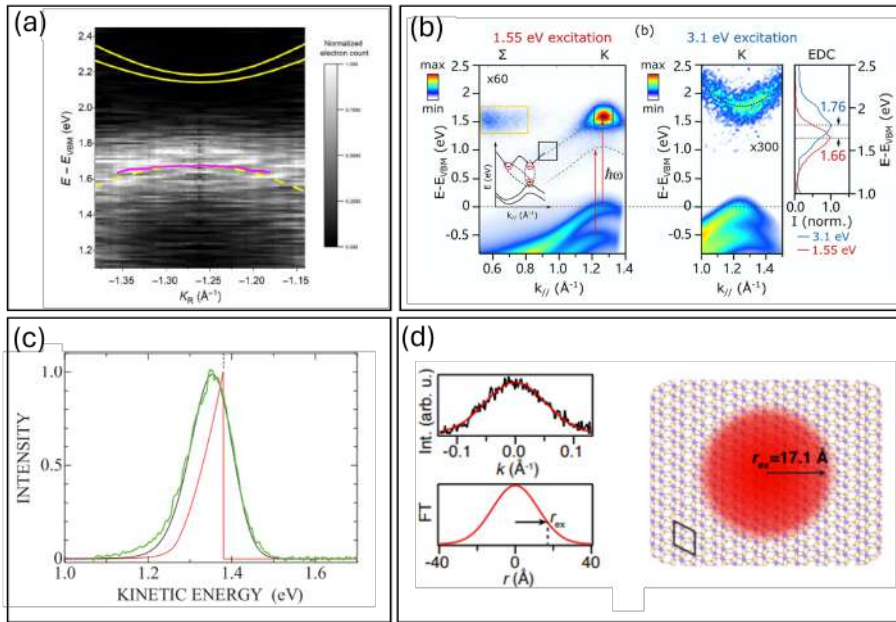


Figure 2.5: (a) k-dispersion of the exciton in ARPES. Adapted from [99]. (b) ARPES intensity collected with two photon energies. The comparison unveils the exciton binding energy. Adapted from [43]. (c) Energy-dependent photoemitted intensity from an excitonic level. Adapted from [178]. (d) Space extension of the exciton wave function. Adapted from [188].

From an experimental point of view, observing strongly bound, few-particle

and short-lived excitonic states is not straightforward, and in the past two decades, only a few papers studied excitons in bulk as well as in bidimensional semiconductors via time-resolved photoemission [13, 194, 195, 41, 178, 95, 189, 43, 99, 188, 177]. In summary, excitons in ARPES show a downward dispersion in the momentum, which mirrors the hole-like dispersion of the conduction band, as shown in Fig. 2.5(a). Its position in the kinetic energy is substantially lower than expected for the conduction band minimum (Fig. 2.5(b)). Furthermore, the photoemission intensity from the excitonic state exhibits an asymmetric line shape characterized by a tail toward the lower-energy side (Fig. 2.5(c)) and a strong momentum dependence. The excitonic feature was explored in bulk crystals (Si(100) [194, 195], ZnO [41], Cu₂O [178] and ReSe₂ [188], and how they manifest in presence of a surface ([177]). Recent studies have focused on dark excitons ([95, 189]) and the connection between the momentum-dependent photoemitted intensity and the real space-dependent excitonic wave function [43, 99, 188] as shown in Fig. 2.5(d).

2.2 Brief overview of transient optical spectroscopies

Static and ultrafast spectroscopies are fundamental in disentangling the contribution of the degree of freedom (such as exciton, phonon, and magnon) to the response of the material under photoexcitation.

The interaction between an electromagnetic field and the electrons inside the matter manifests macroscopically as a polarization $\mathbf{P}$. As a first approximation, the polarization is linear with respect to the electromagnetic field:

$$\mathbf{P} = \epsilon_0 \chi \mathbf{E} \quad (2.11)$$

The optical susceptibility, χ accounts for the electron, vibrational and rotational modes. Optical spectroscopies are sensitive to the optical susceptibility of the material, which is related to the dielectric function of the material as follows: $\epsilon = 1 + \pi \chi$.

Advances in optical spectroscopy technology have enabled the use of a broader range of light, expanding optical detection to uncover a wider variety of processes that were previously hidden. For instance, visible and near-infrared light provides information on the electronic structure, while mid- and far-infrared light provides information on the crystal structure.

In static measurement, after the interaction of the light with intensity I_0 with the material, a part of the light is reflected (I_R) by the surface, and a part is transmitted through the sample (I_T). The light-matter interaction also results in light absorption with an attenuation by Lambert-Beer law.

Therefore, the incident light is split with several contributions as follows: $I_0 = I_a + I_T + I_R + I_S$, where I_S and I_a represent the scattered and the absorbed light. The transmittance T and the reflectance R are calculated as the transmitted and reflected light normalized on the incident light, respectively. Explicitly, $T = \frac{I_T}{I_0}$ and $R = \frac{I_R}{I_0}$. From the Lambert-Beer law, the optical absorption A is related to the transmittance through a logarithmic: $A = -\ln(T)$.

While in ultrafast spectroscopy, the interaction between an ultrashort laser and the sample via dipole allowed processes produced a population of electrons in the CB. Initially, the energy is distributed among themselves and then they transfer their energy to other degrees of freedom of the system. The evolution of the electronic population and the other degree of freedom via scattering processes constitute the incoherent response of the materials. Simultaneously, the absorption of a pulse triggers collective motion such as coherent phonons, which is the coherent optical response of the material. The variation in intensity (ΔI) is related to the change of the electronic population ($\Delta \bar{n}$) and to the lattice displacement ($Q(t)$), through the optical susceptibility as follows [42]:

$$\Delta I(t) = \frac{\partial I}{\partial \bar{n}} \Delta \bar{n}(t) \simeq \frac{\partial I}{\partial \chi} \frac{\partial \chi}{\partial N_{eq}} N_{eq}(t) + \frac{\partial I}{\partial \chi} \frac{\partial \chi}{\partial Q} Q(t) \quad (2.12)$$

The first part of the equation is related to the incoherent response of the material under photoexcitation, which results in a change in the electronic occupation. The second part is related to the coherent response of the material. The coherent response of the material is due to the generation of coherent phonons.

2.2.1 Photoinduced dynamics

From the incoherent point of view, the photoinduced change in band occupation leads to the appearance of several effects, i.e. ground state bleaching (GSB), excited state absorption (ESA), stimulated emission (SE) and band gap renormalization (BGR). Each of these effects has a characteristic signature in transient optical spectroscopy. The absorption of the pump pulse (shown in Fig. 2.6 (a)) generates a population of electrons in the conduction band and holes in the valence band. In the ground state bleaching (Fig. 2.6(b)), the arrival of the probe, there are fewer electrons in the initial state for the transition; therefore, a decrease in absorption is observed with respect to the equilibrium case. The ground state bleaching effect has the same manifestation as band filling (BF), where the transient occupation of the excited state due to filling effects produces a reduction of the absorption of the probe pulse. Here, since the absorption of the probe pulse in the pump excited sample decreases with respect to the case of the sample in the equilibrium condition, the sign of the transient absorption is negative. In ESA (Fig. 2.6(c)), the probe beam

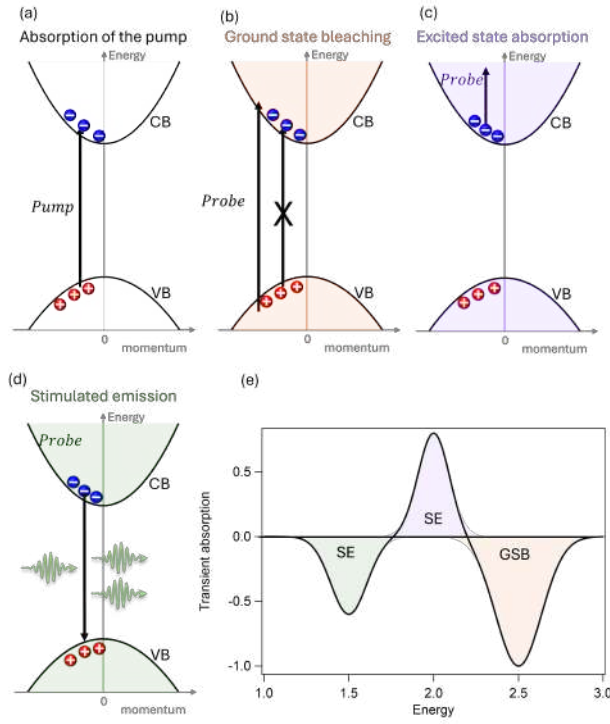


Figure 2.6: (a) Effect of the pump. Scheme of the ground state bleaching effect (b), the excited state absorption effect (c) and the stimulated emission (d). In (e) there is an example of a transient absorbance spectrum (black solid line) with ground state bleaching (orange area), excited state absorption (violet area) and stimulated emission (green area) contributions. Adapted from ([27]).

can be absorbed by the sample to excite electrons to higher energy states. In this case, there is the activation of a further absorption channel since the pump pulse can be absorbed by electrons located in the excited states. This results in a positive transient absorption. In SE (Fig. 2.6(d)), a photon from the probe pulse induces a sudden relaxation of the electrons in the valence band with the emission of a photon [12]. The photon is emitted in the same direction as the probe, so both will be detected. Negative transient absorption is observed because of the increase in the light intensity on the detector. To sum up all the processes, an example of the transient absorption spectrum is shown as a black line in Fig. 2.6 (e). Moreover, the ground state bleaching, excited state absorption and stimulated emission contributions to the total spectrum are shown in Fig. 2.6 (e) as orange, violet and green areas, respectively. The band

gap renormalization is a consequence of the excitation of free electrons in the conduction band that modifies the electrical properties of the material. The change of the screening produces a redshift in the band edge, so the transient absorption below the band edge is positive [141]. The scheme of the band gap renormalization is shown in Fig. 2.7.

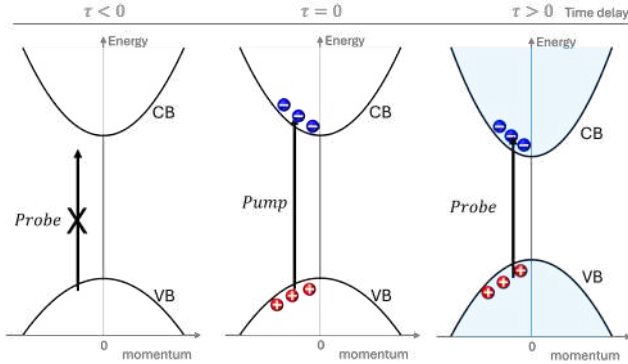


Figure 2.7: Scheme of the band gap renormalization. The pump pulse induces a population of electrons in the conduction band (CB). The high density of negative carriers in the CB creates a screening effect that results in a decrease in the band gap.

2.2.2 Photoinduced excitonic dynamics

We take as an example the case of GaAs, to describe the photoinduced dynamics in a semiconductor with an optical spectrum dominated by an excitonic resonance. The transmission before the arrival of the pump shows the behavior of Fig. 2.8 (a), where three regions emerge [163]. These traces were measured at wavelengths labeled A, B, and C in Fig. 2.8 (a). The decrease of the transmission at the A position is the free-exciton resonance. At shorter wavelengths than B, the increase of the transmission is due to the band-to-band transition. C indicates the position of the band edge, and at wavelengths longer than C, the material is essentially transparent.

At the free-exciton energy (A), the trace in Fig. 2.8(b) exhibits an abrupt increase as the exciton is screened within 0.5 ps, which is the time resolution of the experiment. This is followed by a more gradual increase as the carriers come into equilibrium with the lattice. At C, which is the long-wavelength side of the free exciton, there is an initial fast decrease followed by a slow increase.

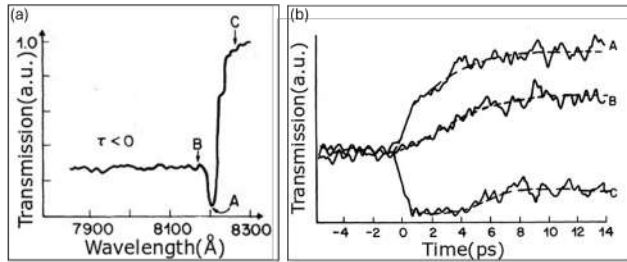


Figure 2.8: Transmission as function of wavelengths(a) and time delay (b) of a GaAs sample([163]).

These are generated by band-gap renormalization followed by band filling. At B, corresponding to the short-wavelength side of the free exciton, band-gap renormalization does not affect the signal significantly. Therefore, the relatively slow increase in transmission is attributed to the effects of band filling.

Now, we focus on how the photoexcitation can induce changes in the excitonic peak to understand better the out-of-equilibrium analysis that will be described in the discussion of the transient optical spectroscopy measurements. As described in chapter 1, exciton are Drude-Lorentz oscillators, which manifest in the absorption as a Lorentian peak (orange structure in Fig. 2.9(a) and (b)). Under photoexcitation, two main effects are observed: (i) broadening and quenching and (ii) shift of the energy position. In the broadening and quenching situation, the photoinduced effects result in a reduction of the oscillator strength and a concomitant broadening of its line width (Fig. 2.9(a)). It manifests as a decrease of the transient absorption at the exciton position flanked by an increase of the transient absorption. As we will discuss in Chapter 5, an increase in the oscillator strength is also possible in the presence of a coherent state. Moreover, the collective effect can also produce an increase in emission at the exciton position. The photoinduced shift results in a change in the central energetic position, usually produced by concomitant effects such as band gap renormalization and a change in the binding energy resulting from the dynamical screening effect. Moreover, during the pump-pulse cross-correlation the exciton can also undergo to a shift due to dynamical optical Stark effect or Franz-Keldish effects. The shifting manifests in the transient absorption as an increase-decrease (or decrease-increase) pattern with a node at the excitonic energy position. In general, the photoinduced variation of the excitonic resonance manifests as a combination of the two effects.

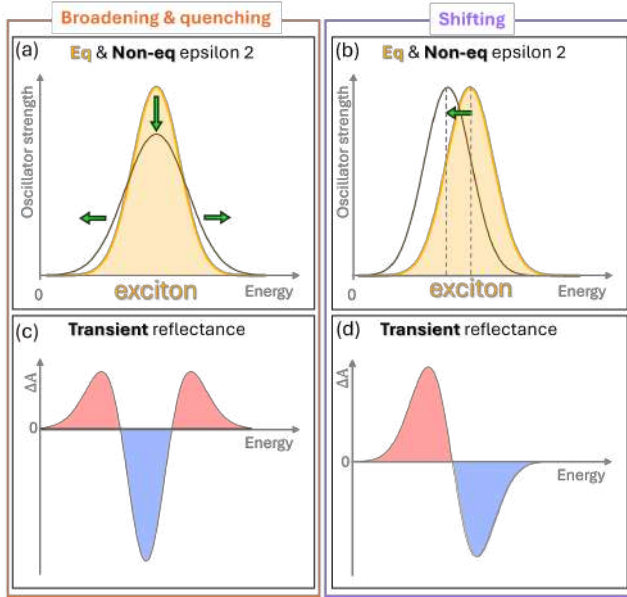


Figure 2.9: Broadening and quenching of the exciton observed in absorption (a) and transient absorption (c) Photoinduced shift of the exciton position observed in absorption (b) and transient absorption (d).

2.2.3 Phonon excitation

The optical spectroscopy is also sensitive to the phonon response of the system. Usually, as in Raman spectroscopy, light is able to excite a motion of the atoms in the crystal structure along the vibrational mode in an incoherent way. However, ultrafast laser pulses, as the ones used in transient optical spectroscopy, can induce a collective motion of the atoms in the crystal and then generate coherent phonons [70].

There are two types of coherent phonons with different lifetimes: the acoustic one and the optical one. The acoustic phonon can reach a lifetime of a microsecond at low temperature, the phonons from the optical branch can have a lifetime less than a nanosecond. The coherent acoustic phonons propagate as ballistic strain pulses in crystals. On the contrary, the coherent optical phonons are delocalized and non-propagating as light couples directly with phonons only at the Γ point of the Brillouin zone ($k = 0$) where the group velocity is nearly 0. The classical equation of motion of coherent phonons is a driven harmonic oscillator in a small nuclear displacement $Q(t)$:

$$\mu^* [\ddot{Q}(t) + 2\gamma\dot{Q}(t) + \omega^2 Q(t)] = F(t) \quad (2.13)$$

Where μ^* is the reduced lattice mass (or effective mass), γ is the phonon damping constant and ω_0 is the undamped phonon frequency. The generation of coherent phonons could be of two types: impulsive or displacive. The discrimination between them is based on the temporal profile and origin of the force $F(t)$. The driven time-dependent force $F(t)$ on the lattice results from a sudden change in the electronic distribution. The first is called *impulsive stimulated Raman scattering* (ISRS), and it is shown in Fig. 2.10(a). The second is named *displacive excitation of a coherent phonon* (DECP), and it is shown in Fig. 2.10(b). The excitation energy and the electronic band structure of the sample are responsible for which of the two cases dominates.

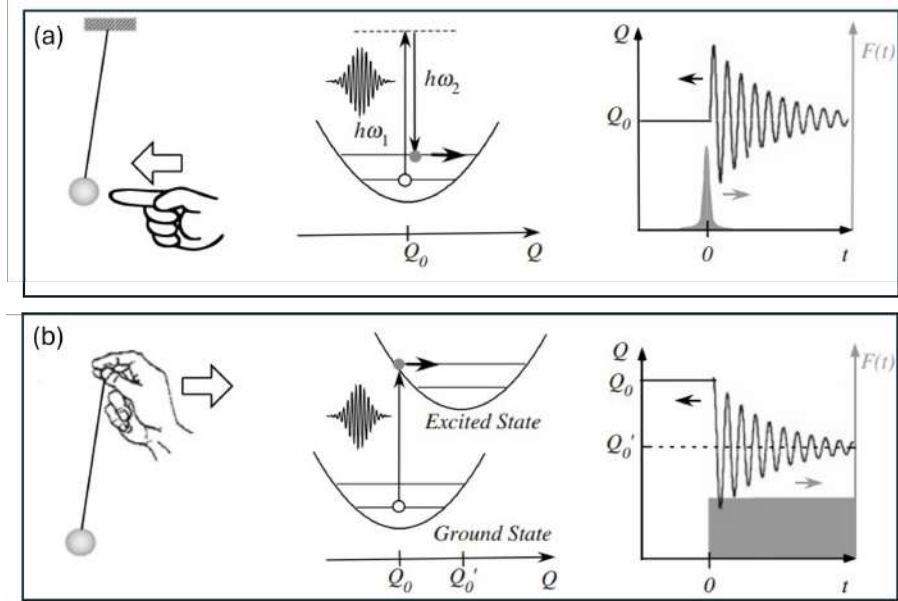


Figure 2.10: (a) ISRS generation model. The graph on the right displays the time evolution of the driving force (grey line) and that of the displacement (solid line). (b) DECP generation model. The graph on the right displays the time evolution of the driving force (grey line) and that of the displacement (solid line) [69].

In general, when a solid is excited by an under-resonance photon energy, i.e. the photon energy is lower than the energy band gap, ISRS is the only mechanism

of coherent phonon generation.

Some requirements should be fulfilled to have the generation of coherent phonons: (i) the phonon mode has to be Raman active, and (ii) the pulse duration has to be lower than the period of the oscillation associated with the phonon mode.

Due to the uncertainty principle, the pulse generated by a femtosecond laser pulse is broadband in energy. The pulse holds multiple combinations of two photons whose energy difference ($\hbar\omega_1 - \hbar\omega_2 = \hbar\omega_0$) matches the vibrational energy and gives an impulsive driving force to start the coherent motion of the atoms. A δ -like force kicks the atoms that start to oscillate around their equilibrium position as shown Fig. 2.10(a). When the pulse arrives, they start to move from their equilibrium position, and thus, they move in time following a sine function trajectory. The corresponding classic picture is a kick of the pendulum, resulting in a change in its kinetic energy.

The displacive excitation of coherent phonons usually occurs in an absorbent medium. A resonant transition occurs when a femtosecond pulse impinges on the samples with an energy larger than the energy gap of the sample. In this case, electrons are photoinduced in real states, which affects the crystal structure until they recombine. This type of force has a step-like shape, as shown in Fig. 2.10(b), and its application results in a shift of the equilibrium point for the phonons. The shift in equilibrium coordinate ($Q'_0 - Q_0$) is assumed to be a linear function of photoexcited electron density $n_e(t)$. Then, at the momentum of the photoexcitation, the atoms start to move from their new equilibrium position, and the result is a cosine function of time. Also, in this case, to generate coherent phonons, the pulse duration has to be lower than the period of oscillation. The classic picture is a quick translation of the suspension point of a pendulum, which results in a sudden change in the potential energy. As described in Equation 2.13, the reflectivity depends linearly, in the first approximation, on the phonon coordinates $Q(t)$ [69] as follows:

$$\Delta R = \frac{\partial R}{\partial n_e} \Delta n_e(t) \approx \frac{\partial R}{\partial \chi} \frac{\partial \chi}{\partial Q} Q(t) \quad (2.14)$$

where n is the refractive index, and χ is the electric susceptibility. The $\frac{\partial \chi}{\partial Q}$ is a first-order Raman tensor, which is non-zero only in the Raman active mode. Therefore, only Raman active modes are revealed by linear optical spectroscopy.

Chapter 3

Bismuth tri-iodide

Bismuth tri-iodide is a layered semiconductor known for its quasi-direct band gap and absorption dominated by a strongly bound bright exciton. The initial interest of the scientific community for BiI_3 was related to the application as a gamma-ray detector at room temperature [105, 147], since the high density and atomic number of iodine is promising for radiation absorption [152]. In recent years, due to its optoelectronic properties, it has become attractive for photovoltaic applications both in its single crystal and thin film form [179, 14, 87]. The presence in the electronic structure of a well-isolated excitonic state in the monolayer as well as in the bulk makes this material an ideal platform for studying the exciton physics. In the first part of this section, we will describe the state-of-art on BiI_3 static and out-of-equilibrium properties. In the second part, we provide a description on how the exciton phonon coupling influencees the excitonic resonance by changing the temperature.

3.1 Structural, optoelectronic and vibrational properties: state of art

BiI_3 is a metal halide semiconductor composed of bismuth atoms, with electronic configuration $5d^{10} 6s^2 6p^3$, and iodine atoms, $5s^2 5p^5$. Bi^{3+} cations have the electronic configuration $5d^{10} 6s^2 6p^0$ as the divalent Pb, making the first the right candidate for the substitution of lead in photovoltaic devices. Each layer of BiI_3 interacts with the neighbouring one with a weak van der Waals force, while within the layers, the Bi and I atoms show a high ionic bound. It has a rhombohedral crystal structure, so it belongs to the space group $R\bar{3}$ (no.148)

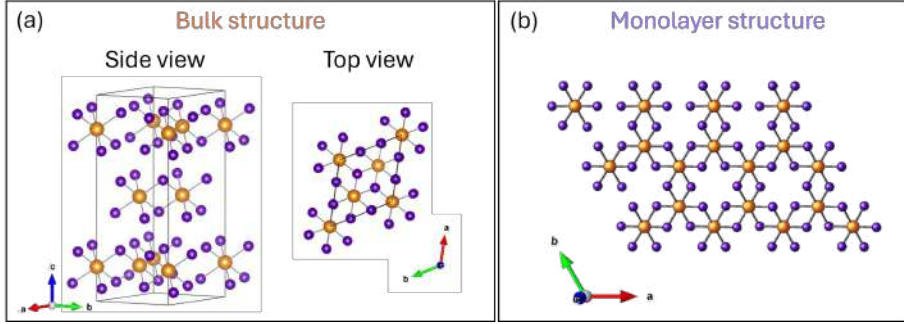


Figure 3.1: Representation of (a) BiI_3 bulk structure and (b) single layer of BiI_3 .

with an ABC stacking of the layer. The bulk BiI_3 crystal structure shows a double-point symmetry S_6 . The iodide anions form an almost hexagonally close-packed lattice, whereas the bismuth cations occupy two-thirds of the octahedral voids in the second layer. The bismuth atom is octahedrally coordinated with iodide atoms.

In bulk (shown in Fig. 3.1 (a)), the interlayer distance is $3.38 \text{ \AA}$ and the Bi-I bond length is $3.046 \text{ \AA}$. The BiI_3 unit cell is rhombohedral, the lattice parameters are $a = b = c = 8.926 \text{ \AA}$ and $\alpha = \beta = \gamma = 52.063^\circ$ [136]. The conventional cell is rhombohedral as described in Fig. 3.1 (a) with $a=7.517 \text{ \AA}$ and $c=20.716 \text{ \AA}$ [121]. This has been used as a starting point for the *ab initio* calculation that complements our results in this thesis. Ma et al. [94] explored the stability of BiI_3 nanosheets in order to isolate a single layer of BiI_3 . They estimated cleavage energy was similar to that of graphene. This result proves the possibility of exfoliating BiI_3 up to the monolayer form.

Single-layer BiI_3 (shown in Fig. 3.1(b)) is composed of a consecutive plane of I-Bi-I with a Bi-I bond length of $3.1 \text{ \AA}$, which is similar to the I-Bi bond of bulk BiI_3 [94]. For monolayer BiI_3 the crystal structure belongs to P_31m (n 162) and has a double point symmetry D_{3d} , characteristic hollow of trihalides like CrI_3 [67]. The single-crystal BiI_3 is featured by an indirect band gap of 1.67 eV with a weak absorption coefficient ($\alpha \sim 100 \text{ cm}^{-1}$) and a direct band gap of 1.96 eV with a higher absorption coefficient that can reach more than 10^5 cm^{-1} above 2 eV [158].

Starting from the bulk crystal structure in Fig. 3.1(a), the band structure inserted in Fig. 3.2 (a) has been simulated by the group of theorists who collaborate with us. The calculation was carried out from the first principle calculation. It used the DFT formalism that exploited $8 \times 8 \times 8$ supercells. The

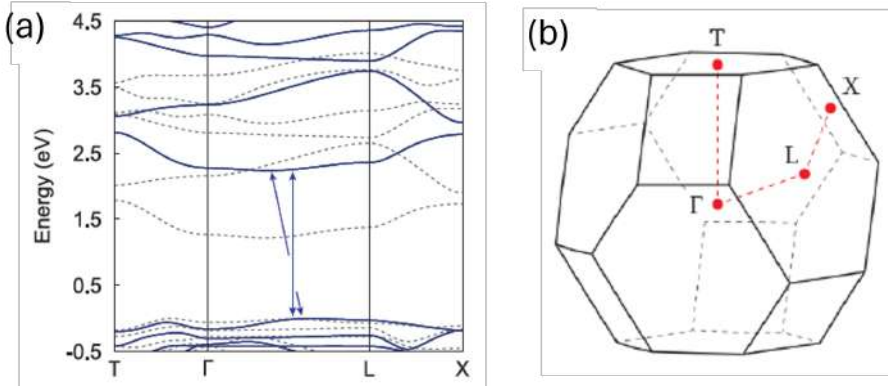


Figure 3.2: (a) Calculated electronic band structure for a bulk BiI_3 . The solid lines are calculated using the GW approximation, while the dashed ones are calculated using DFT. (b) Brillouin zone of bulk BiI_3 . Taken from [21].

Perdew-Burke-Ernzerhof (PBE) exchange-correlation function has been used. The van der Waals interaction has been evaluated using the Tkatchenko-Scheffler model (TS-vdW). Podraza et al. demonstrate a strong spin-orbit coupling (SOC) in BiI_3 , so a DFT calculation was performed including fully relativistic effects [21]. The crystal structure at the equilibrium used in the calculation has a length of edges of $a=7.823 \text{ \AA}$ and $c=22.812 \text{ \AA}$, which are consistent with the x-ray diffraction calculations of $a=7.519 \text{ \AA}$ and $c=20.721 \text{ \AA}$ [140]. The inherent overestimation of the DFT band gap is corrected using the GW method. The resulting band dispersion is shown in Fig. 3.2, where on the y-axis there is the calculated energy and on the x-axis is reported the position of the high symmetry points of the first Brillouin zone of a primitive hexagonal unit cell displayed in Fig. 3.2. The direct and indirect gaps are indicated by the arrows. The band structure shows a fundamental indirect band gap of 2.24 eV and a direct gap close in energy (2.26 eV) and momentum, being both located on the line between Γ and L.

The conduction band is formed of highly covalent I 5p and Bi 6p hybridized states split due to the spin-orbit coupling, while the valence band is mainly composed of I 5p orbital with a minor contribution from Bi 6s electrons [173]. The conduction band is more dispersed in momentum than the valence band as a result of spin-orbit coupling promoted by Bi^{3+} ions. This results in a lighter effective mass of electrons in comparison to that of the holes and, thus, a higher electron mobility. The effective electron mass is 5 times lower than that of holes, and the electron mobility is 30 times higher than that of the holes; the latter can reach $250 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [179]. All in all, the valence band is

mainly composed of I atomic levels and the conduction band is dominated by the orbitals of the bismuth atoms. The band structure can also be calculated for the monolayer BiI_3 . Also, in this case, the SOC effect is important because

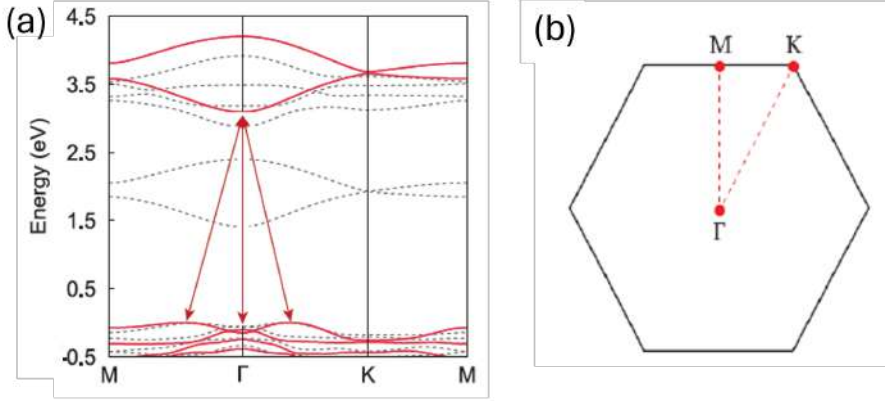


Figure 3.3: (a) Calculated electronic band structure for a monolayer of BiI_3 . The solid lines are calculated using the GW approximation, while the dashed ones are calculated using DFT. (b) Brillouin zone of a monolayer of BiI_3 . Taken from [21]

it can induce a reduction of the band gap of 1eV and a consecutive downward shift of the conduction band. Band structure for the single-layer BiI_3 is shown in Fig. 3.3(a). The band structure is less flat, and the direct gap located at Γ is 3.18 eV. The fundamental gap is still indirect, with a value of 3.09 eV.

Due to its sixfold symmetry, BiI_3 is optically uniaxial with a c -axis perpendicular to the basal plane, and it requires two dielectric functions: an ordinary dielectric function and an extraordinary dielectric function. In ordinary dielectric function, the light is polarized parallel to the optical axis c ($E \parallel c$), while in extraordinary dielectric function, the light is polarized perpendicular to the optical axes ($E \perp c$). Using a two-modulator generalized ellipsometry, Jellison et al. [73] obtained the ordinary and extraordinary dielectric function of a 1 mm thick BiI_3 single crystal grown by vapor-transport method. The real and imaginary part of the complex dielectric function ($\epsilon = \epsilon_1 + i\epsilon_2$) measured by Jellison et al. and its relative absorption coefficient (α) calculated using:

$$\alpha = \frac{4\pi k}{\lambda} \quad (3.1)$$

are shown in Fig. 3.4 (a). Below the direct band gap $\epsilon_2 = 0$ while ϵ_1 is highly dispersive. The refractive index n and k are related to the complex dielectric

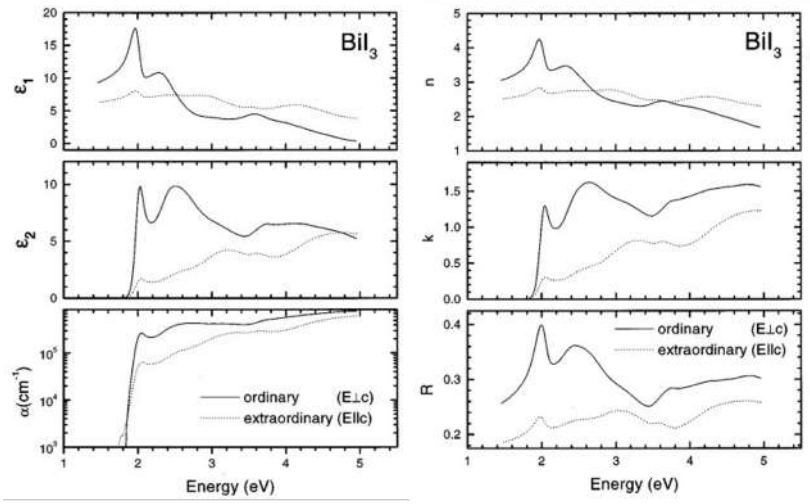


Figure 3.4: Optical function of BiI_3 collected by ellipsometry. Taken from [73].

function by

$$\epsilon = (n + ik)^2 \quad (3.2)$$

and the normal incidence refractivity R is:

$$R = \frac{(n - 1)^2 + k}{(n + 1)^2 + k} \quad (3.3)$$

In (Fig. 3.4), the real and imaginary part of the dielectric function, the absorption coefficient α , n and k , and R are plotted for both the ordinary and extraordinary axes. Komatsu and Kaifu [84] identified the first peak of ϵ_2 located at $\sim 2\text{eV}$ with a strong exciton associated with the direct absorption edge. The absorption coefficient shows a long tail, which is an Urbach tail. The absorption coefficient dependence on the photon energy is described by:

$$\alpha(E) = \alpha_0 e^{-\frac{\sigma(E_0 - E)}{kT}} \quad (3.4)$$

The value of the direct and the indirect band gap can be extrapolated by the absorption coefficient using Tauc's plot. The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) near the fundamental absorption edge is:

$$(\alpha h\nu)^{\frac{1}{n}} = A(h\nu + E_g) \quad (3.5)$$

Where A is a constant, α is the optical absorption coefficient, h is the Planck constant, ν is the frequency of the incident photon energy, and E_g is the optical

band gap. The exponent n depends on the optical transition, in particular for the direct transition $n = \frac{1}{2}$ while for the indirect $n=2$ [140]. An example of Tauc's plot, performed by Podraza et al., is displayed in Fig. 3.5.

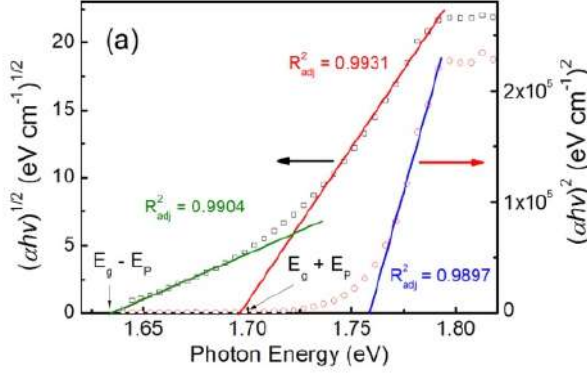


Figure 3.5: Analysis of the UV-Vis measurement as a function of the energy to evaluate the direct and indirect behavior. Taken from [140].

The plot $(\alpha h\nu)^{\frac{1}{2}}$ versus $h\nu$ has been interpolated by two straight lines (red and green) with different slopes that take into account the absorption and the emission of phonons during the interband transition. This behavior is consistent with the presence of an indirect gap, and the two intercepts of the energy axis correspond to $E_g + E_p$ and $E_g - E_p$, where E_g is the indirect energy gap and E_p is the phonon energy. The plot $(\alpha h\nu)^2$ versus $h\nu$ shows only a straight line. The intercept on the energy axis is the value of the direct energy gap E_g . From a theoretical point of view, the absorption and excitonic band structure are calculated by solving the Bethe-Salpeter equation.

Fig. 3.6(a) shows the calculated excitonic resonances with perpendicular and parallel polarization, blue and light blue lines, respectively. The yellow lines are the position of the bright excitons. The absorption is calculated by inserting a fictitious broadening. The quasiparticle band gap is shown at 2.26 eV as a vertical black dashed line. Below the fundamental gap, the absorption is dominated by the bright excitonic resonance located at 2.12 eV. To fully explore the excitonic panorama in BiI_3 , also the excitonic band structure has been calculated by including all the excitons with zero and non-zero center of mass. The lowest bright exciton is indicated by the red dot in Fig. 3.6 (b). Its calculated binding energy is 140 eV, which is higher than conventional 3D semiconductors. The exciton extends over multiple unit cells as described in Fig. 3.6(c). The lowest exciton is dark, and it is located 50 meV below the

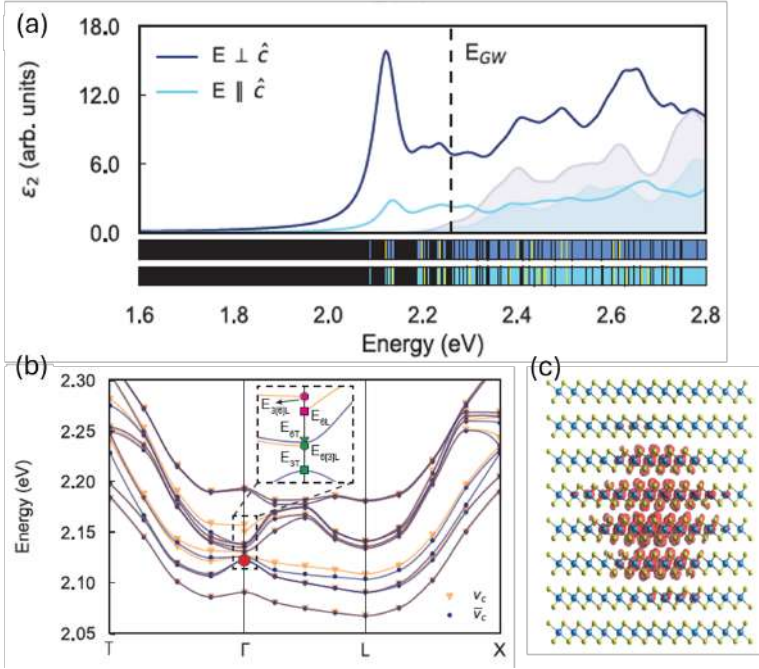


Figure 3.6: (a) Calculated imaginary part of the dielectric function for a bulk BiI_3 . (b) Exciton band structure of BiI_3 . (c) Exciton wave function extension in real space. Taken from [21].

lowest bright exciton.

The space group symmetry $R\bar{3}$ (no.148) associated with the BiI_3 crystal manifests twelve Raman active modes: four non-degenerate A_g modes and four doubly degenerate E_g modes ([153], [158]). An indicative Raman spectrum is shown in Fig. 3.7(a) where the different vibrational modes are indicated.

The modes at 98 and 113.3 cm^{-1} are LO phonon modes at the Γ and Z special points of the Brillouin zone, respectively [179]. A sketch of the A_g mode and of the E_g mode is reported in Fig. 3.7 (c) and (b), respectively.

3.2 Out-of-equilibrium properties

The out-of-equilibrium properties have been investigated in the literature by means of transient absorption spectroscopy in a thin film [158] and using time-

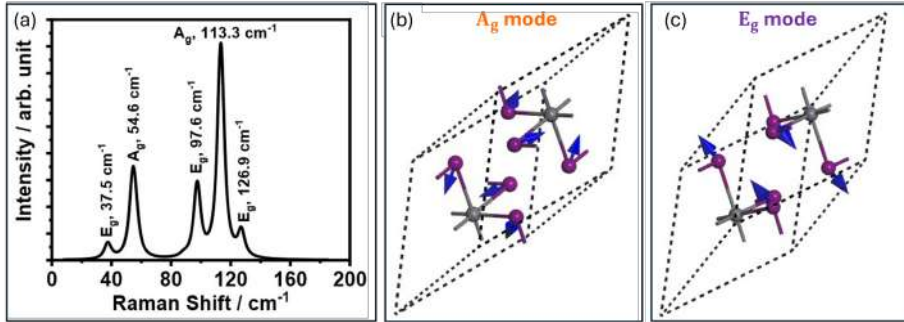


Figure 3.7: (a) Active Raman mode of BiI_3 . (b) and (c) Visualization in the real space of the A_g and E_g mode. Taken from [179].

resolved photoluminescence in a single crystal [14]. In the first, Scholz et al.[158] presented broadband transient pump-supercontinuum probe absorption measurements on BiI_3 under excitation with a pump pulse at 400 nm. The sample used is composed of a substrate of TiO_2 , which is a mesoporous scaffold material, and a thin film of BiI_3 is grown on this substrate. The contribution of the substrate to the study of the BiI_3 dynamics has been neglected. The transient absorption is measured as the variation of the optical density between 260 nm and 670 nm.

Fig. 3.8 (a) and (b) show the probe wavelength and time-dependent variation of the optical density, respectively. At zero delay time, a bleaching feature is observed below 530 nm and an oscillatory structure above. The bleaching arises from two contributions, the photoexcited electrons that relax around the minimum of the conduction band corresponding to the indirect gap at 1.67 eV, and the holes that gather together at the valence band maximum corresponding to the direct gap at 1.96 eV. Up to ten picoseconds (green spectrum), the band-edge feature shifts to the blue, and the bleaching region shows a small decay. Therefore, the dynamics involve predominantly carrier-optical phonon scattering processes, the beginning of the decay of optical into acoustic phonons, and also some electron-hole recombination. The estimated relaxation time for this process is about 3.6 ps.

At times longer than 200ps, the electron-hole recombination dominates. The decay can be well described by the time constant $\tau_3 = 260$ ps and another very slow component, which we can only roughly estimate as $\tau_4 > 5$ ns.

This long-lived dynamic was also observed by photoluminescence measurements [14]. The spectrum in Fig. 3.8 (a) has a minimum located at about 2.0 eV, which corresponds to the position of the direct band edge, and it is dominated by the exciton localized at 610 nm. After 0.52 ps a fast disappearance of the exciton

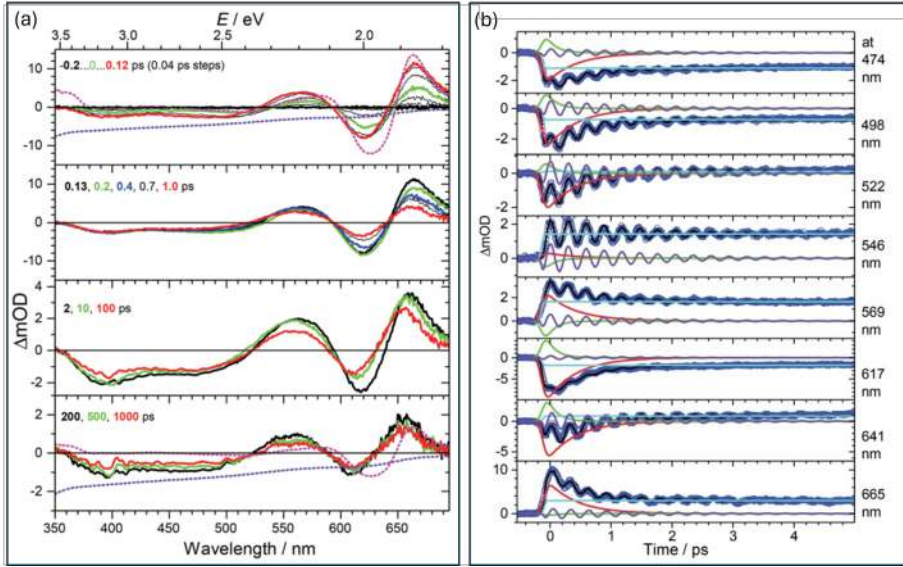


Figure 3.8: (a) Behavior of the transient absorption as a function of probe wavelengths at several time delays. (b) The behavior of the transient absorption as a function of time delay at several probe wavelengths.[158]

absorption is observed due to the Coulomb screening by photoexcited carriers. The horizontal line profiles performed in the spectral range of 474 nm - 665 nm are linecuts shown in Fig. 3.8 (b). The traces show a strong oscillatory feature persisting until 5 ps. This periodic modulation of the measured transmission is due to the coherent optical phonons generated by photoinduced collective motion of the atom around their equilibrium position, as discussed in Section 2.2.3. In this case coherent phonons are generated by impulsive stimulated Raman scattering. The short-time kinetics traces are described by a damped cosine, with dumping time constant τ_d and a wavelength-independent phase shift, and a double exponential, with time constants τ_{e1} e τ_{e2} , that take into account of the electron-optical phonon scattering. The experimental time resolution was included by convolving this total fit function with the Gaussian instrument response function. The prominent oscillation has 114 cm^{-1} Raman shift, which corresponds to the $\text{C}(\Gamma)$ longitudinal optical phonon mode of A_g symmetry. The calculated dumping time constant is $\tau_d = 1.1 \text{ ps}$. The time constants of the two exponential decays are $\tau_{e1} = 0.16 \text{ ps}$ e $\tau_{e2} = 0.48 \text{ ps}$.

The Fourier transform, shown in Fig. 3.9, shows that the oscillations are due to the excitation of the A_{1g} phonon mode at 114 cm^{-1} . Moreover, the low-frequency Raman activity is mainly found in the wavelength region above

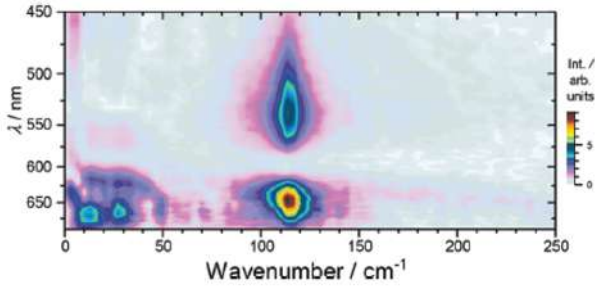


Figure 3.9: FT intensity as a function of the probe wavelength and wavenumber.

620 nm in the transparent regime.

3.3 Characterization of the steady state optical response of BiI₃

Before starting the time-resolved measurements, we collected the reflectance and transmittance at equilibrium on BiI₃ crystals by a VIS-UV spectrophotometer. Fig. 3.10 shows the collected reflectance (solid blue curve) and the calculated absorbance ($A = -\log_{10}(T)$, solid red curve).

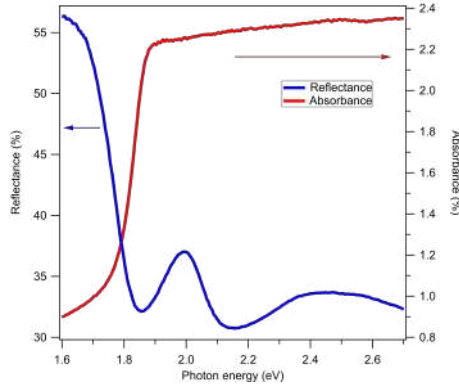


Figure 3.10: Collected reflectance (blue curve) and absorbance (red curve).

The absorbance starts to increase at 1.6 eV, reaching the maximum at 1.9 eV.

The excitonic resonance is not visible due to the thickness of the sample. The reflectance shows an initial decrease at 1.7 eV, a resonance at 2 eV and a broader one at 2.5 eV. The structure at 2 eV is assigned to be the lowest bright exciton, while the second feature is a collection of higher-order excitons. The nonzero intensity below 1.8 eV does not have a counterpart in the literature. Since the increase is similar to the transmittance, we assign it to residual intensity due to the backscattering of the sample holder. To corroborate it, we collected the entire reflectance spectrum (blue markers in Fig. 3.11(a)) and the scattered reflectance (yellow markers in Fig. 3.11(a)).

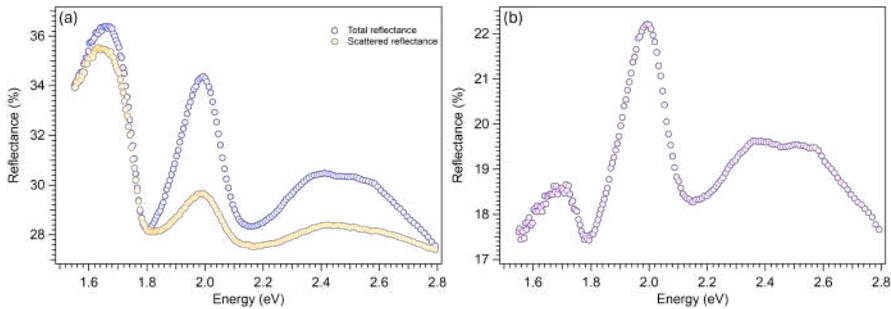


Figure 3.11: (a) Collected entire reflectance (blue marker) and scattered reflectance (yellow markers). (b) Residual reflectance calculated as the difference between the total and scattered reflectance.

The two spectra present the same spectral features with a significant difference in the ratio between the intensity below 1.8 eV and the excitonic peak at 2 eV. Indeed, the ratio is higher for the scattered reflectance than for the total curve. Subtracting the scattered reflectance from the total curve, we observe an almost total absence of the intensity below 1.8 eV (violet markers in Fig. 3.11), supporting the previous hypothesis.

The temperature-induced evolution of the static reflectance has been collected by exploiting Fourier-transform infrared spectroscopy (FTIR) measurements. We measure the reflected intensity (I_R) of the bulk and the copper substrate (I_{Cu}) separately. The resulting reflectance is defined as $R = I_R/I_{Cu}$. Fig. 3.12 shows the resulting reflectance as a function of energy collected at various temperatures ranging from 5 K (blue curve) to 300 K (orange curve). The reflectance at 300 K shows an excitonic peak at 2 eV and the beginning of the second peak, which is in agreement with the reflectance collected with the spectrophotometer in Fig. 3.11. Conversely, from the previous case, the geometry of the FTIR does not allow us to collect the scattered light, and therefore, the intensity below 1.8 eV is not observed in this set of measurements. Decreasing the temperature (from orange to blue in Fig. 3.12(a)), the main exciton shows a blueshift, a

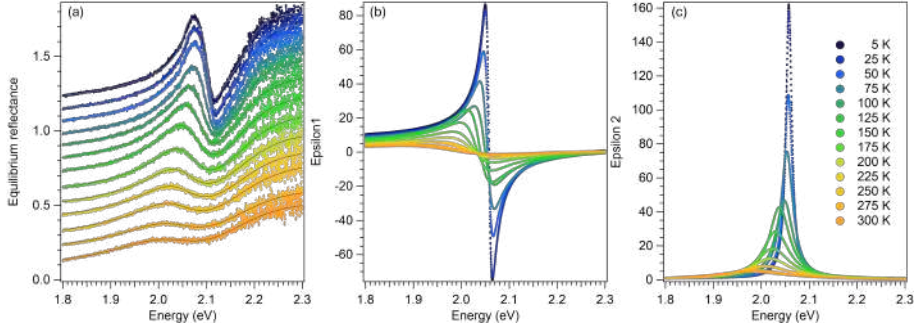


Figure 3.12: (a) Measured reflectance as a function of energy at several temperatures spanning from 5 K to 300 K. The relative fittings are inserted as gray curves. Calculated real (b) and imaginary part of the dielectric function.

shrinkage of its linewidth, and an increase of its intensity. Moreover, the shape of the reflectance changes, i.e. at room temperature, the shape is more similar to the absorption, while around 150 K, the shape becomes more derivative due to the contribution of the real part of the dielectric function.

To rationalize the evolution in the temperature of the excitonic resonance, we decided to fit the collected reflectance spectra with the Lorentz model [198]. In this model, the real and imaginary part of the dielectric function for a series of oscillators is:

$$\epsilon_1 = 1 + \frac{4\pi e^2}{m} \sum_j \frac{N_j(\omega - \omega_j)^2}{(\omega_0^2 - \omega^2)^2 + \Gamma^2\omega^2}, \quad (3.6)$$

and

$$\epsilon_2 = \frac{4\pi e^2}{m} \sum_j \frac{N_j\Gamma\omega}{(\omega_j^2 - \omega^2)^2 + \Gamma^2\omega^2}, \quad (3.7)$$

where e and m_e are the electronic charge and mass, respectively, ω_j is the frequency of the j -th oscillator, and N_j is the density of the electrons. They are related to the complex refractive index ($\hat{n} = n + ik$) through $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$ and to the reflectance following the equation: $R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$. To fit the static reflectance, we used two Lorentian functions. Significant fits are inserted in Fig. 3.12(a) as grey curves. To better describe the temperature dependence of the exciton resonance, the real and imaginary parts of the dielectric function are shown in Fig. 3.12 (a) and (b); as previously reported, the exciton undergoes a blueshift, a shrinkage, and an increase in its intensity. To rationalize these changes, we have explored the temperature evolution of both the main and the second exciton as depicted in Fig. 3.13 (a) and (b).

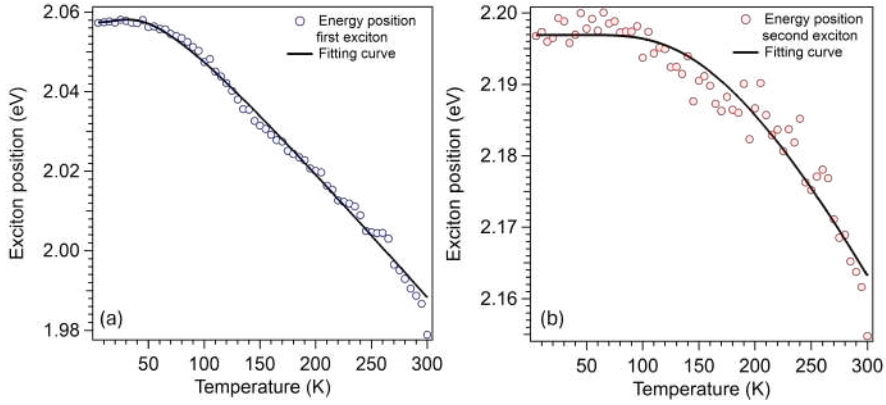


Figure 3.13: (a) Temperature evolution of the first excitonic peak (blue markers) with the relative fitting function. (b) Temperature evolution of the second excitonic peak (red markers) with the relative fitting function.

The temperature evolution of the exciton is driven by exciton-phonon coupling as described in Equation 1.18 reported here:

$$E_X(T) = E_X(0) - S_X < \hbar\omega >_X \left[\coth\left(\frac{< \hbar\omega >_X}{2k_B T}\right) - 1 \right] \quad (3.8)$$

where the $E_X(0)$ is the exciton position at zero temperature, S_X is the exciton-phonon coupling strength and $< \hbar\omega >_X$ is the average phonon energy. The average phonon energy is related to the Debye temperature Θ_X : $< \hbar\omega >_X = k_B \Theta_X$. By fitting the data by Equation 3.8, we found that at zero temperature the exciton is located at (2.058 ± 0.02) eV. The average phonon energy is (15.2 ± 1.7) meV, which is comparable to the A_g phonon energy of 14 meV. The resulting Debye temperature is (176 ± 20) K. The coupling strength between the exciton and the optical phonon is enclosed in the fitting parameter S_X . In this case, the exciton-phonon coupling strength is 1.8, which is comparable to the values found in TMDs [176]. The second peak has another behavior. The average phonon energy $< \hbar\omega >_X = (52 \pm 2)$ meV is much larger than A_g phonon energy. The second peak combines a collection of excitonic features and the absorption band gap edge. Therefore, this behavior is the result of the interaction with a collection of phonons. Fig. 3.14 (a) and (b) show the temperature-induced width variation of the first and second oscillators, respectively. As discussed in Section 1.2, the exciton-phonon coupling affects inhomogeneous exciton broadening. This is described by the Equation 1.19:

$$\Gamma_X = \Gamma_{XI} + \frac{\gamma_{X,ph}}{e^{\frac{< \hbar\omega >_X}{k_B T}} - 1} \quad (3.9)$$

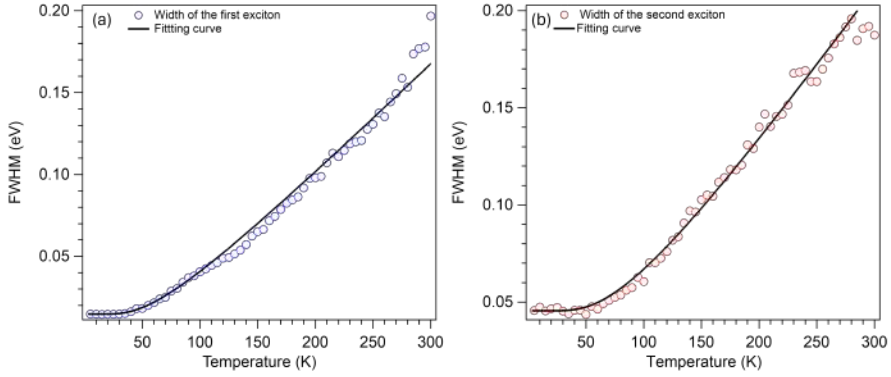


Figure 3.14: (a) Temperature evolution of the first excitonic width (blue markers) with the relative fitting function. (b) Temperature evolution of the second excitonic width (red markers) with the relative fitting function.

The first term Γ_{XI} represents the inhomogeneous broadening induced by temperature-independent mechanisms, such as scattering of excitons with structural defects or impurities. The second term describes exciton-phonon scattering for both absorption and emission of phonons represented by $\gamma_{X,ph}$. The average energy of the phonons that couple with excitons is $\langle \hbar\omega \rangle_x$. We used Equation 3.9 to follow the temperature-induced variation in the exciton broadening; the resulting fitting curves are reported in Fig. 3.14 (a) and (b) as solid black curves. The average phonon energy for the first peak is (14.5 ± 1.2) meV, which is consistent with the previous analysis and the A_g phonon mode. The inhomogeneous broadening driven by the temperature-independent mechanism is (15 ± 2) meV. The second peak behavior is different from that observed earlier. The average phonon energy in this case is (20 ± 2) meV, which is neither comparable with the A_g phonon mode nor with the previous value. This results from the composite nature of the second peak and from a limited probed window in energy. The inhomogeneous broadening driven by the temperature-independent mechanism is (45 ± 5) meV. In conclusion, we explored how the exciton-phonon coupling influences the exciton resonance with changing temperature. In particular, we observe that the first bright exciton is mainly coupled with the optical A_g phonon mode, with a coupling strength of 1.8, similar to other layered semiconductors [176]. The situation with the second exciton is less clear. In fact, it contains several excitonic structures and an absorption edge. Moreover, our probed window does not cover the whole peak.

Chapter 4

Tracking the exciton formation by tr-ARPES

This chapter is partially taken from:

Unveiling exciton formation: exploring the early stages in time, energy and momentum domain

V. Gosetti, J. Cervantes-Villanueva, S. Mor, D. Sangalli, A. García-Cristóbal, A. Molina-Sánchez, M. Tuniz, D. Puntel, W. Bronsch, F. Cilento, V. F. Agekyan, S. Pagliara

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In this chapter, we study exciton formation and relaxation dynamics on BiI_3 using tr-ARPES.

ARPES and tr-ARPES experiments were carried out at the T-ReX laboratory (FERMI, Trieste). ARPES measurements utilizing 10.8 eV photon energy were used to determine the VB edge of BiI_3 . Subsequently, tr-ARPES measurements were used to track the dynamics of photoinduced electrons excited by a pump photon energy of 3.14 eV.

The subsequent exciton formation and localization processes were captured through energy-dependent curve analysis. Experimental observations were complemented by numerical simulations, in which the tr-ARPES signal of BiI_3 was reconstructed by combining the theoretical formulation of tr-ARPES in

the presence of exciton populations with accurate *ab initio* simulations. This approach enables us to discriminate signals arising from bound excitons and free carriers.

The chapter is organized as follows. First, a description of the experimental principle and the data correction will be provided. The results will then be presented and discussed in detail. This will be followed by a section that offers insight into the theoretical results that complement the experimental findings. A final section will be inserted to give an overview of the theoretical results that complement our experimental findings. Eventually, the chapter concludes with a summary and discussion of key outcomes.

4.1 Preliminary measurements

To directly compare the energy of the excited population with the optical transition energies, the energy axis for the experimental data is referred to the VB maximum. To determine its position, we collected the static photoemission spectrum with a photon energy of 10.8 eV¹, larger than the BiI₃ workfunction.

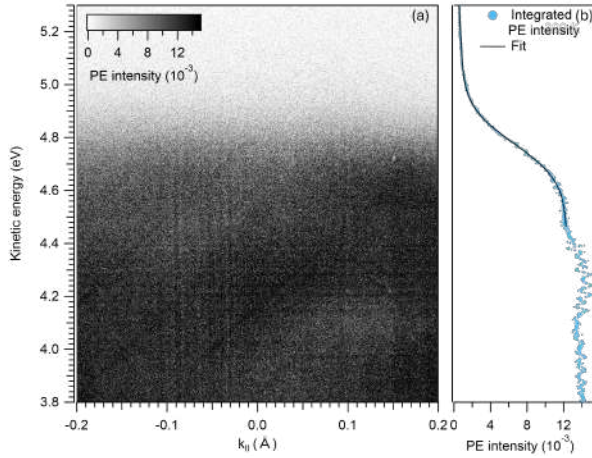


Figure 4.1: (a) ARPES measurement with 10.8 eV photon energy. (b) Integrated PE intensity between $-0.2 \text{ \AA}^{-1}$ and $0.2 \text{ \AA}^{-1}$ as a function of kinetic energy.

¹The setup is described in Appendix A.

Fig. 4.1 (a) shows the resulting photoemitted (PE) intensity as a function of parallel momentum ($k_{\parallel}$) and kinetic energy (E_K). The white (black) color represents the zero (maximum) photoemission intensity. The PE intensity increases around $E_K=4.8$ eV, corresponding to the onset of the valence band, but it does not exhibit any significant $k_{\parallel}$ dependence. We integrated the intensity over the range $-0.2 \text{ \AA}^{-1}$ to $0.2 \text{ \AA}^{-1}$ as shown in Fig. 4.1(b). The resulting curve was fitted using an error function with the central value of the fit ($E_K=4.77$ eV) defining the valence band edge.

To align the valence band edge in the out-of-equilibrium photoemission data collected at 6.2 eV (Fig. 4.3 (a-f)), the kinetic energy was downshifted by 4.6 eV, which corresponds to the difference between the two photon energies (6.2 eV and 10.8 eV). Consequently, the energy was referred to the valence band edge (E_{VB}), introducing a new energy scale called *intermediate state energy* ($E - E_{VB}$). For all measurements, the error bar on the absolute value of the energy was set to 0.1 eV, which is the uncertainty in the evaluation of the zero-energy reference of the system.

4.2 Time resolved photoemission measurements

The tr-ARPES experimental parameters are shown in Fig. 4.2(a). The pump photon energy is 3.14 eV lower than the ionization energy of BiI_3 ($E_I = 5.8$ eV [179]) and significantly exceeds the bottom of the conduction band. This configuration facilitates the excitation of quasi-free carriers into typically unoccupied excited states. The s-polarized probe photons at 6.28 eV are used to photoemit electrons from the transiently occupied excited states. This probe photon energy enables the measurement of the parallel momentum between $-0.12 \text{ \AA}^{-1}$ and $0.12 \text{ \AA}^{-1}$ in a single acquisition.

To understand the feature characterizing the probed region, the BiI_3 electronic structure has been calculated within DFT framework [104], and quasiparticle corrections were applied using the GW method [144, 126]². Since ARPES measurement probes only a few layers of the material (the mean free path is about 20 $\text{\AA}$ at 6.2 eV, while the thickness of each layer and the interlayer distances of BiI_3 are 5 $\text{\AA}$ and 3.38 $\text{\AA}$, respectively), the projected band structure is needed to compare the experimental data and the theoretical simulation. First, the hexagonal-projected path in the Brillouin zone has been calculated at $k_z = 0$, followed by integration along k_z direction. This integration produces the shaded areas in the surface projected band structure shown in Fig. 4.2 (b). The probed region is highlighted by a dashed frame, resulting in the observation of the lowest-energy conduction bands.

²Details about the theoretical calculation are inserted in Section 4.6.

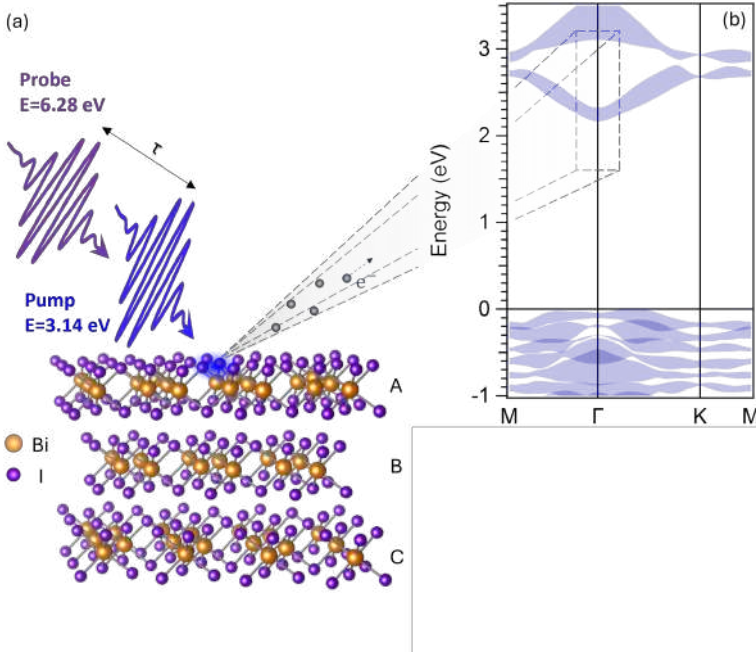


Figure 4.2: (a) Sketch of the tr-ARPES experiment and BiI₃ layered structure. (b) Calculated BiI₃ electronic band structure with the integrated dispersion along the k_z direction indicated by the shaded area.

Fig. 4.3(a-f) shows differential PE intensity maps at several pump-probe time delays after the subtraction of the ARPES intensity recorded before the pump pulse arrival.

The data are plotted as a function of parallel momentum ($k_{||}$, x-axis) and intermediate state energy ($E - E_{VB}$, y-axis). The red (blue) color scale represents the increase (decrease) in photoemitted intensity relative to the equilibrium value. Despite the extremely low fluence ($F = 6 \mu\text{J cm}^{-2}$), we observe a sizable signal. Before the pump pulse arrival ($\tau = -0.15$ ps in Fig. 4.2(a)), no features are observed, confirming that no residual population with a lifetime longer than the inverse repetition rate of our laser source is present. After the pump pulse arrival ($\tau = 0.15$ ps, Fig. 4.2(b)), the photoemitted intensity reveals a circular-shaped feature at a kinetic energy of about 2.5 eV and at $k_{||} = 0 \text{ \AA}^{-1}$. To reference the energy position of the photoexcited population in the BiI₃ electronic band structure, the calculated conduction band structure is overlaid on the data as blue-shaded regions. We note that the excited electronic

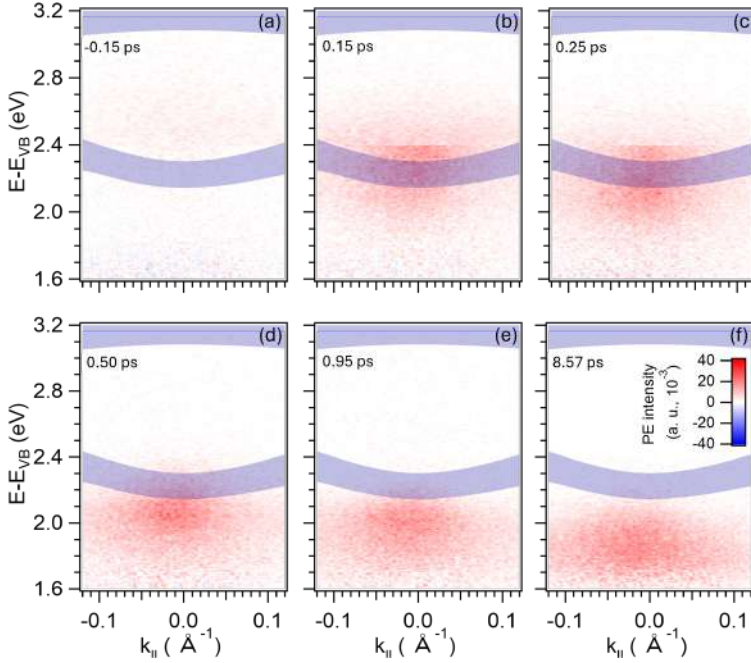


Figure 4.3: (a)-(f) ARPES intensity at selected time delays as a function of intermediate state energy ($E - E_{VB}$) and the parallel momentum, respectively. The blue-shaded areas represent the computed first and second conduction bands.

population predominantly occupies the lowest-energy conduction band. At later time delays (Fig. 4.2 (c-e)), the photoemitted intensity shifts towards lower energies, and it stabilizes at 1.8 eV. At $\tau = 8.57$ ps (Fig. 4.2(f)), the intensity spreads in momentum. Remarkably, this excited population sits a few hundred meV below the conduction band bottom.

4.3 Tracking the exciton formation in the energy domain

Fig. 4.4(a) shows the energy relaxation of the excited electron population, where the integrated PE intensity is plotted as a function of the pump-probe time delay (x-axis) and the intermediate state energy $E - E_{VB}$ (y-axis). This data was obtained after momentum integration between $-0.12 \text{ \AA}^{-1}$ and $0.12 \text{ \AA}^{-1}$.

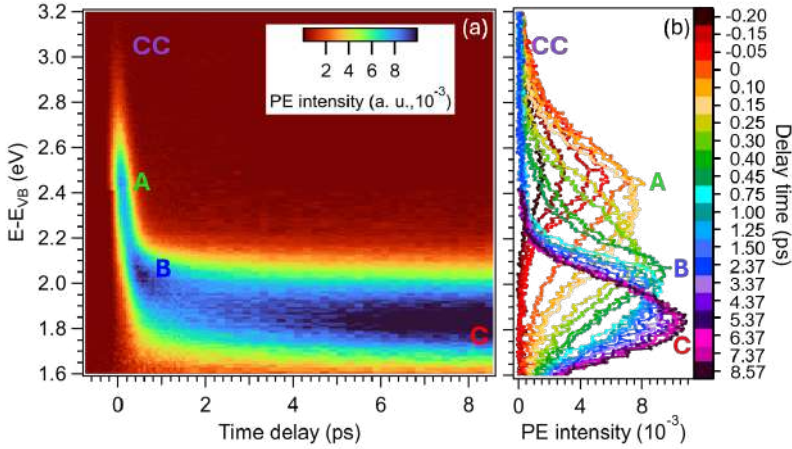


Figure 4.4: (a) PE intensity integrated from the $-0.12 \text{ \AA}^{-1}$ to $0.12 \text{ \AA}^{-1}$ as a function of intermediate state energy ($E - E_{VB}$) and pump-probe time delay (τ). (b) Vertical linecuts of (a) at selected pump-probe time delays. The resonances are labelled with A, B, and C. CC represents the cross-correlation between the pump and the probe.

An initial cross-correlation (CC) intensity appears at $\approx 3.1 \text{ eV}$ at the energy of the pump. During the relaxation process, the PE intensity shows three resonances, more clearly highlighted in Fig. 4.4(b), which displays a set of energy distribution curves (EDCs) collected at various time delays. The three resonances (A, B, C) appear at approximately 2.5 eV , 2.1 eV , and 1.8 eV .

The temporal evolution of these resonances is investigated by fitting the EDCs with a sum of four Gaussian functions, as shown in the inset of Fig. 4.5 (a). The resulting energy and integrated intensity of each resonance are reported in Fig. 4.5 (a) and (b) as a function of the delay time between the pump and the probe. In the fitting procedure CC energy position, A linewidth, C energy position, and linewidth were fixed parameters, and we found that the energy of the A and B resonances shifts toward lower values within the first ps. Although the width of the B resonance is a free parameter of the fit, the A and C widths were fixed.

The intensity of all resonances shows a delayed rise followed by multiple timescale relaxation pathways. These dynamics were fitted globally³ by a convolution of

³To globally fit the A, B and C intensities, the decay of A is kept equal to the rise of B. The two decays of B are equal to the two rises of the C resonance. The time resolution is 200 fs, as corroborated by fitting the CC intensity.

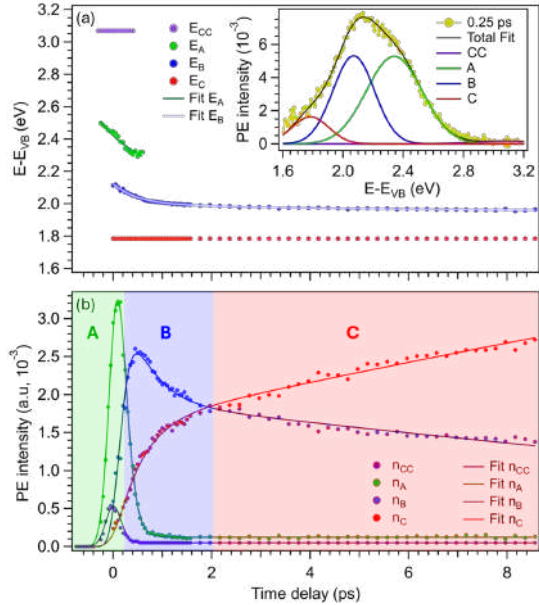


Figure 4.5: Temporal evolution of the energy (a) and the integrated PE intensity (b) of the A, B, and C resonances and the CC feature. The inset shows the EDC at 0.25 ps, the relative four Gaussian fit and the resulting components.

the response function, describing the temporal evolution of the PE signal, and a Gaussian function, accounting for the experimental resolution. The timescales of the dynamics are summarized in the following table:

Resonance	Rise time	Decay time
A	within CC	(120 ± 30) fs
B	(120 ± 30) fs	(520 ± 30) fs (51 ± 1) ps
C	(520 ± 30) fs (51 ± 1) ps	out of the probed window range

Table 4.1: Rise and decay times of the integrated PE intensity for A, B and C resonances.

A thorough analysis of these resonances allows us to track the relaxation process of the excited state population. The CC structure persists only during the cross-correlation time between the pump and the probe, as depicted by the violet markers in Fig. 4.5(b). After the pump pulse arrival and within the

pump-probe CC time, the electronic population relaxes to the first resonance (A) at 2.5 eV corresponding to the bottom of the conduction band. Thus, in agreement with the calculated electronic band structure, the *apparent* energy shift of the A resonance from 2.5 eV to 2.3 eV (green markers in Fig. 4.5 (a)) is ascribed to the conduction band emptying, which takes place in 120 fs, as also observed in previous time-resolved optical measurements [14, 158, 116]). From the conduction band bottom, the electronic population decays toward the B resonance at ≈ 2 eV, thus well within the fundamental bandgap. This is corroborated by the global fitting results, which indicate that the intensity build-up time of the B resonance is comparable with the depopulation time of the conduction band $\tau_A = (120 \pm 30)$ fs. Then, the electronic population in the B resonance decays and is energy-shifted from 2.1 eV to 1.95 eV on a time scale $\tau_{B1} = (520 \pm 30)$ fs. On a longer timescale, exceeding the measured time window, the occupation of the B resonance decays in $\tau_{B2} = (51 \pm 1)$ ps at a fixed energy of 1.95 eV. The intensity build-up dynamics of the C resonance mirrors the two-step depopulation of the B resonance and continues to increase until the end of the measurement time window, while its energy is fixed at 1.81 eV.

To validate our measurements, *ab-initio* simulations were performed in the scheme GW@DFT+BSE by a group of theorists. The modeling of the ARPES signal starts from the reproduction of 500 excitonic bands by solving the BSE equation. The evolution of the occupation is initially reproduced by a Gaussian wave packet representing the absorption and the spread of the pump pulse. The excitonic population evolves toward a Boltzmann distribution located at a lower excitonic level. The employed modeling captures the signal both from the conduction band (free carrier) and from the excitonic resonance (bound electron-hole pairs). The resulting ARPES signal discriminates between the signal resonant to the lowest conduction bands, which is constituted by a population of quasi-free carrier (FC) and an in-gap signal associated with a population of free excitons (FE).

Fig. 4.6 shows the theoretical tr-ARPES signal for different time frames (panels a-c), while the corresponding exciton distribution is represented in red on the exciton dispersion (panels d-f). In Fig. 4.6(a-c), the dashed orange box represents the region of the reciprocal space measured experimentally, and the shaded blue area represents the surface-projected conduction band minimum. Finally, the right-side panels show the $\mathbf{k}$ -integrated PE spectra. In Fig. 4.6(d-f), the right-side panels show the $\mathbf{q}$ -integrated exciton density of states. The theoretical and experimental 2D PE maps as a function of the time are also shown in panes (g-h). The tr-ARPES signal shown in Fig. 4.6(a-b) is generated by BSE eigenstates within the energy range of 2.4 eV to 2.2 eV, as depicted in Fig. 4.6(d-e). Despite being generated by excitons spread over all the Brillouin zone and without any constraint on the momentum of the photoemitted electron,

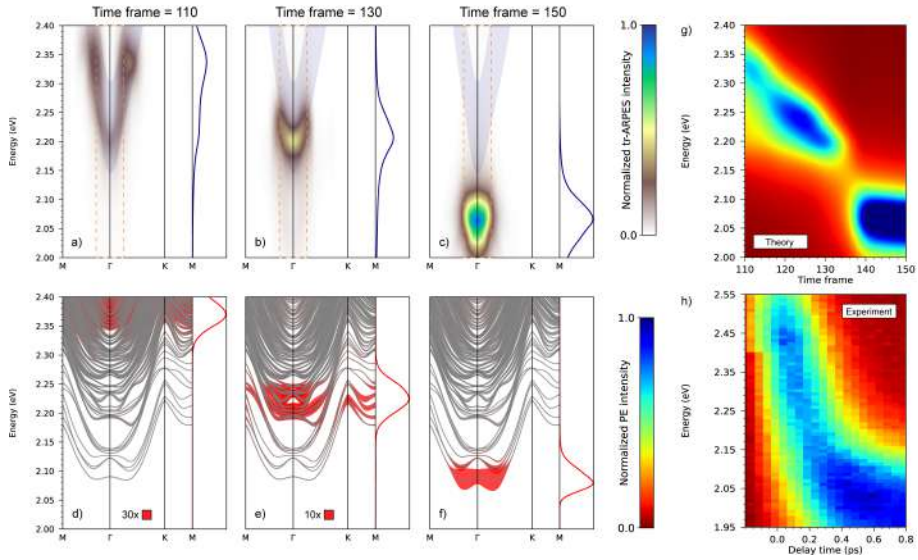


Figure 4.6: (a-c) Theoretical tr-ARPES signal for different time frames. The dashed orange box refers to the area of the reciprocal space measured experimentally. The conduction band minimum with the integrated dispersion along the k_z direction is represented by a shaded area. The adjacent panels represent the momentum-integrated PE spectra. (d-f) Exciton dispersion for each time frame, where the occupied excitons are represented in red. The panels on the right show the occupied-exciton density of states. In panels (d) and (e), the contribution is multiplied by the indicated factors for a clearer view. (h-f) Theoretical and experimental PE colormap as a function of the time.

the signal is mostly centered around the Γ point, e.g. in the window, which is detected experimentally. Moreover, at early times, the signal precisely overlaps with the conduction band minimum, indicating that it is actually due to the free carriers located at the conduction band. This signal corresponds to the A resonance in Fig. 4.5(a), which is associated with the relaxation dynamics of the free carriers along the conduction band. Over time, the signal continues to evolve, leading to the signal represented in Fig. 4.6(c), created by the BSE eigenstates below 2.2 eV, as shown in Fig. 4.6(f). Since this signal is located below the conduction band, it consists solely of bound excitons. In this case, the signal corresponds to the B resonance shown in Fig. 4.5(b), where the exciton cascade captured experimentally is attributed to the contribution of the lower energy excitons. Notably, there is an energy region with no intensity between the signals of Fig. 4.6(b) and Fig. 4.6(c). This is easier to appreciate

when comparing the calculated and experimental time-resolved photoemission colormap in Fig. 4.6(g) and (h), respectively. The absence of PE signal is due to the lack of excitonic states in the energy range around 2.15 eV, as shown in the exciton dispersion reported in Fig. 4.6(d-f). This gap corresponds to the energy jump between the A and B resonances in Fig. 4.5(a), although the theoretical energy jump is smaller than the experimental one. This discrepancy is attributed to surface effects that are neglected in the simulations. Indeed, the signal is collected from the first few surface layers, where a reduced screening is experienced due to the presence of the vacuum. Besides this quantitative difference, the results of the simulations strongly corroborate the identification of the A and B resonances.

Having established the nature of the A and B resonances, we are left with the origin of the C resonance. Two aspects characterize this feature: (i) its energy is much lower than the lowest energy FE calculated at Γ for the layered rhombohedral BiI_3 crystal lattice; (ii) the maximum intensity is reached 520 fs after the pump pulse arrival and delayed by 400 fs with respect to the FE formation (maximum of the B resonance). These observations suggest that the C resonance resulted from a trapping process of initially free excitons. [77, 80, 91, 123, 203, 1]. To discuss the occurrence of this trapping, we first note that, depending on the excitation conditions and the sample quality, different kinds of trapped excitons (TE) could appear in the photoluminescence (PL) spectrum of BiI_3 which is shown in Fig. 4.7 (a) (orange line).

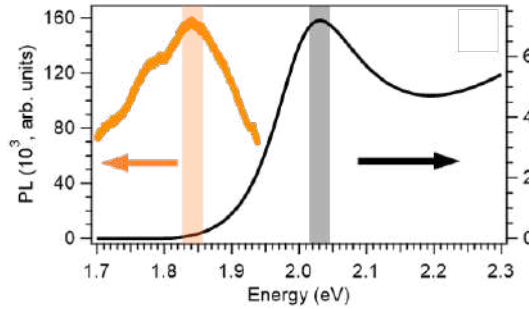


Figure 4.7: PL measurement at room temperature (orange) and calculated imaginary part of the dielectric function taken from [116] (black). The respective central energy positions are marked by vertical shaded lines.

TE usually lead to broadband PL emission characterized by a huge Stoke shift (above 100 meV) with respect to the FE [201, 199, 38, 37]. Indeed, our PL measurement shows a broad PL spectrum with a Stokes shift of 150 meV, as estimated from the energy separation between the PL and FE absorption peak.

Notably, the Stokes shift is comparable with the energy difference between the B and C resonance (0.18 eV). Thus, while we can exclude that excitons can be trapped in stacking fault centres as they appear only at very low temperatures (5K) like sub-meV narrow lines very close (10-20 meV) to the FE peak [80, 1], excitons can be trapped in other native defects [91, 123, 1] or self-trapped in the local photoinduced lattice distortion. In fact, in soft materials like layered semiconductors, the exciton-phonon coupling is strong enough to produce lattice deformations with a consequent localization of FE as STE [199, 78]. In this regard, BiI_3 results to be an ideal platform to host STE, since it is a layered material in which FEs exhibit Frenkel-like character [77], large binding energy, and strong coupling with an A_{1g} optical phonon mode [158, 116, 115].

4.4 Tracking exciton dynamics in the momentum domain

We start this section by describing the time evolution of the PE intensity as a function of the momentum.

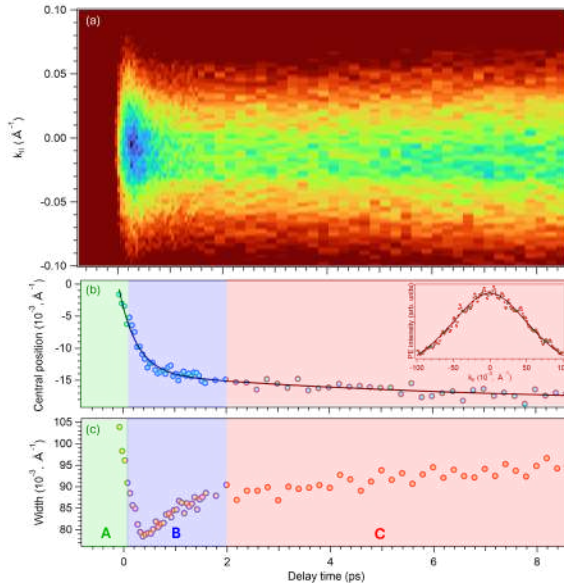


Figure 4.8: (a) Photoemitted intensity integrated between 1.6 eV and 3.1 eV. (b) Temporal evolution of the photoemitted intensity centre of mass. (c) Temporal evolution of the PE intensity spread in momentum.

Fig. 4.8(a) shows the integrated photoemitted intensity as a function of pump-probe delay time (x-axis) and $k_{||}$ (y-axis). The PE intensity was integrated over the total probed energy window (from 1.6 eV to 3.2 eV). At each delay time, we have extracted momentum dispersion curves (MDCs), exhibiting a Lorentian lineshape, as depicted in the inset of Fig. 4.8 (b). At all probed delay times, the momentum dependent PE intensity was fitted with a Lorentian function, defined by its intensity, width and central position. The resulting temporal evolutions of the central position and the spread in the momentum of the PE intensity are inserted in Fig. 4.8(b) and (c), respectively. Three regions are underlined and assigned depending on the dominant resonance as indicated in Fig. 4.5.

At $\tau = -0.15$ ps, the PE intensity is located at $(0.002 \pm 0.005) \text{ \AA}^{-1}$ with a spread in momentum of $(0.100 \pm 0.005) \text{ \AA}^{-1}$. In the first few hundreds of fs, the population shifts towards lower $k_{||}$ values. This behavior is well described by a double-exponential dynamic with time constants of 0.4 ps and a few ps. Simultaneously, it shrinks, reaching the minimum value of $(0.078 \pm 0.005) \text{ \AA}^{-1}$. The shifting of the photoelectron centre-of-mass toward a more negative value is observed in the total probed window. Conversely, the spread shows a trend change during the transfer from an FE to TE. Indeed, the $k_{||}$ -spread of the PE intensity starts to increase again, eventually stabilizing at the end of our probed window at 8.57 ps with a value of $(0.095 \pm 0.005) \text{ \AA}^{-1}$. This suggests a slight localization of the exciton wave function in real space.

We extended our study in the energy vs momentum domain by following the evolution of the $k_{||}$ -dispersion of the photoexcited population energetic center during the relaxation dynamics. For each frame shown in Fig. 4.3 (a-f), we evaluate a set of EDCs at various $k_{||}$ between $-0.09 \text{ \AA}$ and $0.09 \text{ \AA}$ through a fitting with a Gaussian function. In Fig. 4.9 (a) is inserted the Gaussian central energy as a function of $k_{||}$ (color markers) to appreciate the momentum dispersion of the photoexcited population at a selected time delay.

During the pump-probe CC (i.e. at $\tau = -0.15$ ps, grey markers), the conduction band electron population distribute over a parabolic band with upward dispersion and an effective mass of $m_A^* = (0.39 \pm 0.05)m_0$, where m_0 is the electronic mass. This behavior is observed until $\tau = 0.15$ ps (green markers) when the population reaches the bottom of the conduction band (A resonance). The calculated effective mass of the surface-projected conduction band is $m^* = 0.58 m_0$, which is comparable to the experimental value. At $\tau = 0.25$ ps, the $k_{||}$ -dispersion flattens significantly. We note that at this time, the PE intensity of the A resonance equals the B resonance. Therefore, the nearly flat dispersion can be considered as an evolution from a bare conduction-band population to the free-exciton population. Indeed, at $\tau = 0.5$ ps, i.e. when the PE intensity of the B resonance is maximum, the $k_{||}$ -distribution evolves into a downwards-dispersing parabola with effective mass of $m_B^* = (-0.76 \pm 0.05)m_0$

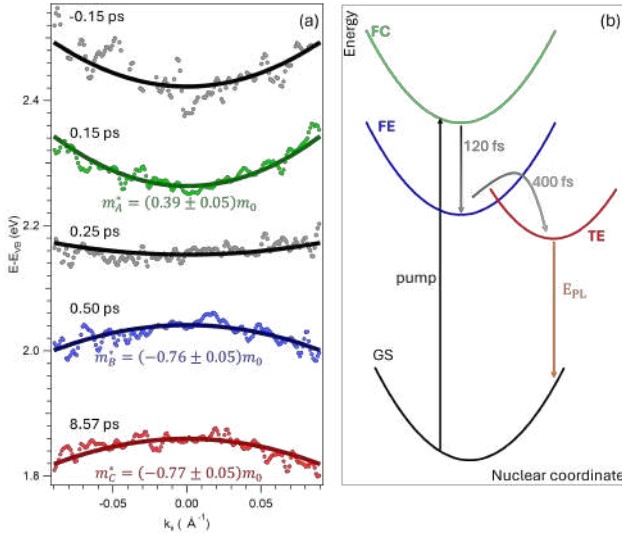


Figure 4.9: (a) Intermediate energy vs parallel momentum dispersion for each frame of Fig. 4.3(a-f). (b) Diagram of the localization process starting from a FC population.

(blue markers in Fig. 4.9(a)). This corroborates the excitonic nature of the B resonance. For direct gap semi-conductors, the PE excitonic signature evolves from the upward excitonic dispersion (high-temperature exciton population) to the downward hole-like parabolic dispersion of the valence band around $\mathbf{k} = \Gamma$ (low-temperature exciton population) [134, 154, 43]. For an indirect gap material and at low temperature, the dispersion of the valence band maximum around $\mathbf{k} = \mathbf{q}_{\min}$, corresponding to the lowest energy exciton, is expected [150]. The case of BiI_3 is more complex due to the presence of many electronic and excitonic bands very close in energy. Therefore, a direct assignment to the excitonic level of the valence band is not straightforward. However, in the theoretical simulation, a concavity switch from A to B resonances is also observed. At even later times ($\tau = 8.57$ ps, red markers), the exciton trapping process maintains the downwards-dispersing parabolic distribution with a comparable effective mass of $m_C^* = (-0.77 \pm 0.05)m_0$.

We then summarize the exciton formation and relaxation dynamics in the sketch of Fig. 4.9 (b). Initially, the photoexcited quasi-free charge carriers are located at about 2.4 eV in the energetic region comparable with the conduction band, at $k_{\parallel} = 0$ and with an upward parabolic dispersion. In the subsequent 120 fs, a part of the quasi-free electrons in the conduction band evolve towards a population of free excitons. The associated ARPES signal shows a maximum just below the

bottom of the conduction band, a slight shrinkage of the momentum spread due to a decrease of the localization of its wavefunction in real space and a downward momentum dispersion. Eventually, FE undergoes a fast trapping process within 400 fs, likely with the aid of coupled A_{1g} optical phonons or due to native defects, which act as trapping sites. This final state shows spectroscopic signatures very similar to the FE, but with a slightly higher spread in momentum, corroborating its excitonic nature and its possible trapping in lattice deformations.

4.5 Exciton wave function in real space

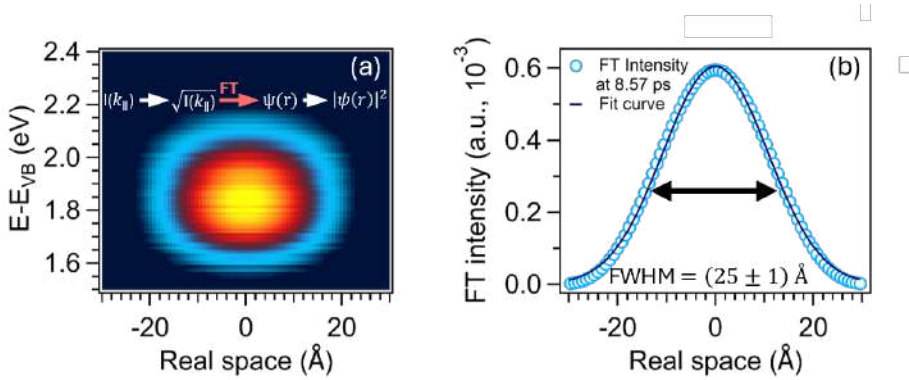


Figure 4.10: (a) FT of the ARPES map collected at 8.57 ps (b) Horizontal linecut of (a) at the maximum of the intensity.

At the longest probed delay time, we estimate the BiI_3 exciton distribution in real space, which provides the exciton wave function, through Fourier Transformation (FT) of the momentum-resolved PE intensity. The procedure is taken from [43]. The exciton wavefunction and the total PE intensity are connected as follows. The total PE intensity is proportional to the squared transition dipole matrix element $|M_{f,i}^k|^2 = |\langle \psi_f | \mathbf{A} \cdot \mathbf{p} | \psi_i \rangle|^2$. This element connects the initial state to the final state via the polarization operator $\mathbf{A} \cdot \mathbf{p}$, where $\mathbf{A}$ is the vector potential of the light field and $\mathbf{p}$ is the momentum operator. Using the assumption that the final state is a plane wave (plane wave approximation), the squared matrix element becomes $|M_{f,i}^k|^2 \propto |\mathbf{A} \cdot \mathbf{k}|^2 |\langle e^{-i\mathbf{k}\mathbf{r}} | \psi_i \rangle|^2$. This expression indicates that the matrix element is proportional to the amplitude of the FT of the initial state wave function. [43]. This procedure retrieves the real space probability density of the electron contribution to the two-particle exciton wave function, which is inserted in Fig. 4.10 (a). The resulting FT intensity is shown in the 2D

plot of Fig. 4.10(a) as a function of real space (x-axis) and intermediate state energy (y-axis). We point out that the intensity at this time delay captures the contribution of co-existing FE and TEs. By taking a horizontal linecut at the FT intensity maximum, a Gaussian lineshape with an FWHM of (25 ± 1) Å is obtained (Fig. 4.10 (e)), which is in agreement with the literature [43, 188]. Considering the volume of a BiI₃ octahedral cluster (composed of one bismuth atom and six iodine atoms), we estimate that the exciton wavefunction spreads over approximately seven clusters.

4.6 Complementary theoretical simulation

In this section, more information is reported on the theoretical simulations that complement our experimental results.

To validate the interpretation of the A and B resonance in terms of quasi-free carriers in the conduction band and an excitonic population, the theoretical tr-ARPES signal has been reconstructed starting from an accurate modelling of electronic and optical properties of BiI₃. First, the exciton dispersion has been computed for a broad energy range within the GW@DFT+BSE scheme (the same as discussed in [21]). Then, the tr-ARPES signal has been modelled using Eq.(4) from Ref. [154], which expresses the electron-momentum resolved signal via an integration over the exciton-momentum:

$$I[N_{\lambda\mathbf{q}}(t)](\mathbf{k}, \omega) = 2\pi \sum_{\lambda\mathbf{q}} N_{\lambda\mathbf{q}}(t) \sum_{cv} |A_{cv\mathbf{k}}^{\lambda\mathbf{q}}|^2 \times \delta(\omega - (\epsilon_{v\mathbf{k}-\mathbf{q}} + \omega_{\lambda\mathbf{q}})) \quad (4.1)$$

where t is the time, $\mathbf{k}$ identifies the electron momentum in the Brillouin zone, ω the energy of the tr-ARPES signal, λ the exciton index, $\mathbf{q}$ the exciton momentum, v and c are the valence and conduction bands indexes. Similarly to the band structure, the ARPES signal is surface-projected by considering the electron $\mathbf{k}$ -parallel momentum. The time-dependent population entering the tr-ARPES signal is described in terms of a Gaussian wave packet initially centred ($t = 0$) at the pumping energy and progressively relaxing towards the exciton dispersion minimum, where it turns into a Boltzmann distribution. Time dependence is determined via a few parameters that enter the time-dependent populations. These parameters are not explicitly fitted to the experimental data, and the time dependence in arbitrary units is reported in Fig. 4.6.

To compare theoretical and experimental results, the surface-projected band structure was calculated. To this end, we first obtain the hexagonal-projected

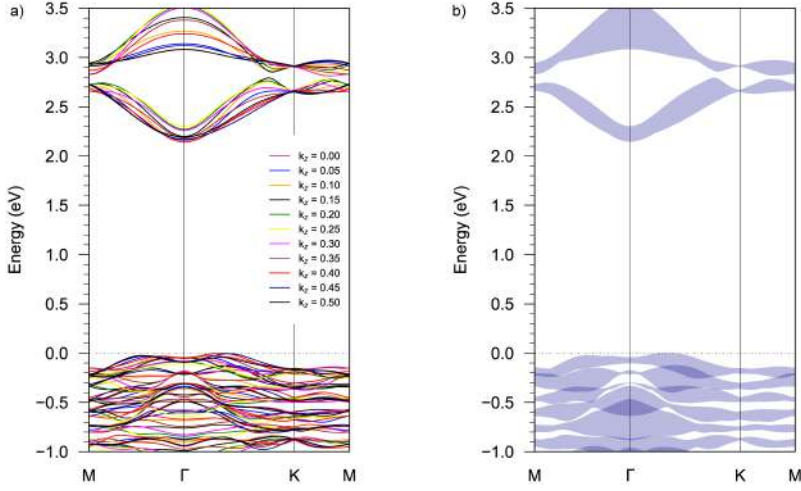


Figure 4.11: Calculation of the surface-projected band structure of bulk BiI₃. (a) Different band structures for each value of k_z . The values of k_z are in crystal coordinates, where $k_z = 0.50$ is the first value in the second Brillouin zone. (b) Surface-projected band structure obtained from the integration of different band structures along the k_z direction.

path in the rhombohedral Brillouin zone. Then, we compute the band structure along the same path for k_x and k_y points of the reciprocal space, and we vary the value of k_z , as depicted in Fig. 4.11(a). In this way, the surface-projected band structure shown in Fig. 4.11(b) is obtained by integrating all the values along the k_z direction. The reconstruction of the tr-ARPES signal was carried out using a GW@DFT+BSE scheme as a starting point. The electronic properties of BiI₃ at the ground-state level were calculated in the framework of DFT, as implemented in the Quantum ESPRESSO package [54, 53, 55]. Quasiparticle corrections were computed through the GW approximation while the optical properties considering excitonic effects were calculated by solving the finite-momentum BSE, as implemented in the Yambo code [102, 155, 103] and reported in Ref [21]. To model the tr-ARPES signal, we employ the expression from Ref [154] and reported in Equation 4.1. $N_{\lambda\mathbf{q}}(t)$ describes the exciton population distribution as a function of the time, $A_{cv\mathbf{k}}^{\lambda\mathbf{q}}$ is the exciton eigenfunction in transition space, $\epsilon_{n\mathbf{k}}$ the band energy. $\epsilon_{v\mathbf{k}-\mathbf{q}}$ is obtained from the GW calculation, while $A_{cv\mathbf{k}}^{\lambda\mathbf{q}}$ and $\omega_{\lambda\mathbf{q}}$ are collected when solving the finite-momentum BSE. The time evolution is not *ab initio* but defined via the following time-dependent excitonic distribution:

$$N_{\lambda\mathbf{q}}(t) = G_{\lambda\mathbf{q}}(t)\alpha(t) + [1 - \alpha(t)]B_{\lambda\mathbf{q}}(t) \quad (4.2)$$

where $G_{\lambda\mathbf{q}}(t)$ is a Gaussian function, $B_{\lambda\mathbf{q}}(t)$ is a Boltzmann distribution function and $\alpha(t)$ defines the weight of each distribution along the time. The Gaussian distribution is defined as a wave packet propagating in energy and spreading both in energy and in momentum space:

$$G_{\lambda\mathbf{q}}(t) = \frac{1}{2\pi\sigma_\omega(t)\sigma_{\mathbf{q}}(t)} \exp\left[-\frac{1}{2}\left(\frac{\omega_{\lambda\mathbf{q}} - \omega_0(t)}{\sigma_\omega(t)}\right)^2\right] \exp\left[-\frac{1}{2}\left(\frac{|\mathbf{q}|^2 - |\mathbf{q}_{\omega_0}|^2}{\sigma_{\mathbf{q}}(t)}\right)^2\right]. \quad (4.3)$$

$G_{\lambda\mathbf{q}}(t)$ is centered on $\omega_0(t)$, which defines the time-dependent propagation of the wave packet. It is defined as

$$\omega_0(t) = \omega_0 - (\omega_0 - \omega_{min}) \frac{Xt}{T} \quad (4.4)$$

with w_0 the initial ($t = 0$) energy, corresponding to the pump energy, ω_{min} the lowest energy exciton, and X/T is the velocity of propagation in energy space. This simulates a time-linear excitonic propagation towards the lowest energy exciton. $|\mathbf{q}_{\omega_0}|^2 \approx 0$ is the momentum at which the distribution is centered. $\sigma_\omega(t)$ and $\sigma_{\mathbf{q}}(t)$ define the time-dependent energy and momentum broadening. The energy and momentum broadening, $\sigma_\omega(t)$ and $\sigma_{\mathbf{q}}(t)$, are defined as:

$$\sigma_\omega(t) = \frac{\sqrt{t}}{b} + \sigma_{\omega,0} \quad \sigma_{\mathbf{q}}(t) = \frac{\sqrt{t}}{c} + \sigma_{\mathbf{q},0} \quad (4.5)$$

with $\sigma_{\omega,0}$ and $\sigma_{\mathbf{q},0}$ the initial values. The variables b and c control a spreading proportional to the time square root.

On the other hand, the Boltzmann distribution, $B_{\lambda\mathbf{q}}(t)$, is defined such that:

$$B_{\lambda\mathbf{q}}(t) = \frac{1}{Z} \exp\left[-\frac{\omega_{\lambda\mathbf{q}}}{k_B T(t)}\right] \quad (4.6)$$

$$Z(t) = \sum_{\lambda'\mathbf{q}'} \exp\left[-\frac{\omega_{\lambda'\mathbf{q}'}}{k_B T(t)}\right] \quad (4.7)$$

where k_B is the Boltzmann constant, $\omega_{\lambda\mathbf{q}}$ the exciton energy and $T(t)$ is the time-dependent temperature. The dependency of the time for the temperature is given by:

$$T(t) = T_0 \cdot \exp[-t \cdot f] \quad (4.8)$$

where T_0 defines the initial value of the temperature at $t = 0$ and f the decay ratio of the temperature with the time evolution.

Finally, the function $\alpha(t)$, which determines the weight of each distribution, is defined as:

$$\alpha(t) = e^{-t/\tau} \quad (4.9)$$

defined in such a way that we have a purely Gaussian wave packet at the initial time, e.g. $\alpha(0) = 1$ and a purely Boltzmann distribution at longer times, e.g. $\alpha(t) \approx 0$ for $t \gg \tau$.

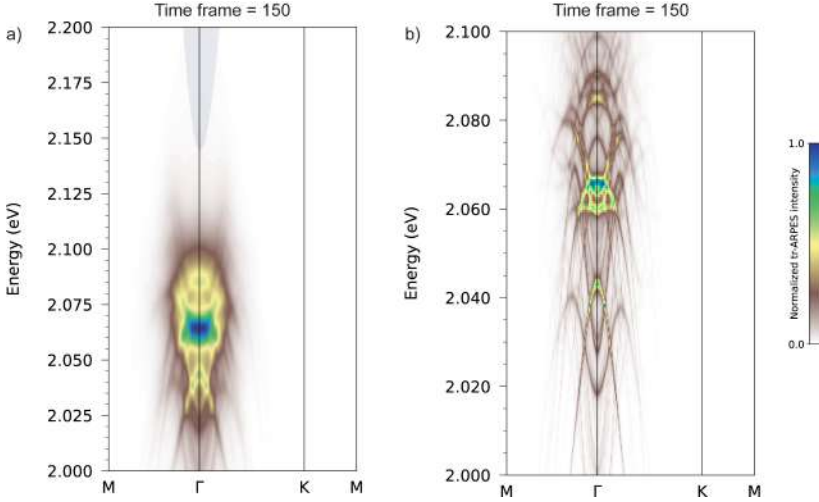


Figure 4.12: Theoretical tr-ARPES signal associated with B resonance obtained using smearing of (a) 0.005 eV, (b) 0.001 eV.

To understand more comprehensively the formation and shape of the B resonance observed experimentally, we analyse the contributions that yield the theoretical B resonance. For this purpose, we compute the tr-ARPES signal as in Fig. 4.6 (c) (time frame = 150 and $T(t) = 139$) using smaller smearings so that we can infer which excitonic and band states originate the B resonance. The results are depicted in Fig. 4.12, where from Fig. 4.12(a) we infer that the signal is more likely to present a concavity switch with respect to A resonance, in agreement with the experiment. A signal with smoother smearing is shown in Fig. 4.12(b), showing that although the concavity switch is still present, it has a very complex origin. Indeed, the B resonance is composed of many excitonic and valence bands, unlike in transition metal dichalcogenides, where the signal presents a dominant contribution [25, 92]. This is due to the small energy difference between the valence and excitonic bands, revealing many different non-zero contributions. As a result, the experimental effective mass for the B resonance cannot be assigned to a specific excitonic or valence band.

4.7 Conclusion

In conclusion, we have successfully reconstructed the formation exciton dynamics in the layered semiconductor BiI_3 in the multidimensional space by a joint experimental and theoretical effort. We have found that an initial population of quasi-free charge carriers excited in the conduction bands evolves within 120 fs into an in-gap population of free excitons at $k_{||} = 0$. These findings have been validated by the theoretical reconstruction of the tr-ARPES signal using a GW@DFT+BSE scheme as a starting point. Concomitantly, the momentum dispersion changes from upward, when the electron population is in the conduction band, to downward, corresponding to the exciton formation and its consequent localization into trapped excitons. From the $k_{||}$ -dispersion, we calculate the exciton wavefunction in real space, which agrees with the free-exciton radius found in the literature.

Chapter 5

Exciton coherence and coherent to incoherent crossover

The chapter is partially taken from:

Detection of a coherent excitonic state in the layered semiconductor BiI₃

V. Gosetti, J. Cervantes-Villanueva, D. Sangalli, A. Molina-Sánchez, V. F. Agekyan, C. Giannetti, L. Sangaletti, S. Mor, S. Pagliara
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In this chapter, we identify an incipient coherent excitonic state by investigating the sub-picosecond exciton dynamics in BiI₃ under quasi-resonant excitation. By combining broadband transient reflectance spectroscopy with simulations based on many-body perturbation theory, we reveal a transient enhancement of the excitonic line intensity. This enhancement originates from photoinduced coherent polarization phase-locked with the interacting electromagnetic field. Our findings allow us to define the spectral signature of a coherent excitonic state and enable the experimental tracking of the dynamical crossover from coherent to incoherent excitons.

The chapter is organized as follows. The first section details the experimental

setup and data correction. Next, we describe the acquisition and parametrization of the static reflectance equilibrium at 50 K and its variations with temperature. The out-of-equilibrium properties are then discussed, focusing on the spectroscopic manifestation of the coherent excitonic state in BiI_3 . Eventually, the theoretical results supporting our experimental findings are presented.

5.1 Setup and preliminary measurements

A transient optical setup has been used to collect the measurement of the transient reflectance of BiI_3 . It was first employed to measure the static reflectance at different temperatures by using the supercontinuum probe.

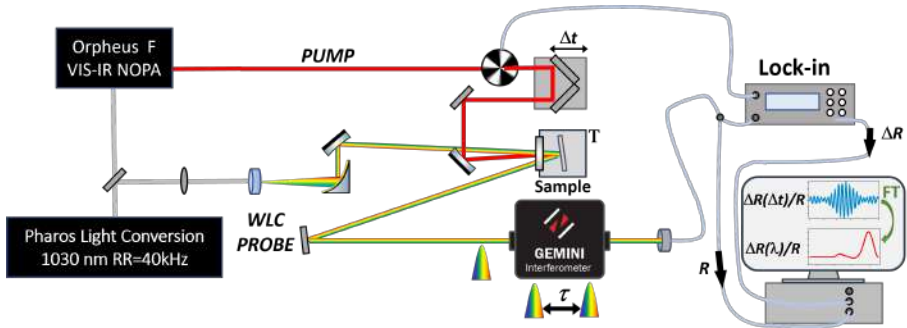


Figure 5.1: Scheme of the optical setup exploited for the acquisition of both the transient and the equilibrium reflectance.

A schematic picture of the setup is shown Fig. 5.1. The first building block of our experimental setup is the femtosecond pulsed laser LIGHT CONVERSION PHAROS, which delivers 280 fs long pulses with a 1030 nm central emission wavelength and 37.5 $\mu\text{J}/\text{pulse}$ energy per pulse. By an optical pulse picker, PHAROS has a tunable repetition rate of up to 400 kHz. A 20/80 beam splitter divided the PHAROS output into two beams. 30 $\mu\text{J}/\text{pulse}$ of the PHAROS emission is used to pump the non-collinear optical parametric amplifier (NOPA) ORPHEUS-F, which generates an output spanning from 640 nm (1.94 eV) to 900 nm (1.37 eV). The beam is then compressed by a double prism compressor. The remaining 7.5 $\mu\text{J}/\text{pulse}$ is used for the probe line. The energy per pulse is reduced to 1.5 $\mu\text{J}/\text{pulse}$ by using a quarter-wave plate and a polarizer. The outgoing beam is focused on a 4-mm-thick YAG (Yttrium Aluminum Garnet) crystal to generate a supercontinuum (WLG). A motorized line delay stage is used to

control the pump-probe delay changing the length of the optical path of the pump. The acquisition is made by using a GEMINI interferometer by NIREOS. To collect the reflectance, we used a silicon-based photodiode. The acquired signal is split into two components: a lock-in amplified signal that filters out the pump-probe correlated signal (ΔR), modulated at the frequency of the pump beam chopper and a DC signal that is the non-correlated reflectance component of the sample. The two collected interferograms are Fourier transformed, and the transient reflectance $\frac{\Delta R}{R_0}$ is acquired. A closed-cycle helium cryostat allows performing transient optical measurements at low temperatures down to 17 K. The sample was cleaved *in situ*. The instrumental response function, defined as the cross-correlation between the pump and the probe measured at the sample position, is limited by the temporal duration of the pump pulse and results in 70 fs. The measurements presented in this chapter were carried out at 50 K and with 10^{-6} mbar pressure to prevent photo-oxidation. As a pump, we used the 650 nm (1.90 eV) output of the ORPHEUS-F with a spectral bandwidth of $\Delta\lambda = 12$ nm and a fluence of $50 \mu\text{J cm}^{-2}$. The repetition rate was set to 40 kHz. For comparison, we have also collected one transient reflectance map with the same pump photon wavelength at 300 K and one with a pump photon wavelength of 445 nm (created by doubling the ORPHEUS output at 890 nm by a second harmonic generation in a BBO crystal, the final energy is then 2.78 eV) at 50 K.

To collect the transient reflectance of BiI_3 as a function of pump-probe delay and probe energy, a continuum white light probe in the 1.9 eV-2.3 eV range was exploited. The use of a broad probe energy window induces a temporal chirp of a few hundred femtoseconds in the response of BiI_3 . To study the probe-energy-dependent response, the dispersion of the chirp has to be taken into account in the analysis. To evaluate the temporal chirp, the transient reflectance of highly-oriented pyrolytic graphite (HOPG) was collected as a function of pump-probe delay time and probe energy with a 2.79-eV- and 1.9-eV-pump photon energy, Fig. 5.2 (a) and (b) respectively. The HOPG sample was located in the closed-cycle helium cryostat at low pressure and room temperature. The HOPG is used due to its instantaneous response and its fast relaxation dynamic, shorter than the setup resolution. Therefore, HOPG is useful to evaluate the pump-probe correlation time and the dispersion of the time zero in the probed energy region. To evaluate these quantities, horizontal line cuts were extracted from the map. The horizontal linecuts at 1.7 eV for the two colormaps are inserted as blue and red markers curves in Fig. 5.2 (c) and (d) respectively. To fit the transient reflectance evolution with the pump-probe time delay, we used a convolution between a Gaussian function, that takes into account the pump-probe-cross-correlation, and a response function, which is a Heaviside function located at the pump-probe overlap time multiplied by a fast exponential decaying function. As a result, the cross-correlation between the pump and the

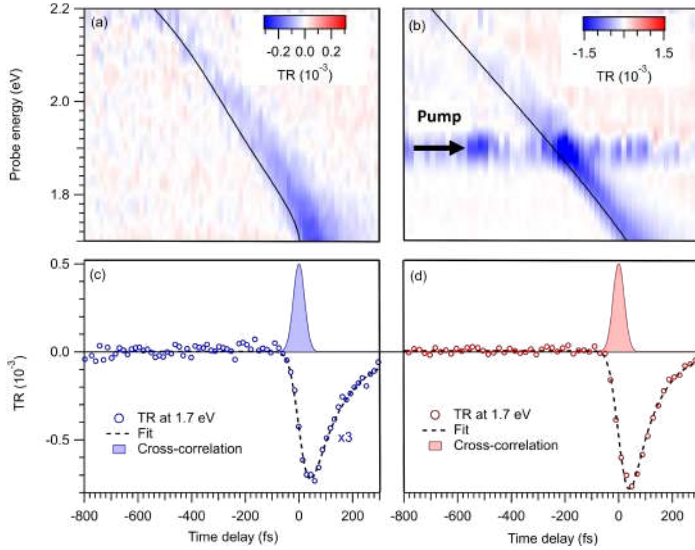


Figure 5.2: Transient reflectance of HOPG as a function of probe energy left axis and delay time bottom axis collected with a photon energy of 2.79 eV (a) and 1.91 eV (b). The solid black curves are the time zeros dispersion. Horizontal linecuts at 1.7 eV with the relative fit are inserted in (c) and (d) for the non-resonant and resonant pumping conditions, respectively. The blue and red shades feature are the resulting pump-probe cross-correlation.

probe is (70 ± 10) fs, and the temporal chirp is the black line shown in Fig. 5.2. The resulting fitting curves are reported as black dashed lines in Fig. 5.2 (c) and (d), and the cross-correlation intensity profiles are the shaded blue and red features. The chirp is determined by the experimental setup and the white light generation (WLG); therefore, the extrapolated time-zero-dispersion is considered for BiI₃. The time zero of BiI₃ transient reflectance was aligned according to the extrapolated temporal chirp.

White-light supercontinuum pulses between 1.55 eV and 2.48 eV were exploited to record the equilibrium reflectance of BiI₃. The setup is the same used for the transient reflectance acquisition, shown in Fig. 5.1, where the pump was blocked after ORPHEUS-F output by a beam blocker. A BiI₃ sample was mounted on a Cu sample holder inside a helium closed-cycle cryostat to control the temperature. To collect the reflected intensity (I_R) we used the GEMINI interferometer by NIREOS. The reflected intensity is collected with a silicon-based photodiode, and the DC signal is acquired by a lock-in amplifier. Then, to have the energy-dependent reflectance, the acquired output is Fourier

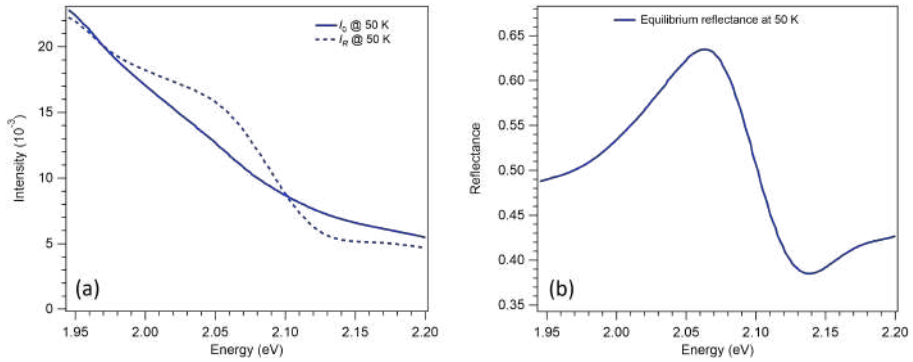


Figure 5.3: (a) The acquired intensity of the supercontinuum I_0 (solid blue line) and the reflected light I_R by BiI_3 at 50 K (dashed blue line) (b) Reflectance spectrum of BiI_3 at 50 K.

transformed. An example of the reflected intensity is the dashed blue line in Fig. 5.3 (a). As a reference, the spectrum of the non-interacting supercontinuum (I_0 , for instance, the solid blue line in figure Fig. 5.3 (a)) was collected. The final reflectance R is, then, the ratio between the reflected light and the incident light ($R = \frac{I_R}{I_0}$). The collected reflectance at 50 K is shown in Fig. 5.3 (b). For completeness, we have also collected the reflectance following the same procedure at several temperatures covering a range from 25 K to 300 K. The resulting spectra are shown in Fig. 5.4.

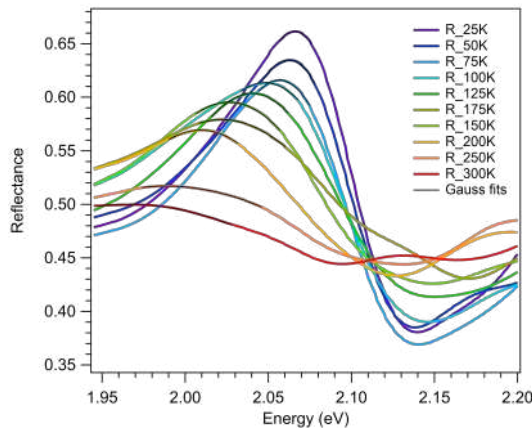


Figure 5.4: Equilibrium reflectance at several temperatures from 25 K to 300 K.

The differential procedure used to interpolate the transient reflectance analysis involves several steps: (i) determining the appropriate parametrization of the BiI_3 equilibrium reflectance $R_{par,eq}$, (ii) reproducing the out-of-equilibrium reflectance $R_{par,neq}$ by modifying the equilibrium parametrization to include the transient effects that account for the out-of-equilibrium properties; and (iii) fit the experimental transient reflectance with the following:

$$\Delta R_{par} = \frac{R_{par,neq} - R_{par,eq}}{R_{par,eq}}. \quad (5.1)$$

To reproduce R_{eq} , we choose to use a Tauc-Lorentz (TL) model. As part of this model, the complex dielectric function is described by:

$$\tilde{\epsilon}_{TL} = \epsilon_{r,TL} + i \cdot \epsilon_{i,TL} = \epsilon_{r,TL} + i \cdot (\epsilon_{i,T} \times \epsilon_{i,L}) \quad (5.2)$$

The Tauc term in the imaginary dielectric function ($\epsilon_{i,T}$) represents the response of the direct gap material caused by the inter-band transition, while the excitonic resonances are described by Lorentzian oscillators ($\epsilon_{i,L}$). In our case, three Tauc-Lorentz oscillators have been exploited to reproduce the excitonic resonances. The complete imaginary part of the dielectric function is:

$$\epsilon_{i,TL} = \epsilon_{i,T} \times \epsilon_{i,L} = \begin{cases} \sum_{i=1}^3 \frac{1}{E} \frac{A_i E_{0i} \Gamma_i (e - E_g)^2}{(E^2 - E_{0i}^2)^2 + \Gamma_i^2 E^2} & \text{if } E > E_g \\ 0 & \text{if } E \leq E_g \end{cases} \quad (5.3)$$

where A_i , Γ_i , and E_{0i} are the amplitude, the full-width-half-maximum (FWHM), and the centre of the i -th oscillator, respectively. The real part of the dielectric function is retrieved by the Kramer-Kronig integration:

$$\epsilon_{TL,r}(E) = \epsilon_r(\infty) + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \cdot \epsilon_{TL,i}(\xi)}{\xi^2 - E^2} d\xi \quad (5.4)$$

where P is the Cauchy principal value. For the Tauc-Lorentz model, the real part of the dielectric function ($\epsilon_{TL,i}$) is the one reported by Jellison and Modine in 1996 [74]. The reflectance is then defined as:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5.5)$$

where n and k are the real and imaginary parts of the complex refractive index $\tilde{n} = n + ik$. These are related to the dielectric function:

$$n = \left\{ \frac{1}{2} [(\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} + \epsilon_1] \right\}^{\frac{1}{2}} \quad (5.6)$$

$$k = \left\{ \frac{1}{2} [(\epsilon_1^2 + \epsilon_2^2)^{\frac{1}{2}} - \epsilon_1] \right\}^{\frac{1}{2}} \quad (5.7)$$

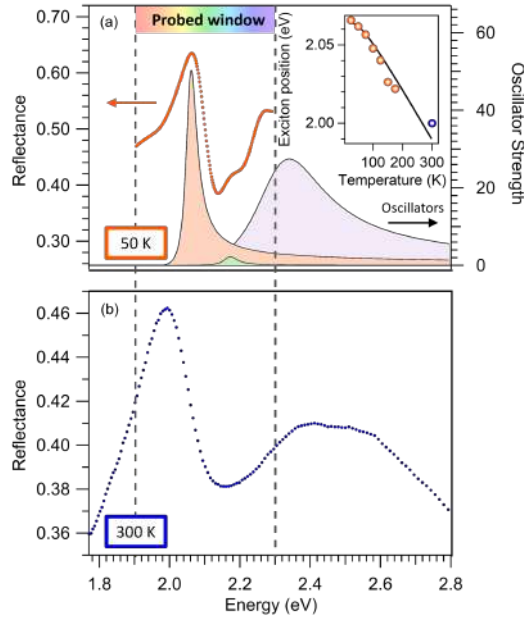


Figure 5.5: (a) On the left axis, the equilibrium reflectance (orange markers) collected at 50 K by using the continuum probe. On the right axis, the three oscillators (orange, green, and violet shades) result from a Tauc-Lorentz analysis. The inset shows the temperature dependence of the first excitonic resonance measured with the continuum probe (orange markers). The data point at 300 K is extracted from the equilibrium reflectance collected by the UV/VIS spectrophotometer and shown in (b).

Thereby, the reflectance at 50 K is fitted using the Tauc-Lorentz procedure. The components of the fit are shown in Fig. 5.5 (a). The first Tauc-Lorentz oscillator, located at (2.06 ± 0.01) eV (orange-shaded peak) with a FWHM of (40 ± 5) meV, is assigned to the first bright exciton. It has a Frenkel-like character [77, 116], and its calculated binding energy is 140 meV [21]. The second oscillator at (2.17 ± 0.01) eV and with a linewidth of (60 ± 5) meV is ascribed to the second bright exciton (green-shaded peak), according to absorption measurement on BiI_3 thin film [203]. We note that the total linewidth of the first excitonic resonance also includes the experimental resolution of 37 meV. The deconvoluted linewidth of the first exciton is (15 ± 5) meV. Moreover, the third oscillator located at (2.31 ± 0.01) eV (violet-shaded peak) has a broader width of (240 ± 5) meV and represents a collection of the higher-order excitons, that in our analysis, acts as a background since it is outside our probed energy window (highlighted at the

top of Fig. 5.5). The estimated Tauc energy gap is (1.97 ± 0.01) eV, and it is the same for all the oscillators. The excitonic nature of the discussed oscillator and the presence of excitons at higher energies are confirmed by comparison with the equilibrium reflectance collected at room temperature in a broader energy range using a spectrophotometer (Fig. 5.5(b)). For completeness, the inset of Fig. 5.5(a) shows the continuous shift of the main excitonic resonance from (2.06 ± 0.01) eV at 50 K to (2.00 ± 0.01) eV at 300 K with increasing temperature. This is evaluated by fitting the structure in the energy-dependent reflectance in Fig. 5.4 with a Gaussian function.

5.2 Transient reflectance at low temperature

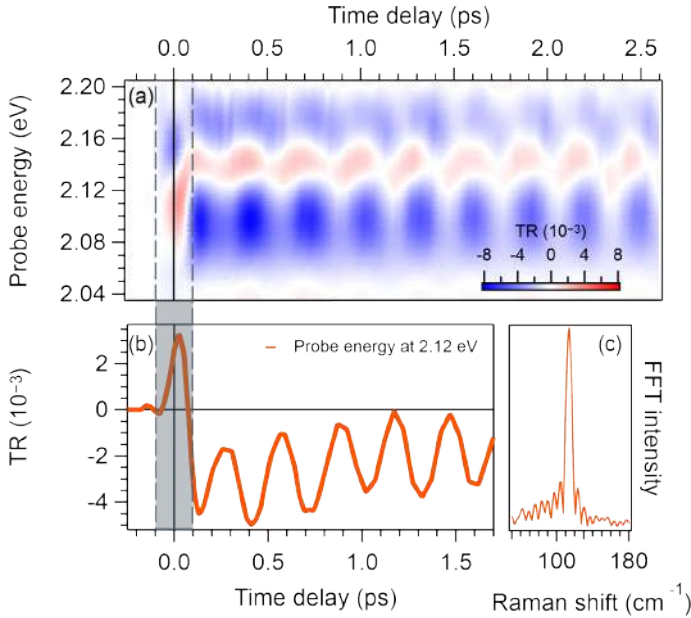


Figure 5.6: (a) TR of BiI_3 , under quasi-resonant excitation (1.91 eV) at 50 K as a function of pump-probe time delay (bottom axis) and probe photon energy (left axis). (b) Time-resolved line cut at 2.12 eV of the TR map in (a). (c) FT of the periodic modulation of the time-resolved linecut in (b).

Fig. 5.6(a) shows the transient reflectance (TR) collected on a BiI_3 single crystal as a function of pump-probe time delay (bottom axis) and probe photon energy (left axis). We choose a pump photon energy of 1.91 eV to minimize the

excitation of quasi-free carriers to the conduction band continuum in favor of the quasi-resonant generation of excitons that will be initially phase-locked with the absorbed photons. We identified two temporal regimes in the TR color map: one starting with at the pump pulse arrival and persisting up to approximately 100 fs, and a second one longer than 100 fs. In the early-time regime (< 100 fs), the TR signal is positive below 2.12 eV and negative at higher energies. During the late-time regime (> 100 fs), the TR intensity is (i) negative in the spectral region below 2.12 eV, (ii) positive up to 2.16 eV, (iii) negative at energies higher than 2.16 eV. Finally, at all time delays and at any probe photon energy, the TR intensity oscillates periodically, as highlighted by the horizontal line cut at 2.12 eV reported in Fig. 5.6(b). The FT in Fig. 5.6(c) shows a Raman shift of (113.60 ± 0.02) cm^{-1} , which corresponds to the dominant A_g phonon mode of BiI_3 coherently generated by the pump pulse [158, 116].

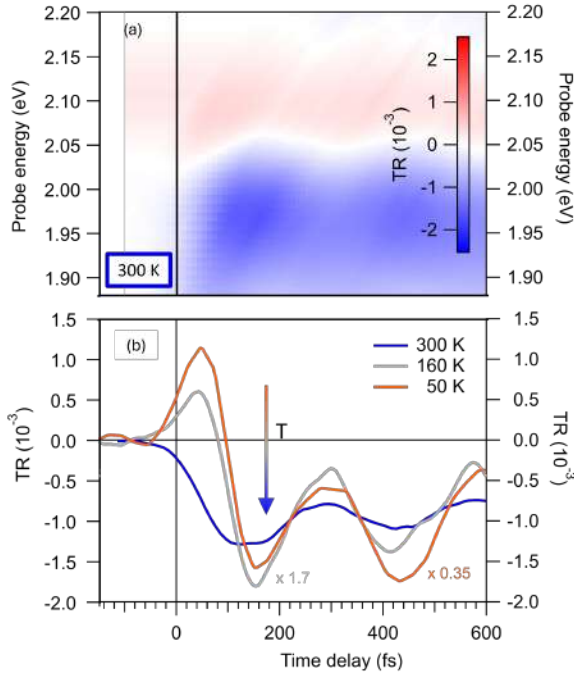


Figure 5.7: (a) TR map of BiI_3 under quasi-resonant pumping (1.91 eV) as a function of probe energy (right axis) and time delays (bottom axis) at 300 K. (b) Time-resolved line cuts at the energy where the intensity is minimum for three temperatures: 50 K, 160 K, and 300 K. The traces are normalized on the negative TR signal at 200 fs.

To determine the energy region of the TR map connected to the dynamics of the main excitonic resonance, we measure the equilibrium reflectance at 50 K in the TR energy region and interpolate the spectrum by the sum of three Tauc-Lorentz oscillators, as discussed in Section 5.1. Consequently, the TR intensity observed in Fig. 5.6(a) below 2.12 eV at 50 K is assigned to the photoinduced dynamics of the main exciton. To rationalize the drastic TR sign change from the early- to late-time regime, we explored different environmental conditions of the exciton dynamics, which mainly affect the dephasing process of any initial coherent excitonic state. We start with a study of the effect of the temperature on the TR map. Fig. 5.7(a) shows that the TR change observed at low temperature is completely absent in the TR map at 300 K, with the TR signal at the excitonic resonance negative for all time delays. The TR response at the probe energy of the excitonic resonance, collected at different temperatures ($T = 50$ K, 160 K and 300 K) and under quasi-resonant pumping, confirms that the initial positive signal vanishes with the temperature, while the negative bleaching of the late-time regime and the periodic oscillations due to the coherent phonons persist (Fig. 5.7(b)). In this light, we can assert that the low temperature, reducing the scattering mechanisms with thermal phonons [5], is a necessary requirement for the observation of the early-time exciton dynamics.

Fig. 5.8(a) singles out the early-time TR response at 50 K to introduce a more quantitative analysis that allows us to extract the photoinduced changes in both the oscillators parameters and the energy gap through differential fitting of the TR spectra at various pump-probe time delays. The interpolation of the energy-dependent TR traces is done through a fitting function (ΔR) exploiting the Tauc-Lorentz oscillators. The fitting function is ΔR_{par} as shown in Equation 5.1. To include the out-of-equilibrium properties in $R_{par,neq}$, we consider a shift in the energy position (ΔE_i), a change in the linewidth ($\Delta \Gamma_i$), a variation of the peak intensity (ΔA_i) for each oscillator, and a modification in the Tauc energy gap (ΔE_g). The resulting imaginary part of the dielectric function is:

$$\epsilon_{i,TL,neq} = \begin{cases} \sum_{i=1}^3 \frac{1}{E} \frac{(A_i + \Delta A_i)(E_{0i} + \Delta E_i)(\Gamma_i + \Delta \Gamma_i)(E - E_g - \Delta E_g)^2}{(E^2 - (E_{0i} + \Delta E_i)^2)^2 + (\Gamma_i + \Delta \Gamma_i)^2 E^2} & \text{if } E > E_g + \Delta E_g, \\ 0 & \\ \text{if } E \leq E_g + \Delta E_g & \end{cases} \quad (5.8)$$

The out-of-equilibrium reflectance ($R_{par,neq}$) is then calculated following the procedure illustrated in Section 5.1. In transient spectra analysis, the third exciton, being a background, is kept fixed for all the time delays. In addition, due to the suppression of photoinduced free carriers ruled by the quasi-resonant pumping, the Tauc energy gap is also fixed for all the delays. Two vertical

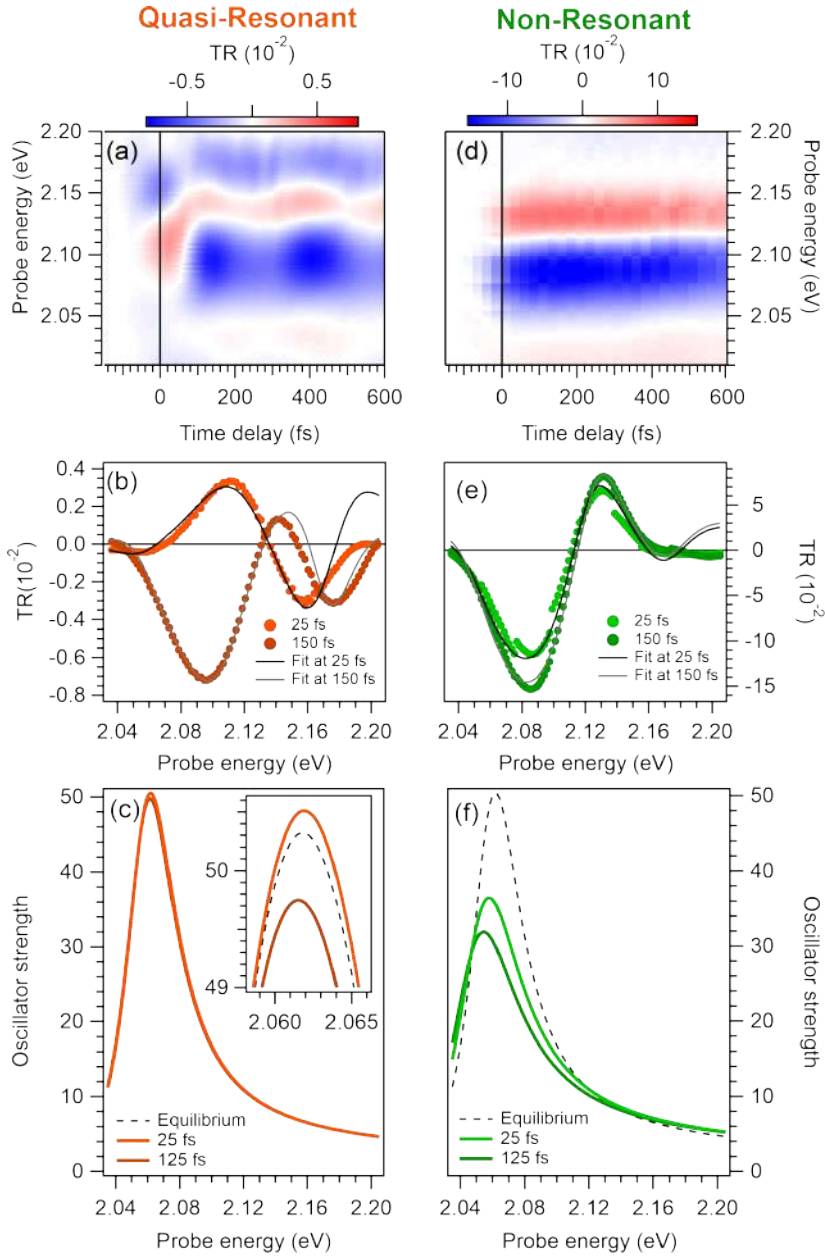


Figure 5.8: TR of BiI_3 at 50 K under photoexcitation with 1.91 eV (a) and 2.79 eV (d) pump photons. Vertical line cuts, (b) and (e), of the color map in (a) and (d), respectively. Oscillator strength of the first exciton at equilibrium, 25 fs and 150 fs under photoexcitation with (c) 1.91 eV and (f) 2.79 eV pump photons.

line cuts of the TR map are shown as markers in Fig. 5.8(b) superimposed on the relevant best-fit curves (solid lines). The positive signal of TR in the early-time regime (25 fs) results from the combination of a blueshift and an intensity increase of the main oscillator. Conversely, the negative TR signal in the late-time regime (150 fs) originates from the bleaching of the oscillator strength accompanied by a redshift of the exciton energy (dark orange line in Fig. 5.8(c)).

We now examine the TR map at 50 K pumping with photons at 2.79 eV (Fig. 5.8(d)), which exceeds the energy of the optical gap of BiI₃. By that, we intend to enable the excitation of quasi-free carriers to the conduction band. As a consequence, unlike the quasi-resonant excitation condition, here, carrier-carrier and exciton-carrier scattering processes are promoted. The relevant data are shown in Fig. 5.8(d). The time- and energy-resolved TR intensity preserves the same sign at any time delay: it is dominated by a negative TR in the region of the main excitonic resonance (below 2.12 eV) and a positive intensity at higher energies. Two vertical line cuts at distinct pump-probe time delays are shown Fig. 5.8(e) to highlight that under non-resonant excitation, the TR signal does not exhibit any drastic sign change over time. Rather, at any time delays the TR spectra result from both the bleaching and the redshift of the lowest-energy exciton oscillator (light and dark green traces in Fig. 5.8(f)). We note that these results are in line with the dynamics initiated on quasi-resonant excitation and observed at late time delays. In this case, the Tauc energy gap is left free to change in the fitting procedure due to the free-carrier-induced band-gap renormalization in the out-of-resonant pumping. The comparison between the TR under quasi- and non-resonant excitation highlights that the exciton dynamics occurring at early time delays is a unique feature. In fact, it solely appears when the laser pump pulse coherently excites excitons, while the excitation of quasi-free carriers in the continuum is kept negligible. Moreover, we recall that the low temperature minimizes, as previously discussed, the scattering processes with thermal phonons. All these elements, together with the short timescale of the relevant dynamics, agree that the early-time regime is the manifestation of a coherent excitonic state. To support our claim, a modelisation of the absorption in the presence of a virtual exciton and a slight detuning has been calculated by the group of theorists, and it is inserted here. In order to confirm this hypothesis, the optical properties of BiI₃ were computed both at equilibrium and out-of-equilibrium with an *ab initio* approach based on many-body perturbation theory. First, the equilibrium absorption is computed via the GW+BSE scheme. This leads to a direct gap of 2.24 eV and a series of excitonic peaks, with the low energy in-plane spectrum dominated by a bright exciton at 2.12 eV. Although temperature effects are not considered in these calculations, the theoretical excitonic peak is in good agreement with the low-temperature measurement shown in Fig. 5.5(a). Then, we perform

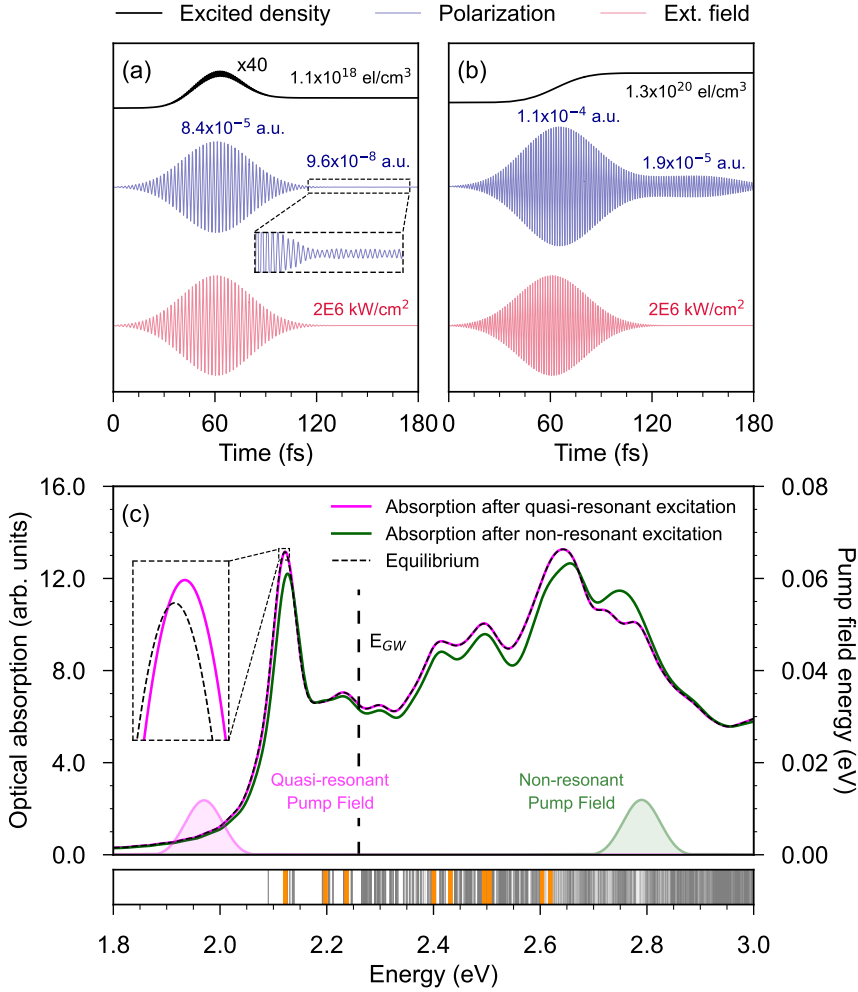


Figure 5.9: Equilibrium and non-equilibrium optical properties of BiI_3 from first-principles calculations. (a-b) Excited density, polarization and pump field for (a) the pump at 1.97 eV and (b) the pump at 2.79 eV. In (a), the excited density has been multiplied by a factor of 40 to be easily observed, whereas the inset shows the non-zero polarization after the pump field. The values for the residual total excited density, the maximum polarization, the residual polarization and the pump field intensity are displayed. (c) Optical absorption spectrum for the equilibrium and non-equilibrium cases. The dashed vertical line represents the direct gap and the shaded areas of the different pump fields. The inset in (c) shows the increase in the intensity of the excitonic peak for the quasi-resonant case, while the inset at the bottom of the figure shows the bright (yellow) and dark (gray) excitons.

real-time simulations based on the equation of motion for the density matrix, $\rho(t)$ [154]. The simulation includes two key ingredients: (i) the long-range screened electron-hole Coulomb interaction to account for the generation of coherent excitons, and (ii) both the pump and the probe laser pulses to model the optical signal accounting for the coherent polarization, i.e. the coherent excitonic state, induced at early times. The non-equilibrium optical spectrum changes were investigated by varying the excitons or carriers injected into the material. Thus, the two pumping conditions used experimentally were considered: (1) quasi-resonant case with a pump pulse with a detuning of 150 meV with respect to the theoretical excitonic peak for the quasi-resonant case ($\omega_P = 1.97$ eV), and (2) non-resonant case with a pump pulse in the continuum of the absorption spectrum ($\omega_P = 2.79$ eV). The corresponding results are depicted in Fig. 5.9, where in panel Fig. 5.9 (a-b), the output of the simulations including only the pump pulse is shown, with the field of the pump laser pulse, the induced polarization, and the total excited population density. In the quasi-resonant case displayed in Fig. 5.9(a), both population and polarization reach a maximum slightly delayed compared to the maximum of the pump pulse, and then the decay to a much smaller value. This decay is due to the detuning between the pump frequency and the excitonic peak and can be described in terms of a large portion of virtual coherent states which do not survive beyond the pump laser pulse. The residual population and polarization instead correspond to real states excited in the material and exist because the long-range Coulomb interaction allows absorption below the direct gap. This residual polarization oscillates at a frequency which exactly matches the excitonic frequency, thus indicating that the residual population density corresponds to a population of coherent excitons [135, 154]. The situation is significantly different when the system is excited by a laser pulse with a frequency well above the fundamental gap, Fig. 5.9(b). In this case, the excited density reaches a maximum at the end of the pump pulse and does not decay subsequently. This means that the laser pulse is completely absorbed, and therefore, only real states are excited. Since the pump frequency lies in the continuum, these states can be described in terms of free carriers, while the associated polarization decays quickly because of the so-called free polarization decay. In the simulations, this does not translate into an actual dephasing, but rather into destructive interference between the many frequencies excited (the residual polarization is due to the fact that numerically only a finite number of frequencies only is available). Therefore, a population of coherent carriers are in the system, although here the coherent nature of the states does not show up in the polarization. Experimentally it is expected that such coherences decay due to dissipative mechanisms. In any case, the free carriers coherences do not have any impact on any result of the simulations. Now, the non-equilibrium optical signal in these two configurations is compared with the equilibrium

absorption spectrum, as shown in Fig. 5.9(c). To this end, a probe laser pulse, which arrives 25 fs after the maximum of the pump pulse was used, as in the experimental setup. To obtain the optical signal, the probe only polarization is defined as $P_p(t) = P_{Pp}(t) - P_P(t)$, e.g. the result of subtracting the polarization induced in presence of the pump-only from the polarization induced in the presence of both pump and probe. The two non-equilibrium spectra obtained have a striking difference: the signal due to the excitonic population leads to an enhancement of the excitonic peak, while the signal due to the carriers results in a bleaching of the same peak. This explains the opposite signal measured experimentally at 25 fs in Fig. 5.8. Moreover, the signal induced by the injected carriers affects the absorption spectrum over a large energy range, whereas the excitonic population only affects the signal near the excitonic peak. The signal in the non-resonant case is not affected by the coherent nature of the states. Indeed, the same signal is obtained either by changing the pump-probe delay or considering a population of non-coherent carriers. Instead, the enhancement of the excitonic peak is largely due to the coherent nature of the excitonic state. By varying the time delay between the pump and the probe pulse, the excitonic peak intensity displays time oscillations with a frequency matching twice the excitonic frequency. This is known as the Dynamical Franz-Keldysh effect [130], and it is caused by the induced polarization. The signal shown in Fig. 5.9(c) is obtained by averaging over two probes with opposite relative phases, which washes out the time-dependent oscillations.

5.3 Exciton coherent to incoherent crossover

Established the spectral fingerprints for the exciton coherence in BiI_3 , now we are interested in capturing their temporal evolution. To trace the dynamical crossover from coherent to incoherent excitonic state, we follow the intensity (Fig. 5.10(a)) and energy (Fig. 5.10(b)) variation of the excitonic oscillator (Fig. 5.10(a)) as a function of time, as obtained from differential fitting of the TR spectra. The intensity variation is positive within approximately 200 fs, then evolves into negative before vanishing on a several ps timescale (not shown). The excitonic resonance shows an initial energy blueshift on the same timescale as the TR intensity increase, followed by a redshift that recovers in a few-ps. Both the intensity and the energy are periodically modulated at the frequency of the A_g phonon mode due to the exciton-phonon coupling [116]. To decouple the contributions of the coherent-to-incoherent crossover dynamics, we *globally* fit the time-resolved intensity variation and the energy shift of the excitonic oscillator through the sum of three terms (shown separately in Fig. 5.10), convoluted with the pump-probe cross-correlation (accounting for the resolution time). The time-resolved dynamics of these two quantities were

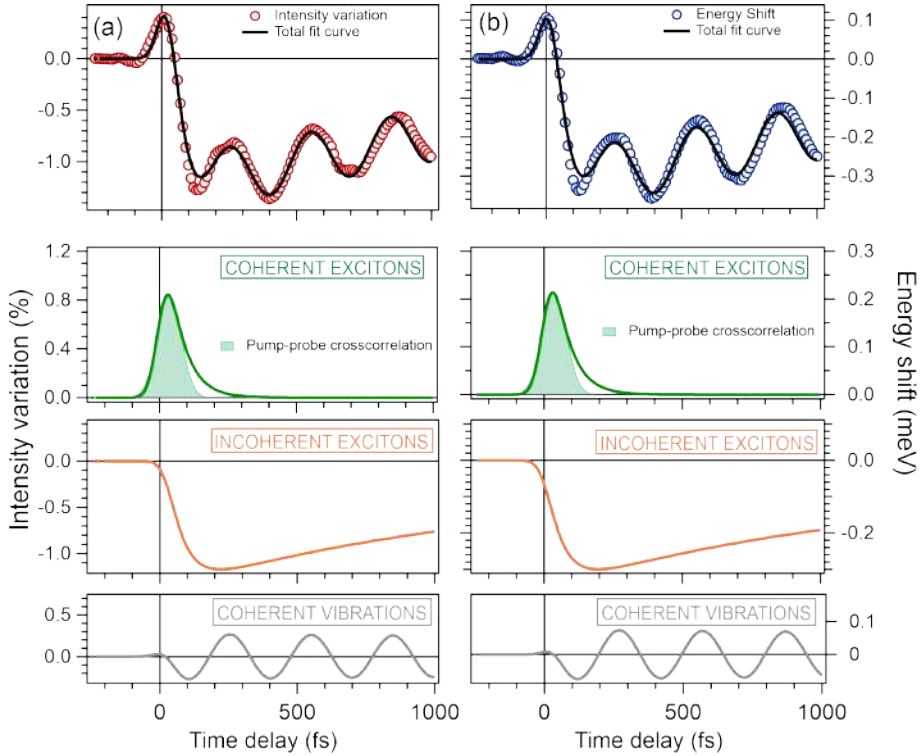


Figure 5.10: (a) Time-resolved intensity variation (red markers) of the excitonic oscillator and relevant fit (solid black line). (b) Time-resolved energy shift (blue markers) of the excitonic oscillator and relevant fit (solid black line). The coherent excitons, incoherent excitons, and coherent vibrations contributions are shown as green, orange, and gray curves, respectively, for both (a) and (b).

evaluated with a global fit through the sum of three terms assigned to coherent excitons, incoherent excitons, and coherent vibrations. The whole response function is convoluted with a Gaussian function with FWHM of 70 fs that represents the experimental resolution. Firstly, the coherent exciton signal rises within the pump-pulse cross-correlation duration and has a single-component decay evolution. Secondly, the incoherent exciton population is described by a single rise time followed by a double exponential decay function. Lastly, the coherent vibrations are periodic modulations described by a damped cosine function, with damped time longer than the probed temporal window. The early-time component (green curve) is associated with the dephasing dynamics of the coherent excitonic state and shows a decay time of (60 ± 10) fs, resulting

in dynamics that outlive the regime of pump-probe temporal overlap (green shade, the full width at half maximum is 70 fs). The orange lines show a delayed minimum, followed by a slow-recover with two component dynamics, one with a time constant of (1.2 ± 0.1) ps and the second longer than the probed window. Notably, the minimum is delayed by the same time as the dephasing of the excitonic coherent state, tracing the crossover from coherent to incoherent exciton population. This is followed by the relaxation and recombination of the incoherent exciton population. Eventually, the cosine-like modulation (grey line) of both the exciton intensity and energy with a period of (300 ± 10) fs (i.e. $(111 \pm 5) \text{ cm}^{-1}$) is indicative of exciton-phonon coupling persisting until coherent optical phonons dephase on a long timescale of several ps by virtue of the low temperature of the system. We note that the estimated dephasing time of (60 ± 10) fs, being much lower than the depopulation one (few nanoseconds), determines a homogeneous exciton broadening of about (11 ± 5) meV. The intrinsic excitonic linewidth, estimated by the equilibrium reflectance measurements, is (15 ± 5) meV, which is in good agreement with the homogeneous broadening estimated by the dephasing time. This result confirms the absence of defects or impurities responsible for the inhomogeneous broadening in our BiI_3 sample and indicates that a further requirement to observe the coherent excitonic state is the presence of an exciton with a linewidth close to the homogeneous limit.

5.4 Conclusion

In conclusion, we have prepared the conditions to track the evolution of the exciton dynamics from a coherent, i.e. phase-locked to the transient electric-field-induced polarization, to an incoherent regime. This is reached by suppressing the scattering with the other degrees of freedom of the system that we obtained by cooling it to low temperature and by tuning the laser pump photon energy on resonant with the exciton. We realize that the coherent state manifests with an increase in intensity and a blue shift of the excitonic oscillator. We find a readable output of the coherent-to-incoherent exciton dynamics crossover that the experiment resolves up to time delays exceeding the temporal overlap of the pump and probe pulses.

Chapter 6

Exciton-phonon coupling in layered semiconductors

The chapter is partially taken from:

Photoinduced modulation of the excitonic resonance via coupling with coherent phonons in a layered semiconductor

S. Mor, V. Gosetti, A. Molina-Sánchez, D. Sangalli, S. Achilli, V. F. Agekyan, P. Franceschini, C. Giannetti, L. Sangaletti, S. Pagliara
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Effect of photoinduced screening on the spectroscopic signature of exciton-phonon coupling

S. Mor, V. Gosetti, V. F. Agekyan, C. Giannetti, L. Sangaletti, S. Pagliara
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This chapter addresses the coupling of excitons with atomic vibrations by means of time-resolved broadband optical reflectivity measurement on BiI_3 single crystal. As a first step, we unravel the universal spectral fingerprints of exciton-phonon coupling in layered semiconductors observing both the coherent optical phonons and the photoinduced variation in reflectance around the excitonic resonance. The experimental observations and the analysis are complemented by *ab initio* calculations carried out in collaboration with a group of theorists. Furthermore, we microscopically relate the photoinduced coherent energy modulation of the excitonic resonance to coherent optical phonons, thereby tracking the extent of the photoinduced atomic displacement in real space. The second part of this chapter is focused on the study of the effect of photoinduced screening on the transient optical signal originating from the exciton dynamics coupled to phonons. Through broadband transient reflectance spectroscopy, we disclose how exciton-phonon coupling manifests in either the presence or absence of dynamical screening due to electrons excited in the CB in a layered semiconductor. We unveil the promoting role of photoinduced screening on these exciton-phonon coupled dynamics as opposed to the case in which the *unscreened* exciton-exciton repulsion likely dominates the non-equilibrium optical response.

This chapter is structured as follows. Initially, the setup will be described. Then, the fingerprints for an exciton-phonon coupling will be presented. Eventually, we will explore the effect of the experimental condition on the manifestation of the exciton-phonon coupling.

6.1 Setup and preliminary measurement

The experimental setup is the same as described in Section 5.1, with some minor modifications. To collect broadband transient reflectance on BiI_3 single crystal, we employ (i) the 650 nm (1.91 eV) output of the ORPHEUS-F NOPA to excite quasi-resonant to the excitonic transition and (ii) the 890 nm (1.39 eV) output to generate its second harmonic at 445 nm (2.78 eV) and to excite BiI_3 above the optical band gap. The second harmonic is generated by a 0.5-mm-thick BBO crystal. In the two experiments, the supercontinuum is generated by two non-linear crystals, i.e. a 4-mm-thick Sapphire crystal and a 4-mm-thick YAG for the non-resonant and quasi-resonant pumping, respectively. The probe wavelength range between 500 nm (2.48 eV) and 950 nm (1.30 eV) is, then, selected via a Thorlabs filter FESH0950. Measurements are carried out at room temperature and ambient pressure after cleaving the sample *in-situ*. To prevent sample damage, we set the laser repetition rate at 40 kHz.

BiI_3 samples have a high sensitivity to humidity, oxygen and exposure to light. Before proceeding to the measurements, we check the BiI_3 response under

photoexcitation to choose the proper fluence and explore the stability of our sample. The fluence depends on the pump pulse power and the beam size. The incident pump fluence is $F_i = \frac{4\langle P \rangle}{\text{Rep. Rate}(\pi d^2)}$, where $\langle P \rangle$ is the average power of the pump at the sample position, Rep. Rate is the repetition rate of the laser, and d is the beam spot diameter (FWHM). For negligible transmittance, the absorbed intensity is $A = 1 - R = 0.6$, and the absorbed fluence is given by $F_a = F_i A$, where F_i is the incident fluence. To evaluate the damage threshold of the system, we record single-color TR data at a probe photon energy of 1.88 eV under non-resonant excitation for various fluence values (Fig. 6.1(a)).

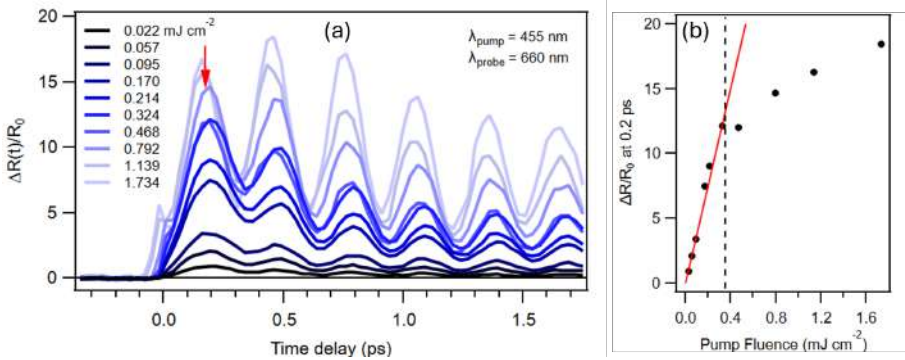


Figure 6.1: (a) TR at 1.88 eV as a function of pump-probe time delay under non-resonant excitation with various incident pump fluence values. (b) Intensity of the TR data in (a) at 0.2 ps as a function of incident pump fluence.

Fig. 6.1(b) shows the first intensity maximum after photoexcitation (i.e. at $\Delta t = 0.25$ ps, as marked by the red arrow in (a)) as a function of the incident pump fluence. This quantity shows a linear behavior up to a threshold fluence of $F^* \simeq 0.4 \text{ mJ cm}^{-2}$ followed by a slope reduction for higher fluences. After the excitation of the system in this high fluence regime, the TR intensity decreases irreversibly. We assigned such persistent change to local damage of the sample due to heating effects and to the low thermal conductivity of BiI_3 compared to other 2D materials [200]. Accordingly, in our broadband TR experiments, we set the excitation of the system to an absorbed pump fluence $< F^*$. Because the range of linear response is rather narrow, fluence variation below F^* results in a bare intensity scaling, as one appreciates in the single-color TR data of Fig. 6.1(a) for the non-resonant case.

Under these considerations, the selected absorbed pump fluence for the non-resonant case is $48 \mu\text{J cm}^{-2}$. The photoinduced free carriers in the conduction band n_c depend on the absorbed fluence and the penetration depth at the pump wavelength. The photon density is $n_{ph} = \frac{F_a}{\xi \hbar \nu}$, where the ξ is the penetration

depth and $\hbar\nu$ is the photon energy of the pump pulse. The penetration depth of BiI_3 at 445 nm (2.78 eV) is $\xi = 2.85 \cdot 10^{-6}$ cm. Assuming that one photon excites one electron in the conduction band, we obtain $n_c = n_{ph} = 2 \cdot 10^{19} \text{cm}^{-3}$. For comparison, we kept the same absorbed fluence in the quasi-resonant pumping measurements.

We have collected transient optical reflectivity measurements (as a function of probe wavelength (energy) and pump-probe delay times on a BiI_3 single crystal sample. The chosen pump are (i) 650nm resonant to the exciton and (ii) 445 nm above the optical band gap, with a fluence of $48 \mu \text{J cm}^{-2}$.

The recorded signal at each probe-pulse wavelength is, then, defined as $(\Delta R/R_0)(t) = ((R_{pump} - R_{nopump})/R_0)(t)$, where ΔR is the pump-probe-correlated reflectivity signal and R_0 is the uncorrelated one. In the text, it will be called transient reflectance (TR). Thus, the signal is expected to be non-zero at positive time delays, i.e. after the pump pulse arrival. However, in our data, a negligible correlated intensity is also observed at negative time delays as the relaxation dynamics of the systems exceed the inverse repetition rate of our laser (1/40 kHz, i.e. 25 μs). This marginal intensity is averaged over the signal at negative time delays and is subtracted from the data.

There is a final remark on the data processing. The broad spectral range of the probe pulses results in a temporal chirp of the transient optical response which is on the order of a few hundreds of femtoseconds. Therefore, to compare photoinduced dynamics at different wavelengths, the 2D data map should be corrected as follows to account for the difference in the pump-probe temporal overlap. We use a single crystal of highly oriented pyrolytic graphite (HOPG) as a reference sample. The material owns an almost instantaneous and intense optical response under photoexcitation with visible pulses with no additional phonon oscillation, and thus it is suitable to extrapolate the pump-probe temporal overlap as a function of probe wavelength. Fig. 6.2(b) shows the transient reflectivity intensity of HOPG as a function of probe wavelength and pump-probe time delay, as measured after passing through the same amount of optics as during the time-resolved measurements on BiI_3 . The black curve indicates the time-zero position at each wavelength. The curve is obtained by fitting the initial signal increase at each wavelength with a convolution function between a Gaussian and a Heaviside function. As a result of this procedure, time-zero is extracted at each wavelength with an uncertainty less than ± 5 fs. The corrected 2D map is plotted in Fig. 6.2(c)). We evaluate the relative shift of time-zero between the 2D maps of HOPG and BiI_3 on the transient reflectivity data of BiI_3 at 620 nm. Indeed, at this wavelength, the response of BiI_3 is very pronounced, abrupt and almost free of oscillations due to the presence of the coherent amplitude node. Thus, we preserved the ± 5 fs accuracy in the estimate of the time-zero position. Accordingly, using the shifted time-zero trace, the transient reflectivity map of BiI_3 is temporally aligned to correct for

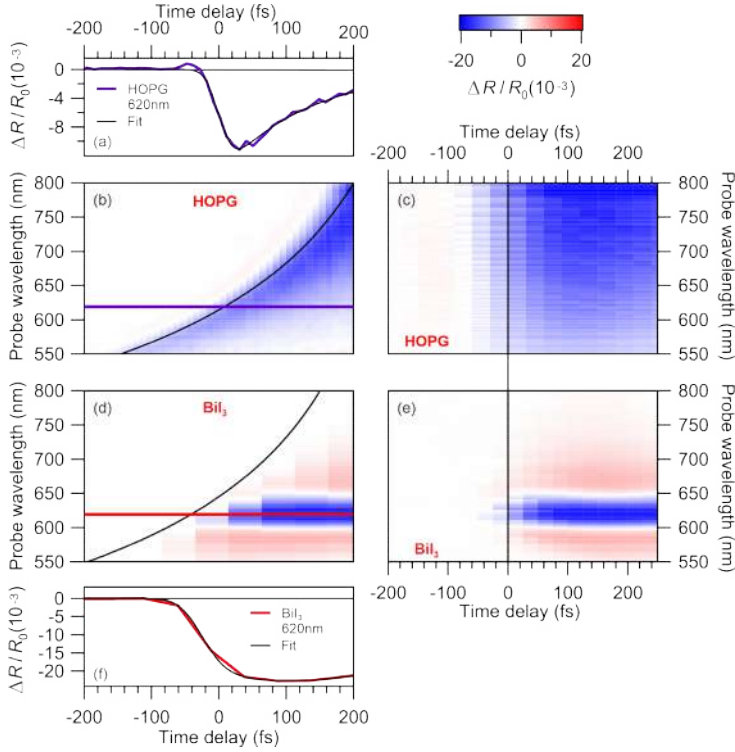


Figure 6.2: (a) Measured transient reflectivity of HOPG as a function of time delay at 620 nm probe wavelength. (b) Measured transient reflectivity map of HOPG. The black curve follows the temporal chirp of the white-light probe pulse. (c) The same map as in (b) after correction of the temporal chirp. (d) Measured transient reflectivity map of BiI_3 superimposed by the HOPG temporal chirp (black curve). (e) Same map as in (d) after correction of the temporal chirp. (f) Measured transient reflectivity of BiI_3 as function of time delay at 620 nm probe wavelength.

the same temporal chirp (compare Fig. 6.2(d) and Fig. 6.2(e)).

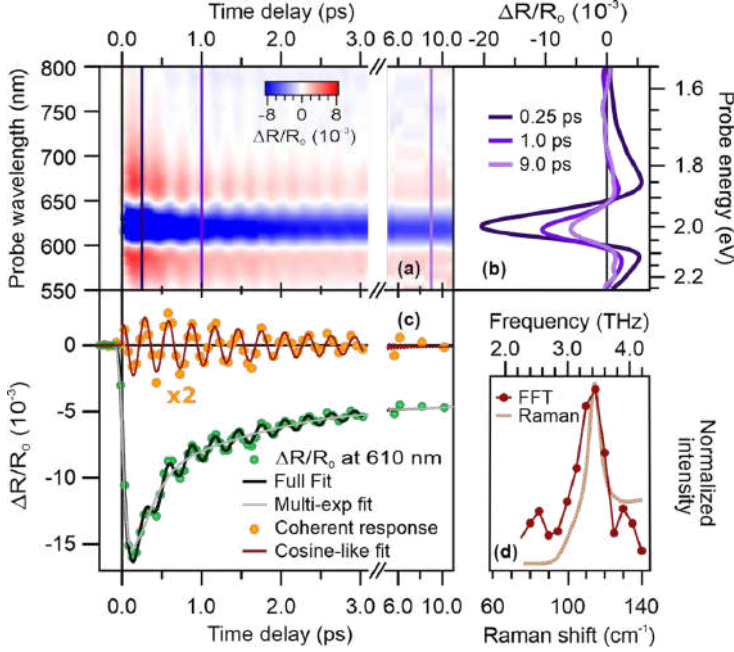


Figure 6.3: (a) Measured $\Delta R/R_0$ as a function of probe wavelength and pump-probe time delay. (b) Vertical linecuts of (a) at selected time delays of 0.25, 1.0 and 9.0 ps. (c) Horizontal linecut of (a) at 610 nm (green circles) with the relative fitting function (black) and the multi-exponential component (grey). The residual periodic modulation is the orange circle, and the cosine-like fit is the brown solid curve. (d) FT of the periodic modulation at 610 nm and the Raman spectrum.

6.2 Non-resonant transient reflectance measurement

Fig. 6.3(a) shows TR as a function of probe wavelength (left axis), probe photon energy (right axis), and pump-probe time delay (top axis), collected with 2.78 eV pump photon energy. The measurements are carried out at room temperature, and the pump photon energy is well above the band gap of BiI_3 . This enables the excitation of $n_c = 2 \times 10^{19} \text{ el cm}^{-3}$ quasi-free carriers into the conduction bands¹. At positive time delays, i.e. after photoexcitation, a pronounced negative (blue) signal with a minimum at 620 nm (2.00 eV) indicates a transient

¹Reported in Section 6.1.

decrease of reflectivity ($(\Delta R/R_0)(t) < 0$) in the spectral range of the excitonic resonance. Above and below this spectral region, the signal is positive (red) as the transient reflectivity increases ($(\Delta R/R_0)(t) > 0$). The spectra reported in Fig. 6.3(b) emphasize the temporal evolution of both the negative and positive spectral features. We note that the red-blue-red pattern is maintained for all the collected time delays, and the absolute intensity decreases with the increasing delay. The monotonic decrease of the signal represents the incoherent response of BiI_3 under photoexcitation. At all probe wavelengths, this incoherent optical response is superimposed by a periodic intensity modulation (represented by the periodic modulation of the false colour in Fig. 6.3(a)) resulting from the generation of coherent optical phonons by the pump pulse.

The transient reflectivity signal at each wavelength is fitted by a sum of four exponentially decaying functions (incoherent optical response) and an exponentially decaying cosine function (coherent optical response) convoluted with a Gaussian function (pump-probe cross-correlation). Fig. 6.3(c) shows the fit (black line) for the data at 610 nm (green circles). The gray line is the multi-exponential fit contribution to the incoherent optical response, only. At all wavelengths, we find that the incoherent optical response decays through multiple relaxation channels with time constants on the order of 200 fs, few picoseconds, hundreds of picoseconds and 1.5 ns, respectively. These values agree with previous measurements of the transient absorption of spin-coated BiI_3 thin films [158] and the luminescence of BiI_3 single crystals [14]. Accordingly, we assign the fastest dynamics to carrier-carrier scattering, and the two intermediate dynamics to electron-phonon scattering processes and the beginning of electron-hole recombination. The slowest dynamics exceed the investigated temporal window, and its time constant has been held during the fitting procedure to the literature value [14] of the electron-hole radiative recombination process. After subtraction of the multi-exponential fit component (grey line in Fig. 6.3(c)), the coherent optical response (orange circles) is retrieved. Its Fourier transformation (FT, red circles in Fig. 6.3(d)) reveals an oscillation at (3.41 ± 0.02) THz matching the frequency of the A_g phonon mode (light brown line) [179]. Moreover, the oscillation intensity is damped, on average, within (1.860 ± 0.075) ps, which provides the dephasing time of the coherent phonons.

To shed light on the nature of the transient optical response, the group of theorists performed a numerical analysis of the optical properties of BiI_3 via *ab-initio* simulations within the GW+BSE scheme.

As shown in Fig. 6.4(a), the imaginary part of the dielectric function is dominated in the optical region investigated in our measurements by an excitonic peak at 2 eV. The exciton wave function [59] is shown in the real-space representation of Fig. 6.4(b). To match the computed reflectance $R^{X_0}(\omega)$ with the experimental reflectance spectrum (thick line), the calculated peaks are shifted here by

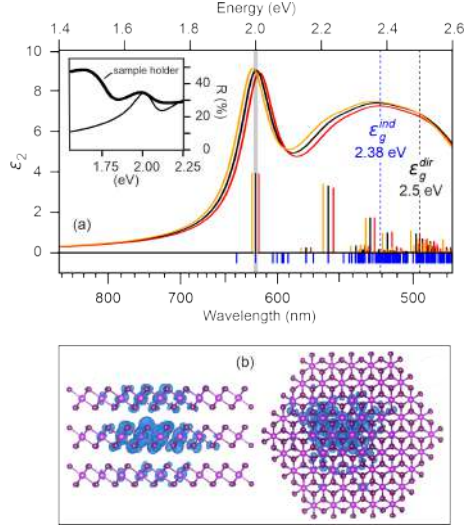


Figure 6.4: (a) BSE absorption spectrum of BiI_3 computed at equilibrium (black line) and with the atoms displaced along the A_g phonon mode with $\pm\Delta_0 = 0.05$ Bohr ≈ 2.6 pm (red and orange line). The corresponding equilibrium reflectivity is shown in the inset (thin line) and compared with the experimental measurement (thick line). At low energy, the two differ by the back reflection of the sample holder. The blue vertical lines represent the excitonic energies at equilibrium, while the black, red, and orange bars are the same poles weighted by the oscillator strengths. The blue and black dashed lines mark the position of the indirect ϵ_g^{ind} and direct ϵ_g^{dir} electronic gap. (b) Real-space representation of the exciton wave function. In the side view, three layers of the bulk are shown, with the hole fixed in the central layer.

0.35 eV. Thus, our calculations clearly show that the optical reflectivity is mostly dominated by the imaginary part of the dielectric function, in agreement with previous works [73, 140]. We then interpret the incoherent optical response as follows: the negative peak at 620 nm (2.00 eV) is assigned to the pump-induced photobleaching of the excitonic resonance; the positive signal at shorter and longer wavelengths to a combination of photoabsorption between transiently excited states, screening-induced optical gap renormalization [158], and increase of the exciton linewidth.

6.2.1 Exciton-phonon coupling: phonon point of view

We now focus on the bare coherent optical response of BiI_3 . Firstly, we singled out only the phononic response by subtracting the incoherent response from the total map.

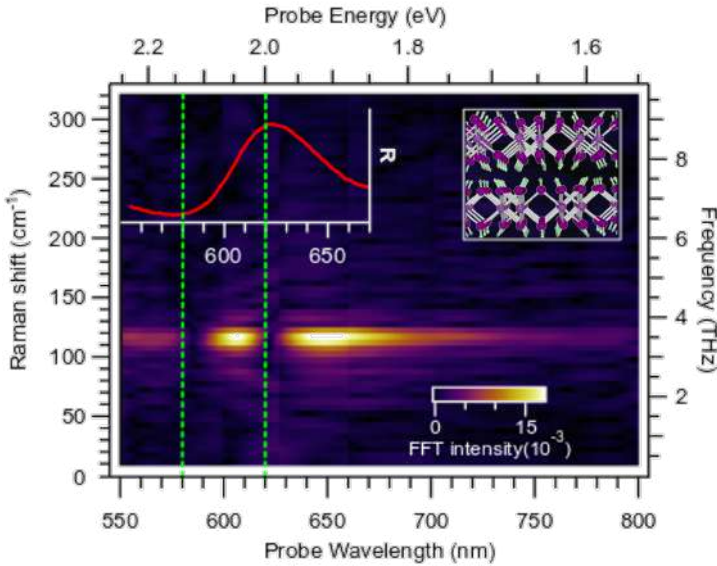


Figure 6.5: FT of the coherent response of BiI_3 .

The frequency-resolved coherent optical phonon map is obtained by FT at each probe wavelength and plotted in color scale in Fig. 6.5(a). It exhibits one intense feature centred at 3.41 ± 0.02 THz, i.e. at the frequency of the A_g phonon mode whose calculated real-space representation is depicted in the inset. A closer look at the FT-spectrum intensity reveals two peculiarities: an enhancement in the exciton-wavelength region and quenching at 580 nm (2.14 eV) and 620 nm (2.00 eV). We argue that the enhancement and quenching of the A_g phonon mode intensity point at an interaction between this vibrational mode and the excitonic transition.

To describe the generation of the coherent phonons, the transient reflectivity collected at selected wavelengths around the two positions where the coherent optical response exhibits a node (i.e. 610 nm and 580 nm) have been extracted from Fig. 6.3(a) and are inserted in Fig. 6.6. The data are shown both before and after the subtraction of the multi-exponential fit accounting for the incoherent optical response to retrieve the bare coherent part. First of all, we note

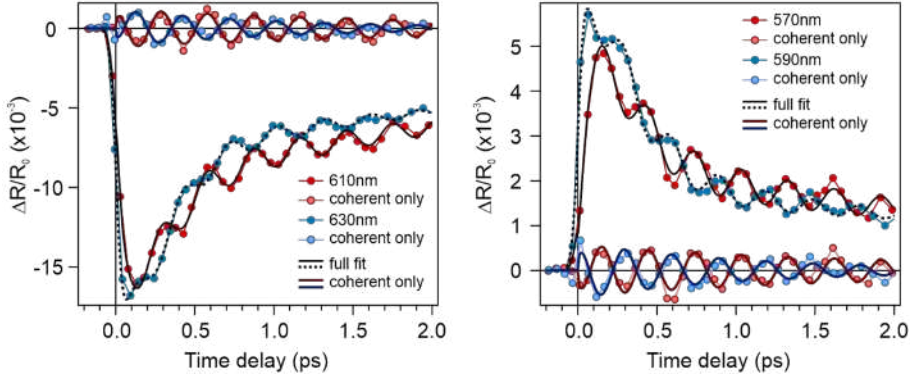


Figure 6.6: Transient reflectivity at selected wavelength prior and after subtraction of the incoherent response fit. The black lines are the full fits, and the red and blue lines are the fits to the coherent part only.

that the periodic modulation is well-fitted by a cosine function in all the probed wavelengths, supporting the idea that coherent phonons are generated by dispersive generation. In both cases, the traces show that the transient reflectance oscillates with the same A_g frequency, but a π -phase shift across the two sides of each node is observed.

The fit parameters of the initial phonon amplitude and phase for all the probed wavelengths are plotted on the left axes of Fig. 6.7(a) and (b), respectively. As a first result, we observe that the coherent phonons are generated by dispersive excitation since the phase is π or 0 (Fig. 6.7(b)). This is consistent with the full symmetry of the A_g vibrational mode and the absorptive excitation regime of our experiment [26, 208, 69, 70]. The calculated amplitude and phase are obtained as follows. First, the GW+BSE reflectivity is recomputed with the atoms displaced by an amount $\Delta X_{A_g} = \Delta_0 u_{A_g}$ along the direction of the eigenvector u_{A_g} of the A_g phonon mode (green arrows, inset of Fig. 6.7(a)). Assuming that the atoms oscillate according to $X(t) = X_0 + \Delta X_{A_g} \cos(\omega_{A_g} t)$, the reflectivity, $R^X(\omega)$, and thus the reflectivity variation, $F(\omega) = (R^X - R^{X_0})/R^{X_0}$ are obtained for distinct positions of the displaced atoms. The atomic displacement induces a change in the band gap, ΔE_{gap} . This affects the dielectric function and, thus, the exciton binding energy, which responds to the modified Coulomb screening with a change ΔE_{be} in the opposite direction. The resulting shift of the excitonic peak is $\Delta E = \Delta E_{gap} + \Delta E_{be}$. The overall picture is of an excitonic resonance that oscillates back and forth in energy as shown in Fig. 6.4(a) (yellow and red spectra). We now compare the calculated $|F(\omega)|$ and $F(\omega)/|F(\omega)|$ with the measured initial amplitude and phase of the coherent optical response, respectively. The calculated quantities are inserted in the right axis in Fig. 6.7

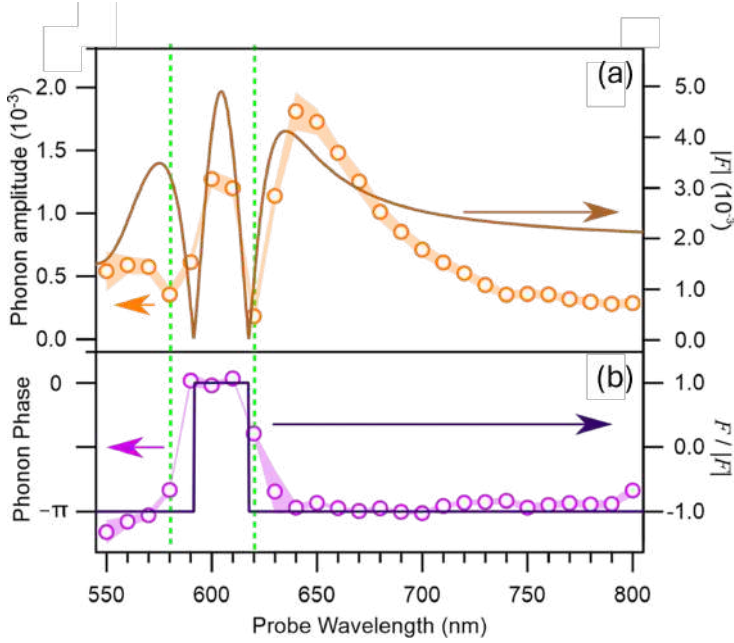


Figure 6.7: (a) Experimental fit parameters of the initial amplitude and (b) phase of the coherent optical phonon as a function of the probe wavelength (left axis) and corresponding calculated quantities (right axis).

(a) and (b). Both quantities confirm the amplitude enhancement as well as the two nodes at the wavelengths of the π -phase shift. The node at the exciton wavelength (620 nm) is due to the opposite sign of the reflectivity variation generated by the shift of the excitonic peak. Concerning the other node, a bunch of excitons with strong exciton-phonon coupling is found to produce a broad peak centred at 525 nm (2.35 eV). Thus, the second node at 580 nm results from the combination of the displacements of the two excitonic peaks. The concomitant observation of the predicted amplitude enhancement and π -phase shift [183] provides, for the first time, unambiguous proof of coupling between coherently activated A_g phonons and excitons. Furthermore, by exploiting the excellent agreement between theory and experiment, we provide a quantitative estimate of the photoinduced atomic displacement and the associated energy shifts. An intensity variation of the coherent optical response on the order of $F(\omega) \approx 10^{-3}$ is obtained in the simulations under atomic displacement in the range of $\Delta_0 \approx 10^{-1}$ pm. To have an idea of the scales involved, for $\Delta_0 = 0.05$ pm the excitonic peak is predicted to shift by $\Delta E = 0.2$ meV as a result of an upshift of the band gap edge by $\Delta E_{gap} = 0.3$ meV and an opposite shift of the

binding energy of $\Delta E_{be} = 0.1$ meV.

6.2.2 Exciton-phonon coupling: exciton point of view

To unravel the impact of exciton-phonon coupling on the dynamics of the excitonic resonance, we follow the transient energy position of the excitonic peak. This is obtained by differential fitting of the transient reflectivity spectra (inset of Fig. 6.9) after parametrization of the equilibrium reflectance.

The parametrization has been modeled on the equilibrium reflectance of BiI_3 collected with a PerkinElmer Lambda 950 spectrophotometer at 300 K and inserted in Fig. 6.8. We observed that the static reflectance is dominated

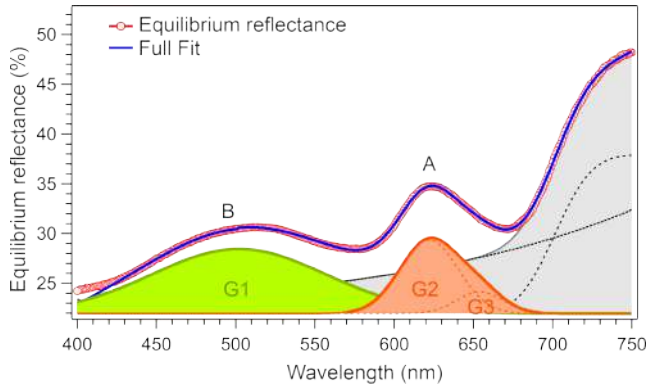


Figure 6.8: Equilibrium reflectance of BiI_3 (red markers) and the relative parametrization (blue line). G_{1-3} are the Gaussians used to parametrize the features A and B. The black line takes into account the background composed by the exponential function (dotted line) and the error function (dashed line).

by two features. A sharp one at 620 nm (2 eV, feature A) is ascribed to the excitonic resonance, and it is the focus of our time-resolved experiment. A broad one at 500 nm (2.48 eV, feature B), partially exceeding our probed energy region, which is composed of a bunch of high-energy excitons that overlap with the band gap edge. As a result, the bare phonon-mediated band gap renormalization and the photoinduced dynamics of the high-energy excitons will be spectrally intertwined. To parametrize the equilibrium reflectance, we use a sum of the following contributions (inserted in Fig. 6.8: a Gaussian peak (green shade, G1) accounting for the broad feature B; a peak (orange) reproducing the exciton A, which is composed of a main Gaussian function (G2) and a minor one (G3) taking into account a slight asymmetry in the peak tails; a background given by the superposition of an off-set exponential function and

an error function (the latter to account for the long-wavelength reflectance contribution originating from the back reflection of the sample holder). As discussed before, this parametrization holds only in the high-temperature limit, where a resemblance between the absorption and reflectance is observed. Once the parametrization of the static reflectance has been defined, the transient reflectivity spectra have been fitted with a differential fit function dR . The non-equilibrium reflectance R_{noneq} is obtained by the same fit function used to parametrize the reflectance at equilibrium, and in order to reproduce the transient reflectivity spectra, we allowed the least necessary number of parameters to vary, namely the amplitude and position of G1, G2 and G3 and the width of G2.

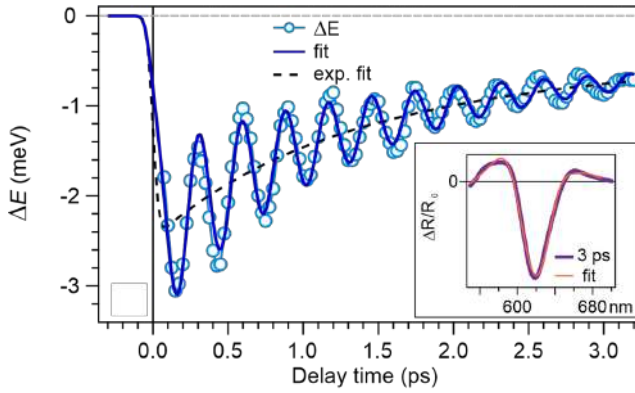


Figure 6.9: Energy shift of the excitonic peak (blue circles). The ΔE fit curve (solid line) is given by a single-exponential decay function (dashed line) multiplied by an exponentially damped cosine function. In inset, spectrum at 3 ps (purple line) and relative differential fit (orange line).

Fig. 6.9 shows the energy shift, ΔE , from the equilibrium position of the Gaussian peak accounting for the excitonic resonance ² (blue circles). The evaluated temporal window spans up to a few picoseconds to cover the phonon dephasing time. Under photoexcitation, the excitonic resonance undergoes an instantaneous redshift (within the pump-probe crosscorrelation) followed by a

²The energy centre of the Gaussian has been calculated as follows: we take the sum of G2 and G3: $G_X = G2 + G3$ at the equilibrium and we take the value of position where the asymmetric peak is maximum x_0 , which is related to the position of the whole exciton at the equilibrium. Then we take G_x inserting the out-of-equilibrium parameters. Therefore, we then find the maximum position $x(t)$ for each pump-probe time delay. The energy shift is then $x(t) - x_0$.

blueshift towards the equilibrium position. The latter evolves on a fast timescale of (1.110 ± 0.075) ps (dashed line), and a slower one that exceeds the evaluated temporal window and is accounted for in the fit by an additional offset. The blueshift is superimposed by a periodic energy modulation at the exact frequency of the A_g -phonon mode, damped on a timescale of (1.420 ± 0.075) ps. Both the red- and blueshifts are rather common in photoexcited semiconductors and typically relate to band-gap renormalization [128, 29, 141, 118] and exciton-binding-energy changes [35, 75] induced by dynamical screening, and conduction-band filling by photoexcited carriers [186, 47, 76]. Conversely, the coherent modulation of the excitonic resonance has been rarely observed in the photoinduced dynamics of semiconductors with strong exciton–phonon coupling [183, 6, 50]. We explain this result by noting that a suitable intensity ratio of the coherent and incoherent optical response is required in order to avoid the exciton energy modulation being buried underneath the photobleaching spectral intensity, as reported, for instance, in [183]. Our measurements indicate that such a ratio is on the order of 1:10 and is achieved by non-resonant photoexcitation with energy above the optical band gap in order to retain from too intense photobleaching of the excitonic resonance.

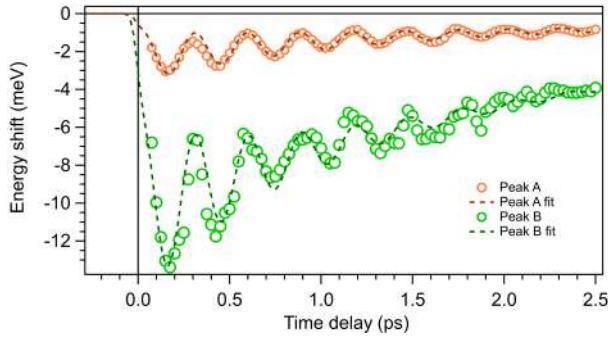


Figure 6.10: The microscopic effect of exciton–phonon coupling: periodic renormalization of the excitonic peak position by the atomic displacement. T_{ph} refers to the phonon period.

Fig. 6.10 compares the coherent energy modulation of the feature B (energy position of G1) and A (peak position of the sum of G2 and G3). Both spectral features undergo an in-phase modulation of their energy position. However, the amplitude of the modulation is larger for feature B (green circles) than for the low-energy exciton A (orange circles). This confirms the theoretical results predicting a phonon-induced exciton binding modulation concomitant

to a phonon-induced band gap change. In particular, the band gap reduces (increases) by a larger amount than the exciton binding energy, resulting in an overall energy downshift (upshift) of the excitonic resonance probed by transient reflectivity.

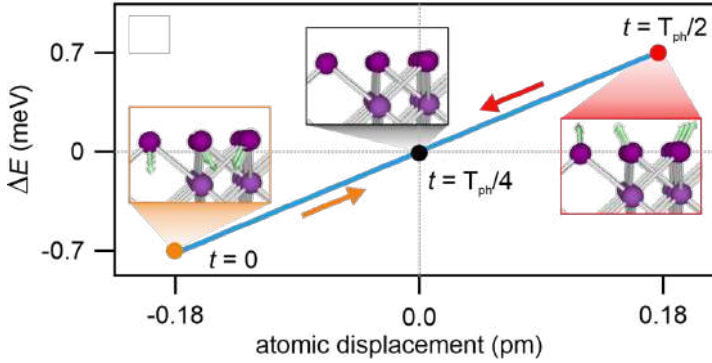


Figure 6.11: The microscopic effect of exciton–phonon coupling: periodic renormalization of the excitonic peak position by the atomic displacement. T_{ph} refers to the phonon period.

The periodic modulation of the excitonic peak exhibits an initial amplitude of $\approx 0.7 \text{ meV}$ ³ in agreement with the simulation with an atomic displacement of 0.18 pm (see Fig. 6.11). The corresponding reflectivity variation is on the expected order of 10^{-3} , differing only by a factor of ≈ 3 from the measured phonon amplitude at the respective probe wavelengths (see Fig. 6.7(b)). All these findings demonstrate that tracking the energy modulation of the excitonic resonance induced by coherent phonons enables the tracking of the atomic displacements along the direction of the phonon mode.

6.2.3 Complementary theoretical results

This section includes the theoretical simulations performed by a group of theorists. These complement our experimental results as anticipated earlier. The electronic structure has been calculated using density functional perturbation theory (DFT) within the framework of the generalized gradient approximation, with the Perdew-Burke-Ernzerhof (PBE) approximation for the

³We note that a periodic modulation of the transient reflectivity minimum is already visible by eye. The high statistics of our transient reflectivity data allow us to resolve relative energy shifts of only a few tens of meV, which are robust against the choice of fit analysis.

Kohn-Sham (KS) equations, as implemented in Quantum Espresso [54]. Norm-conserving pseudopotentials have been produced using the code ONCVSP in the fully relativistic version [60]. The calculations of the electronic density have been performed using an energy cutoff of 80 Ry, a $\mathbf{k}$ -grid of $5 \times 5 \times 5$ and with spinorial wave functions. The parameters for the relaxed rhombohedral unit cell of bulk BiI_3 are $a = 8.94 \text{ \AA}$, and $\cos \gamma = 0.6148$.

Fig. 6.12 shows the band structure of BiI_3 along different paths and with

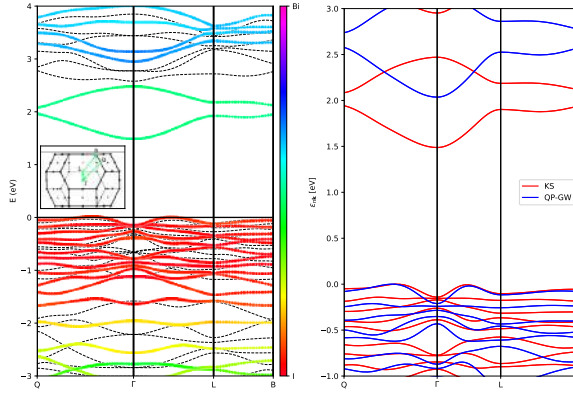


Figure 6.12: (left panel) Band structure of bulk BiI_3 calculated with DFT. The inset shows the path along the Brillouin zone. The colorbar indicates the atomic composition of the electronic bands. The band structure calculated without spin-orbit coupling is represented with dashed lines. (right panel) Band structure of bulk BiI_3 at the KS level, using the PBE functional (red lines), and at the GW level (blue lines).

different levels of approximation. First, at the PBE level, the spin-orbit coupling has a huge impact on the electronic structure [94]. The band gap of the material without spin-orbit coupling (SOC) is 1 eV higher than the one obtained with SOC. This is due to the lowering of two conduction bands, while the valence band region is much less affected. In the left panel of Fig. 6.12, the atomic orbital projections of Bi and I are superimposed to the band structure as a color code. The path along the Brillouin zone is shown in the inset. The valence band is clearly dominated by the iodine orbitals, while the conduction band states are strongly hybridized. GW quasiparticle corrections open the gap by about 0.6 eV, from 1.5 to 2.1 eV, with no significant changes in the band structure. The Mexican-hat shape of the valence band around Γ , which is the source of the indirect band gap of the material, is enhanced. The optical properties are then computed starting from the GW band structure and computing the dielectric function including excitonic effects. The excitonic states are calculated by solving the Bethe-Salpeter Equation (BSE). The Yambo

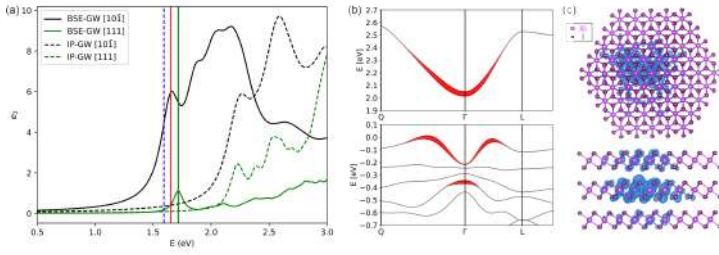


Figure 6.13: (a) Imaginary part of the dielectric function as calculated with BSE-GW (solid line) and IP-GW (dashed line), for light polarization parallel to the ordinary axis ($[10\bar{1}]$ direction in black) and parallel to the extraordinary axis ($[111]$ direction in green). The first dark and bright excitons are indicated with blue (dark exciton), red (bright exciton, ordinary polarization) and green (bright exciton, extraordinary polarization) vertical lines, respectively. (b) Representation of the exciton wave functions (red shadow) on the GW band structure for the first bright exciton. (c) Excitonic wave function in real space of the bright exciton. The hole is located nearby an iodine atom.

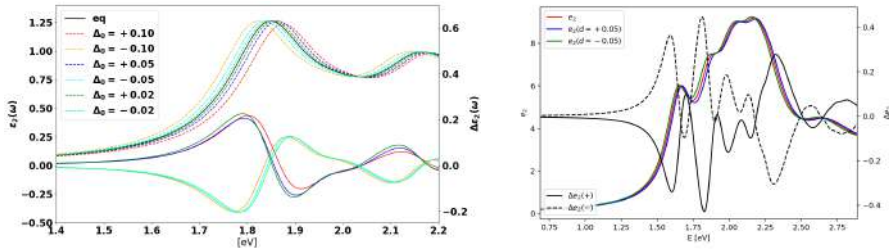


Figure 6.14: Equilibrium absorption and displaced absorption $\varepsilon_2(\Delta_0)$ for different values of Δ_0 . The differential absorption $\Delta\varepsilon_2(\Delta_0, \omega)$ are also shown. In the left panel, calculations with poorly converged parameters for six different displacements. In the right panel, fully converged results for the optimal displacement $\Delta_0 = 0.05$ Bohr.

code [155] is used for the GW-BSE scheme. For the GW calculations, the plasmon-pole approximation for the dielectric screening is used, with 160 bands and a cutoff of 1 Ry. The self-energy is obtained using 160 bands and a cutoff of 15 Ry. We find convergence for a $\mathbf{k}$ -grid of $6 \times 6 \times 6$. The BSE excitonic Hamiltonian is constructed by including 17 occupied (valence) states and 9 empty (conduction) states. The unusually high number of bands needed to converge the spectrum is a fingerprint of the peculiar optical properties of the

material. The absorption spectrum is shown in Fig. 6.13(a) both along the ordinary (in-plane electric field) and extraordinary (out-of-plane electric field) geometry. For both geometries, the spectra, including excitonic effects (BSE-GW), are compared with the ones at the independent particles levels (IP-GW), where excitonic effects are neglected. The calculated spectrum appears shifted by 0.35 eV with respect to the measured one. The shift majorly originates from the temperature renormalization [110] and the absence of self-consistency in the GW calculations [57]. For Fig. 6.13(a), we used a uniform broadening of 0.1 eV for all peaks. In Section 6.2, instead a smaller broadening is used for the lowest energy peak (50 meV) and a higher broadening for the rest of the spectrum (150 meV), in agreement with experimental results from the literature. The exciton wave function representation follows the methodology explained in Ref. [180], and it is shown in Fig. 6.13(b-c) (real-space and k-space representation). At variance with other 2D materials, like transition metal dichalcogenides [111], the exciton here has a remarkably high binding energy also in the bulk and a Frenkel-like character, see Fig. 6.13(a).

Finally, we use DFT (as implemented in QE) to compute the phonon spectrum [9]. The selected phonon eigenmode corresponds to the A_{1g} oscillation and displaces the atoms away from equilibrium along such eigenmode with a prefactor of Δ_0 . The value of Δ_0 is chosen to be as small as possible so that the variation observed in the spectrum is linear with respect to the displacement. However, a too small displacement cannot be used. Otherwise, the difference between the spectrum with atoms at equilibrium and the spectrum with displaced ions is dominated by numerical noise. First, the displaced spectra are computed with 0.10, 0.05 and 0.02 Bohr for low convergence parameters. Defining $\Delta\varepsilon_{\Delta_0}(\omega)$, it was verified that $\Delta\varepsilon_{0.10}(\omega) \approx 2\Delta\varepsilon_{0.05}(\omega) \approx 5\Delta\varepsilon_{0.02}(\omega)$, as shown in Fig. 6.14(a). Then 0.05 Bohr is chosen as the optimal value, and it is further verified that $\Delta\varepsilon_{0.05}(\omega) \approx -\Delta\varepsilon_{-0.05}(\omega)$ with fully converged parameters, as shown in Fig. 6.14(b). According to these results, the spectrum for any displacement with $\Delta_0 < 0.05$ Bohr can be obtained rescaling $\Delta\varepsilon_{0.05}(\omega)$. All differential spectra are dictated by the shift of the peak position, and we verify that the shifts also depend linearly on the value of Δ_0 . For the simulated $\Delta_0 = 0.05$ Bohr, we obtain $\Delta\epsilon_g^d(LDA) \approx 12$ meV for the LDA electronic gap, $\Delta\epsilon_g^d(GW) \approx 17$ meV for the GW electronic gap, and $\Delta E \approx 10$ meV for the BSE optical gap. Extracting the rescaling factor by matching the energy shift of the excitonic peak with the experimental data, the previously discussed values are obtained.

In summary, the strength of this method relies on the ability to calculate the overall effects of lattice vibrations on both the gap and the excitonic states by only performing the calculation of the optical spectra at the GW-BSE level. Nevertheless, different from the microscopic approaches [110, 24], our calculations do not explicitly compute the exciton-phonon matrix elements.

6.3 Effect of the dynamical screening on exciton-phonon coupling

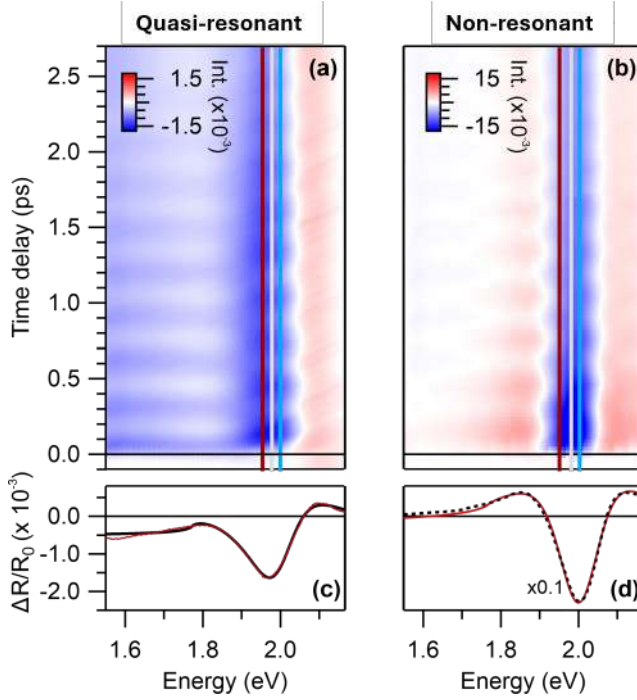


Figure 6.15: $\Delta R/R_0$ intensity maps as a function of pump-probe time delay and probe photon energy for (a) quasi-resonant excitation at 1.91 eV and (b) non-resonant excitation at 2.79 eV. The latter data are adapted from Mor *et al.* [116] On both maps, the red, gray and blue vertical lines mark the position of the time-resolved line cuts reported in Fig. 6.16. The (c) and (d) panels show the energy-resolved line cuts at $\Delta t = 150$ fs for the quasi-resonant and non-resonant excitation cases, respectively.

Fig. 6.15 (a) and (b) show the TR map under quasi-resonant and non-resonant excitation, respectively. Both data are collected at room temperature with absorbed pump fluence of $50 \mu\text{J cm}^{-2}$, which is well within the regime of linear response of the material. For the quasi-resonant case, the pump photon energy is tuned well below the conduction band edge in order to avoid the excitation of quasi-free carriers. At the same time, the pump photons excite resonantly at the low-energy sideband of the excitonic line where the absorbance is still significant. For the non-resonant case, the pump photon energy enables the excitation of

electrons to the conduction-band continuum. $\Delta R/R_0$ under quasi-resonant excitation (Fig. 6.15 (a)) shows two spectral regions of negative (blue) and positive (red) intensity below and above 2.05 eV, respectively. Particularly, an intensity minimum occurs at the exciton energy, and a negative feature extends between 1.55 and 1.80 eV, a region corresponding to the edge of the indirect band gap at 1.67 eV [140]. These features are clearly resolved in the horizontal line cut at 150 fs reported in Fig. 6.15 (c). Moreover, in the TR color map at any probe photon energy, a time-periodic intensity modulation (coherent optical response) superimposes upon the non-periodic evolution of the TR intensity (incoherent optical response). The incoherent optical response reflects the relaxation dynamics of the system towards equilibrium, while the coherent response is due to the generation of coherent optical phonons [139, 42, 61]. $\Delta R/R_0$ induced by non-resonant excitation is shown in Fig. 6.15 (b). The data are the same as discussed in Section 6.2. As previously discussed, the coherent optical response adds up to the incoherent one at any energy. The incoherent optical response shows a double sign change with negative intensity centered at the exciton energy and positive intensity at higher and lower energies. This is also illustrated by the horizontal line cut at 150 fs in Fig. 6.15 (d). All in all, TR reports spectral evidence of the generation of coherent optical phonons as well as excitons under both quasi-resonant and non-resonant excitation conditions. With regard to the incoherent optical response, we assign the negative TR of both data sets to photobleaching of exciton transitions, whereas the positive TR to transient absorption from photoexcited states and photoinduced broadening of the exciton line width. Under non-resonant excitation, free-carrier-induced band-gap renormalization is expected to add a positive contribution in the in-gap energy region [158]. Spectral evidence of these band gap dynamics is discussed later as proof of photoinduced screening. Conversely, under quasi-resonant excitation, these transient band gap dynamics should be marginal due to the lack of a population of photoexcited quasi-free carriers. Consistently, the TR is negative at all energies below the exciton peak, suggesting the optical response in that region is rather dominated by photobleaching of phonon-assisted optical transitions across the indirect band gap.

6.3.1 Coherent optical phonons under quasi-resonant and non-resonant pumping

In this section, we focus on the coherent optical response. We have extracted the bare periodic modulation of the $\Delta R/R_0$ intensity map under subtraction of the incoherent TR contribution. The latter is obtained by applying a smoothing filter to the $\Delta R/R_0$ intensity at each probe photon energy in the window of positive time delays. In Fig. 6.16 (a), the Fourier transformation (FT) of the

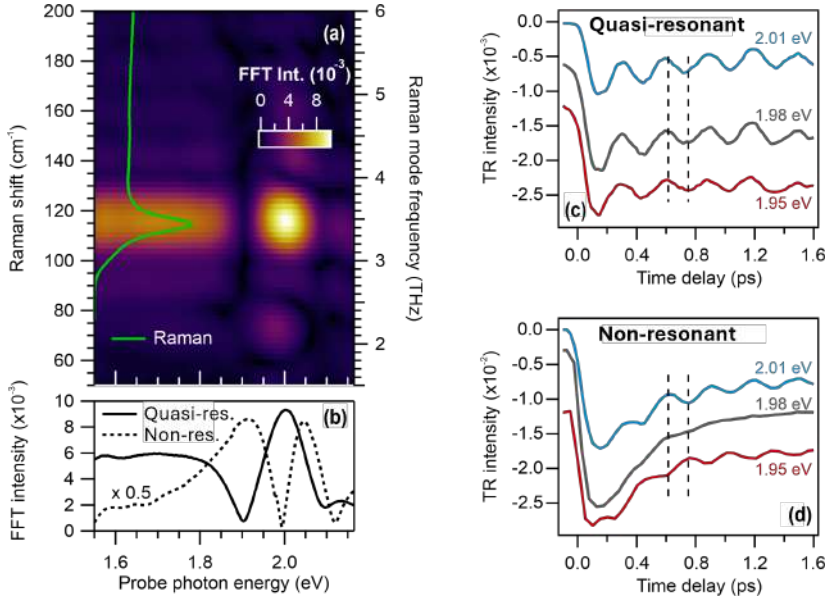


Figure 6.16: (a) Color map of the Fourier transformation of the coherent optical response as a function of Raman shift/mode frequency (left/right axis) for each probe photon energy (bottom axis). The Raman spectrum is shown as a green line for reference. (b) Horizontal line cut at the A_g -mode frequency for quasi-resonant (solid black) and non-resonant (dashed black) excitation. (c) and (d) $\Delta R/R_0$ line cuts at 2.01 eV (blue), 1.98 eV (gray) and 1.95 eV (red) as a function of time delay for quasi-resonant and non-resonant photoexcitation, respectively.

coherent optical response for the quasi-resonant case is shown in false color as a function of probe photon energy. We find a single FT component at 3.4 THz (113.4 cm^{-1}), which corresponds to the A_g vibrational mode, as confirmed by the Raman spectrum (green curve) overlaid on the FT map. In Fig. 6.16 (b), the FT intensity at 3.4 THz is reported as a solid black curve, while the dashed black curve is the corresponding line cut for the non-resonant case ⁴. We observe that for quasi-resonant photoexcitation, the coherent phonon amplitude at the exciton energy shows a maximum, whereas under non-resonant excitation, a node resulting from a periodic shifting of the excitonic resonance due to coupling to coherent optical phonons [116]. Interestingly, such node resembles an antiresonance (dip) obtained from continuous wavelet transformation of the coherent TR of silicon, which was analogously explained by a Fano resonance

⁴For relevant FT map in the non-resonant case, see Section 6.2.

in the Raman spectrum due to coupling of an LO phonon with the exciton continuum [62]. The difference in the photon energy-resolved FT observed in Fig. 6.16 (b) is the first sign that a periodic modulation of the exciton peak energy is hindered under quasi-resonant excitation. More generally, it shows that the coupled exciton-phonon dynamics and relevant TR response are affected by the photoexcitation condition. Further evidence of this is found in the time domain. Fig. 6.16 (c) shows, for the quasi-resonant case, the TR at the exciton energy (gray) and at the low- (blue) and high-energy (red) side of the exciton peak, respectively. The line cuts are extracted from the TR intensity map at the energies marked in Fig. 6.15(a) by vertical lines of the respective colors. All line cuts exhibit an in-phase oscillation persisting for a few ps. Conversely, the intensity oscillation for the non-resonant case shows the opposite phase at the low- and high-energy side of the exciton peak and is completely damped at the exciton peak energy (see Fig. 6.16 (d)). From the discussion in Section 6.2, we know that such π -phase shift of the TR intensity at the exciton energy is connected to the node of the FT intensity and further identifies the coherent phonon-mediated modulation of the energy of the excitonic resonance. The absence of this other fingerprint corroborates that these dynamics induced by exciton-phonon coupling are suppressed under quasi-resonant excitation conditions.

To investigate the mechanism underlying the inhibition of a coherent-phonon-mediated modulation of the excitonic resonance in the quasi-resonant case. We perform differential fitting analysis of the TR spectra at various pump-probe time delays and for both photoexcitation regimes (see red curves in Fig. 6.15(b) and (c)). The analysis consists of two steps. First, we find the best parametrization of the equilibrium reflectance spectrum through the Tauc-Lorentz model. For the investigation of the effect of the screening on the spectroscopic manifestation of the exciton-phonon coupling a more defined parametrization than the one inserted in Section 6.2 is required. We choose to use a Tauc-Lorentz parametrization since it allows us to decouple the resonances of the material from the band gap edge, and therefore to single out the effect of the quasi-free carrier from the photoinduced exciton dynamics. The collected reflectance spectrum is reported in Fig. 6.17 (green curve) together with the best parametrization (black curve), which is based on the Tauc-Lorentz model. A detailed description of the Tauc-Lorentz model is inserted in Section 5.1. To sum up, each excitonic resonance is described by a Tauc-Lorentz oscillator, which carries the information on the band gap edge position (the increasing background in the oscillator) and the oscillator itself. The total fit function comprehends two Tauc-Lorentz oscillators, indicated by the grey-shaded structures in Fig. 6.17 and a background described by an error function. Each oscillator is described by a position, an amplitude and a width. In this parametrization, the first bright exciton is located at (1.99 ± 0.01) eV and a broadening of (0.16 ± 0.01)

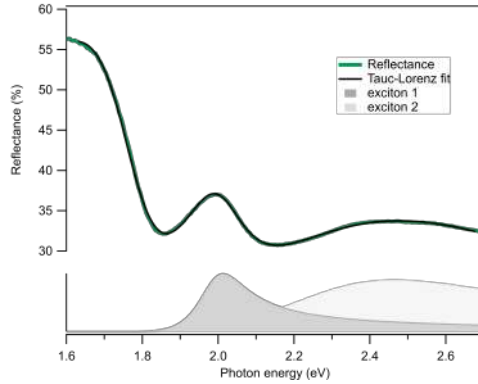


Figure 6.17: Steady-state reflectance spectrum of BiI_3 at 300 K.

eV. The second oscillator takes into account a series of high-energy excitons, which cannot be decoupled at 300 K. The resulting oscillator is located at (2.30 ± 0.05) eV with a broadening of (0.74 ± 0.05) eV. The retrieved band gap is (1.77 ± 0.01) eV, and it is equal for all the oscillators. The latter accounts for a non-constant background due to the partially overlapping tail of the upper band gap edge. The result is shown in Fig. 6.17 as a black curve on top of the equilibrium reflectance data.

Each Tauc-Lorentz oscillator is defined by three parameters: the amplitude, the central energy and the band gap energy. Then, we fit each TR spectra through variation of the least number of parameters. The fit function is given by $(R_{\text{noneq}} - R_{\text{eq}})/R_{\text{eq}}$, where the best-fit parameters for the equilibrium spectrum, R_{eq} , are kept hold in the fitting procedure, while we allow the parameters for the non-equilibrium spectrum, R_{eq} , to adjust to fit the TR spectra. As a result, we obtain the variation in the exciton energy and intensity from the change in the Tauc-Lorentz peak energy and amplitude and in the band gap from the difference with respect to the upper band gap edge at equilibrium. Fig. 6.18 shows the differential fit results under both quasi-resonant (red) and non-resonant (blue) excitation, i.e. (a) the variation of the band gap, and (b) the energy shift and (c) the intensity variation of the Tauc-Lorentz oscillator accounting for the exciton transition at 2.00 eV. The temporal evolution of those observables is obtained using a *global* fitting with the sum of a double exponential decaying function and an exponentially damped cosine function, convoluted with a Gaussian function that accounts for the pulses' cross-correlation. The best fits are shown as black curves on top of the respective data for the quasi-resonant (solid) and non-resonant (dashed) cases. Under non-resonant excitation (blue markers), the band gap is significantly reduced by ca. 12 meV at the excitation time, and the recovery dynamics report two timescales, $\tau_{\text{fast}} = (473 \pm 15)$ fs and

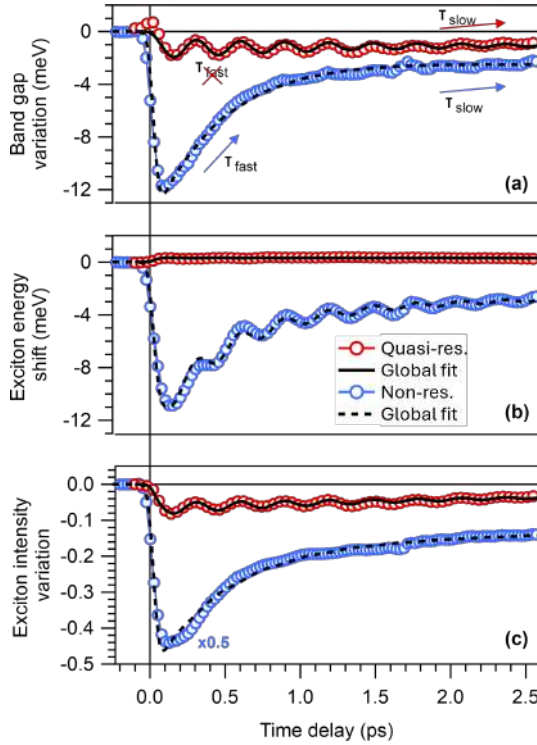


Figure 6.18: Time-resolved variation of (a) the band gap, and of (b) the energy shift and (c) the intensity of the excitonic resonance under quasi-resonant (red) and non-resonant (blue) photoexcitation. The black lines are the fits. (d) Schematic of the spectroscopic signature of exciton-phonon coupling in either absence (top) or presence (bottom) of photoinduced screening.

$\tau_{slow} > 2.5$ ps. The exciton energy shows an initial shift of ca. 11 meV to *lower* energies and an intense periodic modulation at the A_g phonon frequency with an initial amplitude of (1.2 ± 0.1) meV. Eventually, the exciton intensity is strongly suppressed under photoexcitation, and recovers on the two time scales τ_{fast} and τ_{slow} without periodic oscillation at the A_g phonon frequency. Note that the data are scaled by a factor of 0.5 for comparison with the quasi-resonant case. The abrupt band gap renormalization indicates the activation of dynamical screening due to the excitation of quasi-free carriers to the continuum. The fast relaxation is accordingly assigned to carrier-carrier scattering events. The non-periodic evolution of the exciton (both energy and intensity) mirrors the band gap behavior, indicating that the two relaxation dynamics are connected. Finally, the periodic modulation of the exciton energy signifies once more the

coupling to coherent optical phonons in accordance with previous ab initio calculations [116]. The results under quasi-resonant excitation (red markers) are drastically different: (a) the band gap narrows by only 1.5 meV and oscillates at the frequency of the A_g phonon mode, (b) the exciton energy barely reports an almost detection-limited shift by ca. 0.3 meV to *higher* energies at time-zero and does not oscillate, and (c) the exciton intensity variation shows an abrupt suppression followed by a recovery on the single-exponential dynamics τ_{slow} and a periodic oscillation. Now, the marginal band gap shrinking and the missing fast recovery τ_{fast} is consistent with the lack of quasi-free carrier-induced dynamical screening under quasi-resonant excitation. Notably, the small blueshift of the excitonic resonance at the excitation time points towards a repulsive interaction among excitons and it is opposite to the shifting direction of the band gap. Eventually, the coupling of excitons to coherent optical phonons manifests *solely* as oscillations of the intensity (which also appears in the TR intensity at any other energy), while it does not trigger any modulation of the exciton energy. We summarize the effect of exciton-phonon coupling and photoinduced screening

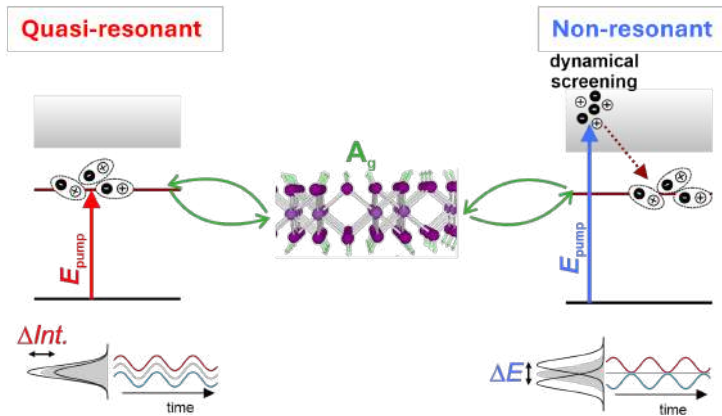


Figure 6.19: Time-resolved variation of (a) the band gap, and of (b) the energy shift and (c) the intensity of the excitonic resonance under quasi-resonant (red) and non-resonant (blue) photoexcitation. The black lines are the fits.

on the TR spectrum in Fig. 6.19. When excitons and coherent phonons are generated in the absence of photoexcited quasi-free carriers (top of Fig. 6.19), the *unscreened* exciton-exciton interaction likely govern the dynamics at time zero leading to the initial blueshift of the exciton energy. Consequently, (1) a photo-induced modulation of the excitonic resonance is suppressed, and (2) the coupling appears in a modulation of the exciton *intensity*. Conversely, the activation of dynamical screening by photoexcited carriers (bottom of Fig. 6.18(d)) plausibly weakens the repulsion among excitons while locking the

exciton energy modulation to the A_g coherent optical phonons. As a result, the *energy* of the excitonic resonance oscillates in addition to following rigidly the massive renormalization of the band gap.

6.4 Conclusions

In conclusion, we prove that the excitonic resonance of the layered semiconductor BiI_3 can be optically modulated via coupling with coherent atomic vibrations of which we are able to estimate the spatial extent with sub-picometer resolution. The present results can be extended to any photoexcited semiconductor with the exciton strongly coupled to a lattice deformation. As a perspective, we propose that ultrafast modulation of excitonic resonances could be experimentally controlled by varying the laser fluence or tuning the pump photon energy across the exciton transition, paving the way towards optical control of the non-equilibrium optoelectronic properties of low-dimensional semiconductors. Moreover, we succeed in experimentally disentangling the distinct contributions of exciton-exciton repulsion, exciton-carriers interaction and exciton-phonon coupling in the TR spectrum in a photoexcited layered semiconductor. We find that the photoinduced screening modifies how exciton-phonon coupling manifests in the TR spectrum. In particular, it promotes the energy modulation of the excitonic resonance, which is phase-locked to the atomic vibration. This is opposed to the case in which the *unscreened* exciton-exciton repulsion sets the shifting dynamics of the excitonic resonance at the excitation time, and exciton-phonon coupling leads solely to an intensity modulation.

Chapter 7

Observation of the coherence by inter-tr-2PPE

In chapter 5 and 4, we identified the spectroscopic signature of the excitonic coherent state in the layered semiconductor BiI_3 , using transient optical spectroscopy and investigated exciton formation through tr-ARPES. In this chapter, we present a proof-of-concept to demonstrate a potential advance that combines information obtained by photoemission spectroscopy on the excitons and the observation of the coherent excitonic state and its decoherence time. In fact, the coherent state can be probed directly using interferometric time-resolved two-photon photoemission spectroscopy (inter-tr-2PPE), which extends pump-probe spectroscopy by scanning the delay between two identical or phase-related pulses interferometrically [193, 137, 138, 145, 146]. This permits us to follow not only the incoherent processes but also the decay of the phase coherences between the initial and excited levels in solid-state systems. The chapter is divided as follows. In the first section, the inter-tr-2PPE principle will be described. Then, the mathematical description will be inserted with the relative simulation that we have performed. Lastly, we introduce preliminary measurements.

7.1 Description of the inter-tr-2PPE

The pump-probe process in photoemission is described as a two-photon photoemission process (2PPE)[184].

Fig. 7.1(a) shows the excitation pathways in a generic a 2PPE process.

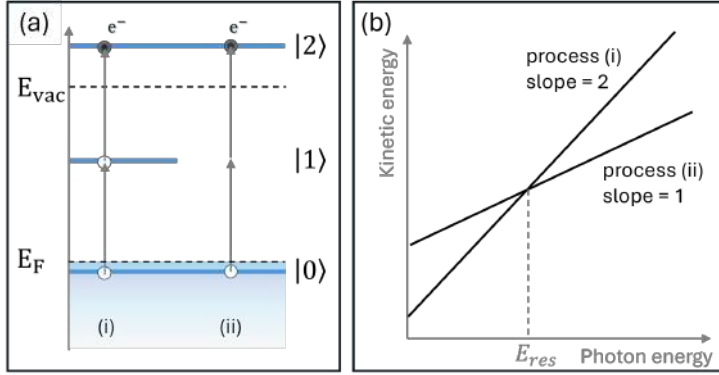


Figure 7.1: (a) Excitation pathways in two-photon photoemission. Two paths are possible: (i) an incoherent step-by-step single photon process and (ii) a coherent direct two-photon ionization process. (b) Photon energy dependence of the photoelectron kinetic energy. Adapted from [184].

The first photon (pump) excites electrons from a state below Fermi, known as the initial state and denoted as $|0\rangle$, to an intermediate state, denoted as $|1\rangle$. The intermediate state is virtual or real and lies between the Fermi energy and the vacuum level, indicating that the pump energy is not enough to overcome the work function ϕ of the material. The second photon, the probe, produces a transition between the intermediate state $|1\rangle$, and the final photoelectron state, which is above the vacuum level and is indicated as $|2\rangle$. To produce a photoemitted intensity, the delay between the pump and the probe pulses must be shorter than the lifetime of the intermediate state. The intensity of 2PPE depends on the initial and intermediate state and the energy of the photon. Two main excitation pathways are predicted as shown in Fig. 7.1: (a) an incoherent process where the kinetic energy of the photoelectron depends on the intermediate state energy position; and (b) a coherent process described as the absorption of two photons with energy $\hbar\omega_1$ and $\hbar\omega_2$ and having the energetic position related to the initial one through both the pump and the probe energy. The two processes show a different slope when the kinetic energy is evaluated by changing the photon energy: the slope is 1 for the incoherent process and 2 for the coherent one as shown in Fig. 7.1(b).

The spectral intensity is defined as

$$P(\hbar\omega_1, \hbar\omega_2, e_p) = \frac{2}{(e_p - \hbar\omega_1 - e_i)^2 + \gamma_i^2} \frac{1}{(e_p - \hbar\omega_2 - e_j)^2 + \gamma_j^2} \quad (7.1)$$

where $\hbar\omega_1$ and $\hbar\omega_2$ are the energy of the pump and the probe, respectively.

The linewidth γ contains information about the depopulation time T_1 and the dephasing times T_2^* associated with the system. The two are related by $\gamma = \frac{1}{T_2} = \frac{1}{2T_1} + \frac{1}{T_2^*}$. The investigation of the PE intensity in the time domain using tr-2PPE permits the tracking of the PE intensity dynamics by changing the delay times between the pump and the probe. Inter-tr-2PPE is then a specific subclass of the tr-2PPE technique where the pump and the probe have a degenerate energy and a well-defined phase. The setup is designed based on the coupling of the PE setup with a Michelson interferometer and, the first results on metals was obtained by Petek et al. [137]. If the two photons are identical with a defined delay, the photoemission process has four excitation pathways (two for the pump and two for the probe) inserted in Fig. 7.2(a) [137]. The diagram shows in the left (right) part the possible excitation pathways of

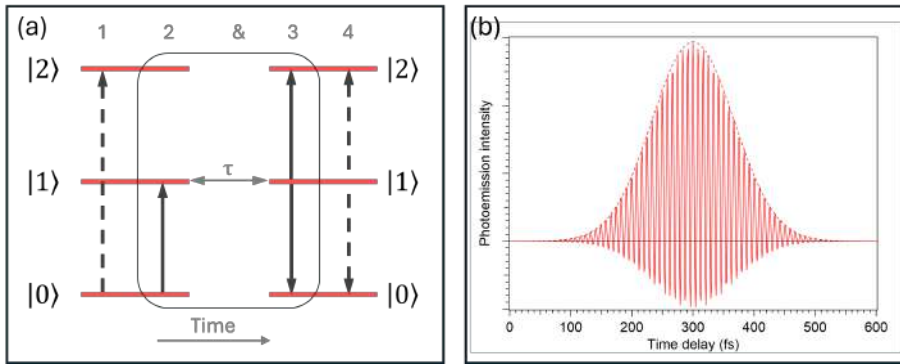


Figure 7.2: (a) Excitation pathways for the inter-tr-2PPE. Adapted from [137]. (b) Example of a typical result of the inter-tr-2PPE.

the pump (probe). The coherent two-photon absorption is indicated by the dashed arrows, which represent the absorption of two photons coming from the same pulse (pump or probe). Increasing the excitation fluences, the coherent two-photon process increases the probability of being observed. Furthermore, channels 2 and 3 in Fig. 7.2(a) are transitions in which a photon from the pump and a photon from the probe are involved. In Fig. 7.2(a), only the intuitive order is inserted. For example, the case where the photon of the probe is absorbed before the photon of the pump is not displayed. If the states are coherent, these channels interfere constructively if the transitions from the pump and from the probe are in the same direction or destructively if transitions go in the opposite direction (indicated by the direction of the arrow). In the coherent regime, the counterintuitive order also contributes to the interference pattern. The interference depends on the difference of the phase between the two pulses and the dephasing rate. The results of inter-tr-2PPE is the spectrum displayed

in Fig. 7.2(b) as the photoemitted intensity as a function of the two-pulse delay time. The spectrum has an interferometric pattern with a Gaussian-like envelope. The shape of the interferogram carries information about the dephasing and depopulation times in the system. However, understanding the connection between the interferometric pattern and the dephasing mechanisms is not trivial. To clarify it, we choose to follow two paths indicated in Fig. 7.3. First, we simulate the time evolution of the photoemitted intensity by solving

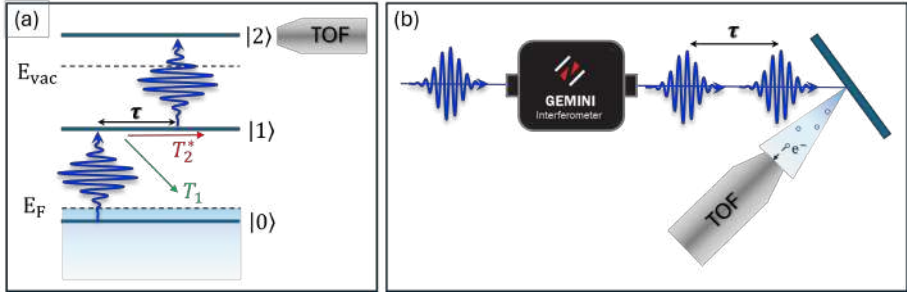


Figure 7.3: (a) Sketch of the photoemission process with two pulses. (b) Picture of the setup for an inter-tr-2PPE.

the optical Bloch equations (OBEs) for a three-level system that interacts with two laser pulses (Fig. 7.3(a)). In addition, we have built the interferometric setup and collected some preliminary results (Fig. 7.3(b)).

7.2 Simulation of the inter-tr-2PPE response

The intensity of the interferometric photoemission is simulated by solving the OBEs for a three-level system.

As reported previously, the photoemission process is described by a three-level system where the levels are (i) the initial occupied level with the eigenvalue E_0 and eigen function $|0\rangle$, (ii) an intermediate level (either real or virtual) with eigenvalue E_1 and eigen function $|1\rangle$ and (iii) the final state which is the photoelectron state with eigenvalue E_2 and eigen function $|2\rangle$. The description of the light-matter interaction for a three-level system is implemented by using the density matrix formalism described in Section 1.3.1.

The density matrix for a three-level system is then:

$$\rho = \begin{pmatrix} \rho_{00} & \rho_{01} & \rho_{02} \\ \rho_{10} & \rho_{11} & \rho_{12} \\ \rho_{20} & \rho_{21} & \rho_{22} \end{pmatrix} \quad (7.2)$$

where ρ_{ii} with $i=0,1,2$ are the populations for each level and the ρ_{ij} with $i,j=0,1,2$ and $i \neq j$ are the coherences between the i and j states. The time evolution of the density matrix elements evolves with Equation 1.24. The interaction Hamiltonian $\hat{H}_{int}$ is related to the electric field as $\hat{H}_{int} = -\hat{\mathbf{d}} \cdot \hat{\mathbf{E}}$. In the weak field approximation, the field does not change the eigenvalues of the system. The interaction matrix is then:

$$\rho = -E(t) \begin{pmatrix} 0 & d_{01} & d_{02} \\ d_{10} & 0 & d_{12} \\ d_{20} & d_{21} & 0 \end{pmatrix} \quad (7.3)$$

The dipole moment is defined as $d_{ij} = \langle i | d | j \rangle$. The two pulses are coherent, and collinear and the electric field is:

$$E(t) = \frac{1}{2} (\mathcal{E}(t) e^{i\omega_l t} + \mathcal{E}^*(t) e^{-i\omega_l t}) \quad (7.4)$$

The electric field has a Gaussian envelope encoded in the complex value $\mathcal{E}$, and ω is the frequency of the laser. The total electric field is composed of two pulses delayed by a time τ , resulting in an amplitude:

$$\mathcal{E}(t) = A_l e^{-\frac{t^2}{2\sigma_l^2}} + A_l e^{-\frac{(t-\tau)^2}{2\sigma_l^2}} e^{i\omega_l \tau} \quad (7.5)$$

where A_l is the amplitude of the pulse envelope, σ_l is the width of the pulse envelope, ω_l is the frequency of the laser and τ is the delay between the pump and the probe. We assume that the final state does not depopulate, so T_1^2 is not included in the calculations and that the dipole momentum between the initial and final states is not included since the transition has to pass through an intermediate virtual state ($d_{02} = d_{20} = 0$).

The resolution of the OBEs is simplified, assuming that the pump photon energy is resonant to the initial-to-intermediate and intermediate-to-final transitions. Hence, the differences are zero. The effect of the variation of the energy position on the final interferogram is discussed in [193]. The initial state is:

$$\rho = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (7.6)$$

which means that the electronic population is entirely in the initial state. We note that the sum of the population must always be 1 at each calculated time.

With these approximations, the OBEs for a three-level system are:

$$\begin{aligned}
\frac{\partial \rho_{11}}{\partial t} &= \frac{i}{2\hbar} (\mathcal{E}^* \rho_{10}^* - \mathcal{E} \rho_{10}) + \frac{1}{2\hbar} d_{12} (\mathcal{E} \rho_{21} - \mathcal{E}^* \rho_{21}^*) - \frac{1}{T_1^1} \rho_{11} \\
\frac{\partial \rho_{22}}{\partial t} &= \frac{i}{2\hbar} (\mathcal{E}^* \rho_{21}^* - \mathcal{E} \rho_{12}) \\
\frac{\partial \rho_{00}}{\partial t} &= -\frac{\partial \rho_{11}}{\partial t} - \frac{\partial \rho_{22}}{\partial t} \\
\frac{\partial \rho_{10}}{\partial t} &= \frac{i}{2\hbar} d_{01} \mathcal{E}^* (\rho_{00} - \rho_{11}) + \frac{1}{2\hbar} d_{12} \mathcal{E} \rho_{20} - \left(i\Delta_{01} + \frac{1}{2T_1^1} + \frac{1}{2T_2^{01}} \right) \rho_{10} \\
\frac{\partial \rho_{21}}{\partial t} &= \frac{i}{2\hbar} d_{12} \mathcal{E}^* (\rho_{11} - \rho_{22}) - \frac{1}{2\hbar} d_{01} \mathcal{E} \rho_{20} - \left(i\Delta_{12} + \frac{1}{2T_1^1} + \frac{1}{2T_2^{12}} \right) \rho_{21} \\
\frac{\partial \rho_{20}}{\partial t} &= \frac{i}{2\hbar} \mathcal{E}^* (d_{12} \rho_{10} - d_{01} \rho_{21}) - \left(i\Delta_{02} + \frac{1}{2T_1^1} + \frac{1}{2T_2^{02}} \right) \rho_{20}
\end{aligned} \tag{7.7}$$

where ρ_{ii} with $i = 0, 1, 2$ are the populations, ρ_{ij} with $i, j = 0, 1, 2$ and $i \neq j$ are the coherences, $\mathcal{E}$ is a complex quantity that carries information about the impinging pulse, d_{01} and d_{12} are the dipole momenta, Δ_{01} and Δ_{12} are the detuning with respect to the $0 \rightarrow 1$ and $1 \rightarrow 2$ transitions, T_1^1 is the depopulation time for the intermediate level and T_2^{01} , T_2^{12} and T_2^{02} are the decoherence times between the initial state and the intermediate state, the intermediate state and the final state, the initial and the final state, respectively. We evaluated the time evolution of the population of the final state at a fixed time delay. Then, we perform the same evaluation by scanning the delay between the pulses. The final interferogram is reconstructed by taking the last calculated value for the final-state population as a function of the two-pulse time delay.

Initially, we explored the threshold for the perturbative regime. Beyond the perturbative regime, the assumption that the electric field does not change the eigenvalue of the system no longer holds. We then explore the effect of changing the amplitude of the electric field A_l and the dipole momenta $d_{12} = d_{10}$. The other parameters are fixed to the value inserted in Table 7.1.

Fig. 7.4 (a), (b) and (c) shows the solution of OBE for several values of amplitude and dipole transitions. Before the arrival of the laser, we observe the equilibrium values, i.e. the electronic population is in the ground state, i.e. $\rho_{00} = 1$, the intermediate and photoelectron states are empty, i.e. $\rho_{11} = \rho_{22} = 0$. In Fig. 7.4(a), the amplitude is $A_l = 0.03$ eV, and the dipole momentum is $d_{12} = d_{10} = 0.08$, resulting in a variation in the population in the ground state is 0.13%. The zero of the time axis is chosen at the maximum of the first peak. At the pump arrival, ρ_{00} and ρ_{11} are populated instantaneously, while ρ_{22} has

τ	245 fs
σ_l	80 fs
$\Delta_{10}=\Delta_{21}$	0
T_1^1	30 fs
T_2^{01}	30 fs
T_2^{12}	10^{15} fs
T_2^{02}	30 fs
ω_l	0.75 PHz

Table 7.1: Set of value used for the simulation in Fig. 7.4.

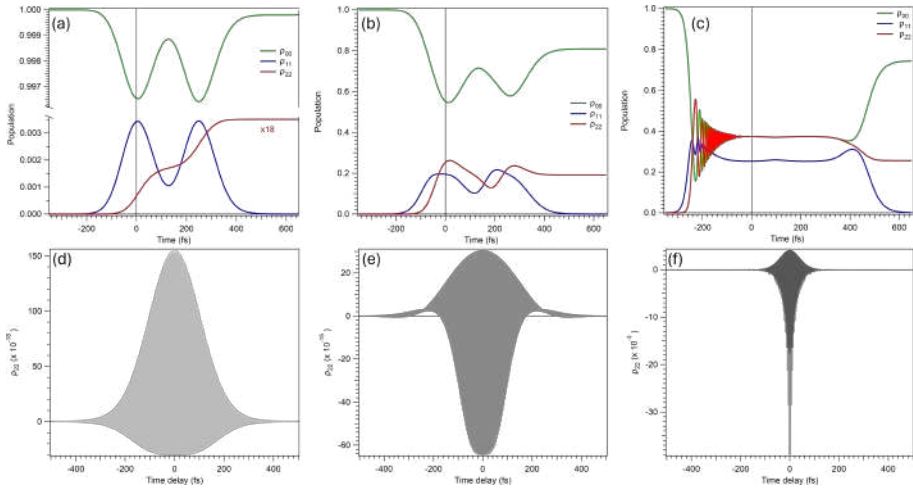


Figure 7.4: OBE solution for a fixed delay to 250 fs, the coefficients used are inserted in Table 7.1 and for (a) $A_l = 0.03$ eV and $d_{01} = d_{12} = 0.08$, (b) $A_l = 0.3$ eV and $d_{01} = d_{12} = 0.1$ and (c) $A_l = 3$ eV and $d_{01} = d_{12} = 1$. (c-e) are the interferograms calculated with the same value of (a-c), respectively.

a rise time. We note that ρ_{22} is also populated by a two-photon absorption. In Fig. 7.4(b) the amplitude is 0.3 eV and the transition momentum is 0.1, the population varies of 14%. A deviation of the pattern inserted in Fig. 7.4 (a) is observed as a periodic modulation of the population. This is an indicator for a deviation from the perturbative regime. In Fig. 7.4(c) the amplitude is 3 eV and the transition momentum is 1. The first pulse produces an intense modulation of the populations, indicating a non-perturbative regime also in this case. Moreover, ρ_{22} shows a decrease at 500 fs, which is totally non-physical and indicates that the photons are absorbed by the system. Fig. 7.4 (d), (e) and (f) show the calculated interferograms for each case discussed before. The

interferogram calculated with the amplitude is $A_l = 0.03\text{eV}$ and the dipole momentum is $d_{12} = d_{10} = 0.08$ is inserted in Fig. 7.4(d). The interferometer is asymmetric with respect to the x-axis, with a Gaussian envelope in the upper part and a lower intensity in the bottom part of the interferogram. The interferogram calculated with the amplitude is $A_l = 0.3\text{eV}$ and the dipole momentum is $d_{12} = d_{10} = 0.1$ is inserted in Fig. 7.4(e). Even if the time evolution of the populations does not differ significantly from the previous case, the interferogram inserted in Fig. 7.4(e) changes. In the non-perturbative regime, the interference pattern is totally destroyed in the upper part, while the bottom lobe dominates the interferogram. Last, the simulated interferogram with the parameters $A_l = 3\text{ eV}$ and the dipole momentum is $d_{12} = d_{10} = 1$ is inserted in Fig. 7.4(f). In this case, the interferogram has a negligible intensity, indicating a total absence of the interferometric pattern.

We decided to use the interferogram in the perturbative regime as the starting point of our systematic investigation, i.e., using the parameters $A_l=0.03\text{ eV}$ and $d_{12} = d_{10} = 0.08$. The parameters used in the following simulation are inserted in Table 7.2. Variations are indicated in the text for each specific case.

A_l	0.03 eV
$d_{12} = d_{10}$	0.08
σ_l	80 fs
$\Delta_{10}=\Delta_{21}$	0
T_1^1	30 fs
T_2^{01}	0.1 fs
T_2^{12}	10^{13} fs
T_2^{02}	0.1 fs
ω_l	0.75 PHz

Table 7.2: Set of values used for all the following simulations.

Fig. 7.5 shows the interferogram resulting from the parameters in Table 7.2. To have a qualitative comparison, the interferograms will be described by the Gaussian envelope

$$y = y_0 + A_g e^{-\frac{t^2}{\sigma_g^2}}. \quad (7.8)$$

where y_0 is the background, A_g the amplitude of the Gaussian and σ_g is the width of the Gaussian. The resulting width is (142 ± 5) fs, which can be compared to the cross-correlation of the pulses. The cross-correlation is calculated from the width of the pulses (80 fs) using the following relation:

$$\sigma_{AC} = \sqrt{2}\sigma_l \quad (7.9)$$

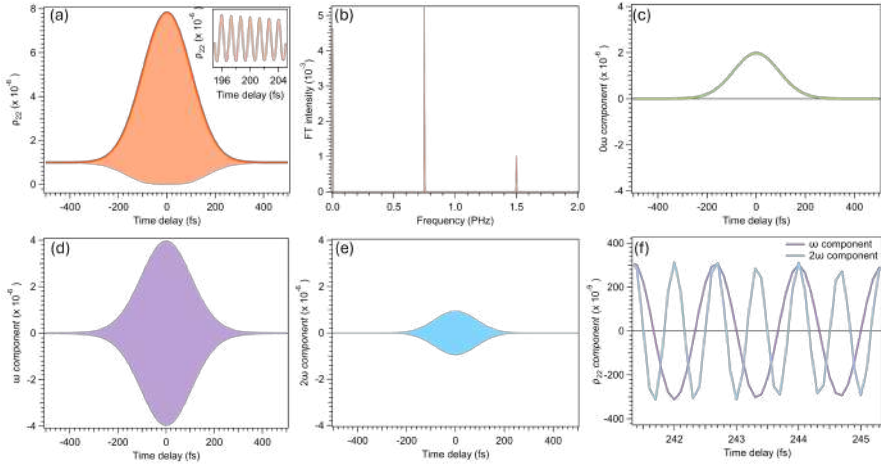


Figure 7.5: (a) p_{22} as a function of the delay time with the value inserted in Table 7.2. (b) Fourier transform of (a) (c) Phase-averaged contribution, (d) ω contribution and (e) 2ω contribution of the interferogram in (a). (f) Comparison of the oscillation in (d) and (e).

and it is equal to (113 ± 5) fs. This shows that the two interferograms are different. To retrieve these interferograms, we selected a frequency $\omega_l = 0.75$ PHz, corresponding to the photon energy used in the experimental setup (3.1 eV). To determine the frequencies of the periodic modulation in the interferogram (inset in Fig. 7.5), we performed a Fourier transform (FT) of the interferogram. Fig. 7.5(b) shows the FT results, where three features are identified. The peak at zero represents the phase-averaged contribution to the interferogram as described in Fig. 7.5 (c). The frequency at 0.75 PHz, matching the frequency of the two excitation pulses, corresponds to channels 2 and 3. The resulting component of the total interferogram is inserted in Fig. 7.5 (c). The last feature, at 1.5 PHz, arises from the coherent two-photon absorption. The resulting component, shown in Fig. 7.5 (e), oscillates at twice the frequency of the pump pulses, as shown in Fig. 7.5 (f).

Fig. 7.6 shows the interferograms simulated by changing the amplitude ((a) and (b)) and dipole momentum ((d) and (e)) to explore the limits of the perturbative regime. Observing Fig. 7.6 (b) and (d), we note that they have the same width (142 fs) with a significant change in the amplitude. This indicates that, in the perturbative regime, the shape of the interferogram does not change even if there is an increase in its amplitude. In the non-perturbative regime (Fig. 7.6 (a) and (c)), the situation is quite different. The width decreases (109

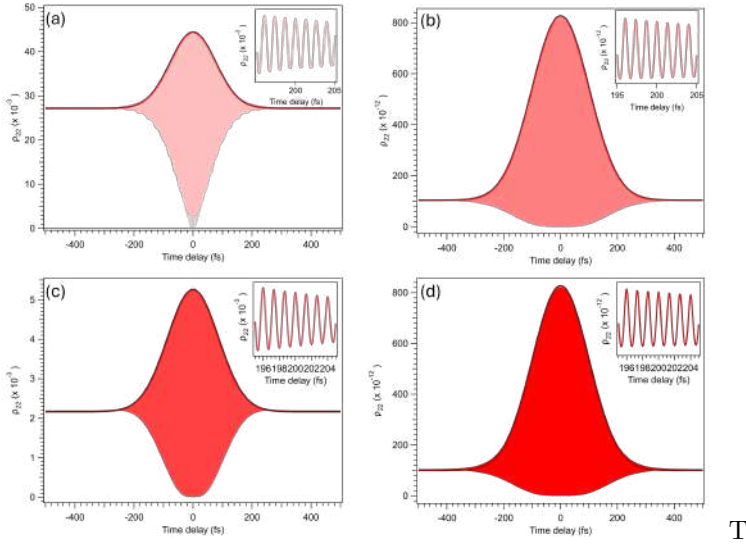


Figure 7.6: ρ_{22} as a function of the delay time with the value inserted in Table 7.2, with the following modification: (a) $A_l = 3$ eV, (b) $A_l = 0.003$ eV, (c) $d_{01} = d_{12} = 1$ and (d) $d_{01} = d_{12} = 0.08$.

fs and 122 fs for Fig. 7.6 (a) and (c), respectively), and, simultaneously, the shape of the interferogram changes, producing a stretching of the bottom part with respect to the top one.

Eventually, we evaluate the effect of the pulse duration on the interferogram.

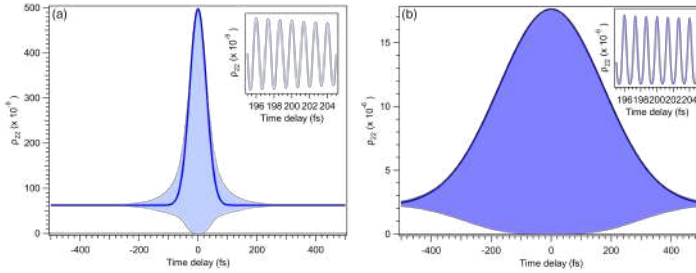


Figure 7.7: ρ_{22} as a function of the delay time considering the value inserted in Table 7.2, with the following modification: (a) $\sigma_l = 20$ fs and (b) $\sigma_l = 150$ fs.

Fig. 7.7 (a) and (b) show interferograms simulated with shorter pulses ($\sigma_l = 20$ fs) and longer pulses ($\sigma_l = 150$ fs), respectively. The interferograms differ from

the one shown in Fig. 7.5(a), resulting in a width of 40 fs and 246 fs for the interferogram in Fig. 7.7 (a) and (b), respectively. The width influences the amplitude of the interferogram, resulting in a more intense signal in the wider spectrum. The shape also differs in the two cases, i.e. the depopulation time of the intermediate state is 30 fs, which is larger than the width in Fig. 7.7 (a) and significantly shorter than the width of the interferogram in Fig. 7.7 (b). This indicates that the deviation from the Gaussian shape is related to the depopulating process.

In the second part, we will report a systematic investigation of how dephasing and depopulation change the shape and intensity of the interferogram.

The first parameter that we want to discuss is T_1^1 , which is the depopulation time of the intermediate state. This describes the time that is needed for the electron to return to the ground state due to the scattering events. In our simulations, this is the only value that changes the occupation of the levels, since the final level is the photoelectron level and the initial one does not decay.

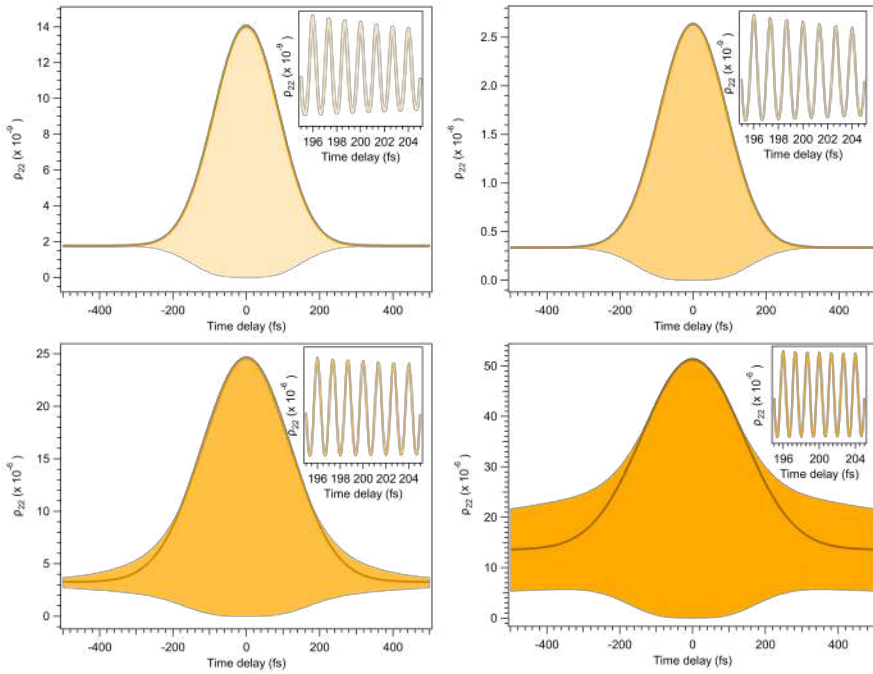


Figure 7.8: ρ_{22} as a function of the delay time with the value inserted in Table 7.2, with the following modification: (a) $T_1^1 = 1$ fs, (b) $T_1^1 = 15$ fs and (c) $T_1^1 = 90$ fs and (d) $T_1^1 = 1000$ fs.

Fig. 7.8 shows the interferogram when we change the depopulation time from 1 fs to 1000 fs. The widths of the interferograms are reported in Table 7.3.

T_1^1 (fs)	σ_g (fs)
1	125
15	130
30	142
90	170
1000	195

Table 7.3: Depopulation time and the relative interferogram width.

The two interferograms shown in Fig. 7.8 (a) and (b) are similar, and the widths are near the autocorrelation value. In Fig. 7.8 (c), a sizable deviation is observed from the Gaussian envelope that becomes extreme in Fig. 7.8 (d). Moreover, there is an increase in the intensity at a larger delay since the electrons remain longer in the intermediate level, producing a nonzero probability of transition. Next, we want to discuss T_2^{01} , which is the decoherence time between the initial and intermediate state.

Fig. 7.9 shows the interferogram when the dephasing time between the initial and the intermediate state varies from 0.1 fs to 1000 fs. The widths of the interferogram are reported in Table 7.4.

T_1^{01} (fs)	σ_g (fs)
0.1	142
15	142
30	147
90	150
1000	154

Table 7.4: Dephasing times and the relative interferogram widths.

We note that the changes in the width are small with respect to the width of the laser pulse. The overall effect is similar to the one observed for the depopulation time, i.e. there is a broadening of the linewidth of the envelope with the increase of the dephasing time. This is due to an increase in the coherence can induce a broadening of the interference fringes at larger time delays.

Next, we want to discuss T_2^{02} , which is the decoherence time between the initial and photoemission states through elastic scattering events. The presence of a coherence time is necessary to have a two-photon absorption. Fig. 7.10 (a) and (b) show that the interferogram calculated with $T_2^{02} = 1$ fs and $T_2^{02} = 1000$

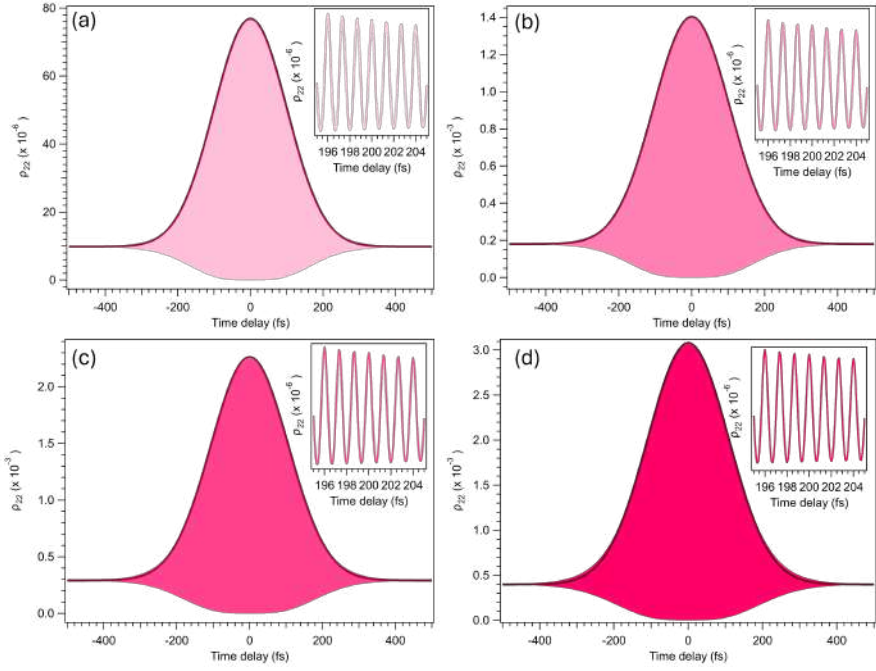


Figure 7.9: ρ_{22} as a function of the delay time with the value inserted in Table 7.2, with the following modification: (a) $T_2^{01} = 1$ fs, (b) $T_2^{01} = 30$ fs and (c) $T_2^{01} = 90$ fs and (d) $T_2^{01} = 1000$ fs .

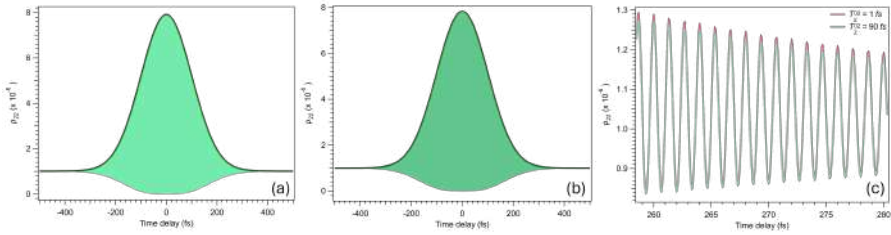


Figure 7.10: ρ_{22} as a function of the delay time with the value inserted in Table 7.2, with the following modification: (a) $T_2^{02} = 1$ fs and (b) $T_2^{02} = 1000$ fs. (c) Comparison between the two interferograms.

fs, respectively. The width of the two interferograms is equal to 142 fs, which is the same value as the reference case. This attests that the dephasing time between the initial and the photoelectron states does not change significantly

the shape of the interferogram. Moreover, the two interferograms oscillate with the same frequency.

The last parameter that we will explore is T_2^{12} , which is the decoherence time between the intermediate and photoelectron states through elastic scattering events. Fig. 7.11(a) shows the interferogram calculated with a $T_2^{12} = 30$ fs and

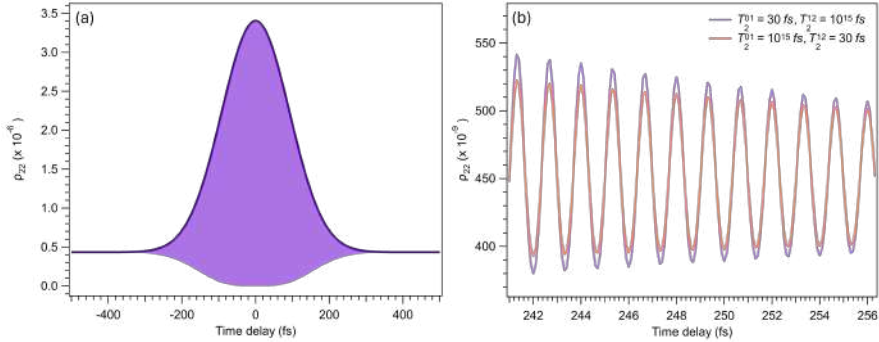


Figure 7.11: (a) ρ_{22} as a function of the delay time with the value inserted in Table 7.2, with the following modification: $T_2^{12} = 30$ fs and $T_2^{01} = 10^{17}$ fs. (c) comparison between (a) and the interferogram in Fig. 7.5 (a) .

$T_2^{01} = 10^{17}$ fs. Also in this case, the interferogram shape does not change by varying the dephasing time between the initial and the photoelectron states. Fig. 7.11(a) shows the comparison of the oscillation between the reference case in Fig. 7.5(a) and the interferogram inserted in Fig. 7.11(a). We note that they oscillate with the same frequency. In summary, through this methodical investigation, we have determined how the interferogram shape deforms in the non-perturbative regime and identified the conditions under which these deformations occur. Additionally, we observed that the dominant mechanism affecting the interferogram is the depopulation of the intermediate state. The effect of decoherence between the initial and intermediate states manifests similarly to the depopulation mechanism but with a lower intensity. The other two decoherence times do not influence the shape of the interferogram.

7.3 Preliminary results

Fig. 7.12 shows the set up for the inter-tr-2PPE. 795 nm pulses are generated by an amplified laser system composed of four components: (i) Coherent Mira 500, (ii) Coherent Verdi, (iii) Coherent Evolution and (iv) the amplifier. The output consists of photons with a 795-nm wavelength, a spectral width of 10

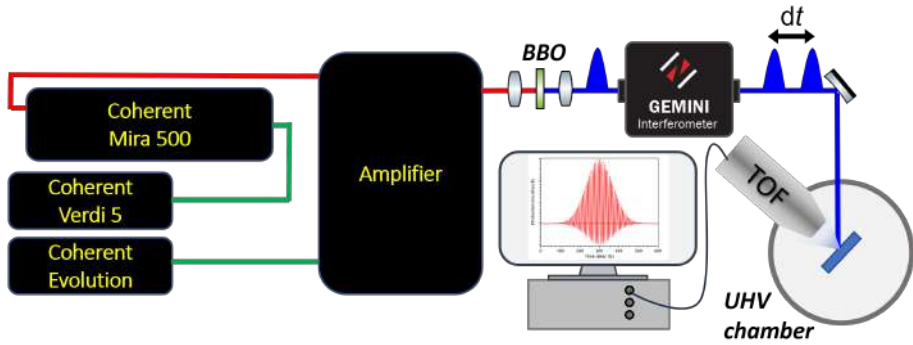


Figure 7.12: Picture of inter-tr-ARPES setup.

nm and a repetition rate of 1 kHz. The pulse duration is 150 fs. A BBO crystal is used to generate the second harmonic, resulting in a photon energy of 3.1 eV. The optical interferometer Gemini is employed to create two pulses with a defined phase difference. The delay between the two pulses is manipulated by changing the thickness of the birefringent medium placed in the beam path¹. The sample is placed inside an ultra-high vacuum chamber with a pressure of $5 \cdot 10^{-10}$ mbar. When the beam interacts with the sample, photoemitted electrons are produced and emitted in all directions. However, in our experiment, only electrons emitted in the direction normal to the surface of the sample were collected. The photoemitted electrons enter in a drift tube, where they travel without experiencing any external field. The detector used is a time-of-flight (TOF) detector, which calculates the electron energy based on the time it takes for the electrons to travel through the tube.

We chose to use Cu(111) as a test sample, which shows an energy gap and the photoemission spectrum is dominated by two features: the image potential state (IPS) and the surface Shockley state (SS). SS state is located at 0.420 eV below the Fermi energy, while the IPS is located at 0.81 eV below the vacuum as shown in Fig. 7.13(a). The work function for a Cu(111) sample is 4.95 eV[19]. Fig. 7.13(b) shows a photoemitted intensity as a function of the kinetic energy. There is the onset of the spectrum at zero kinetic energy, and the subsequent exponential decay is due to secondary electrons. Two structures can be distinguished: the first is due to the SS, and the edge at about 1.6 eV is the Fermi edge (FD), while the second one is due to the IPS. To estimate the energy position, the two peaks are fitted with a convolution between a Gaussian that represents the instrumental resolution and a response function.

¹A detailed description of the GEMINI interferometer is inserted in Appendix D.

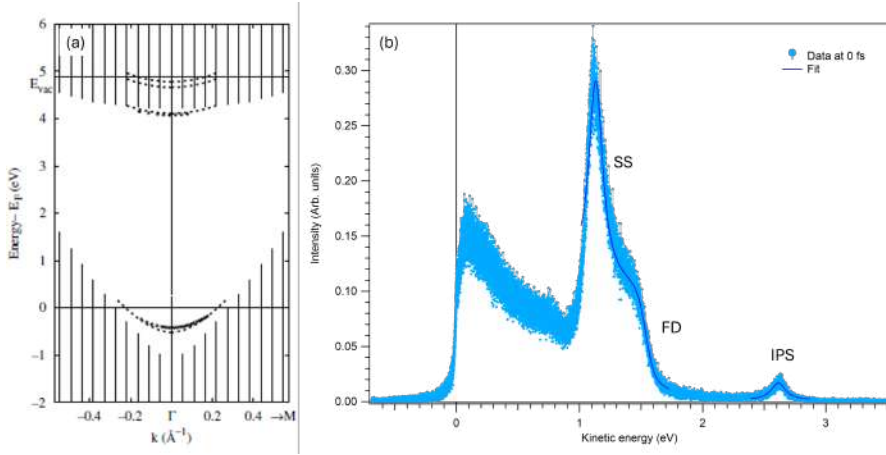


Figure 7.13: (a) Band structure for Cu(111). (b) Collected photoemission intensity as a function of the kinetic energy collected at $k_{||} = 0$.

The response function for the first peak is a sum between a Fermi-Dirac function and a Lorentian, while the response function for the second is a Lorentian. The retrieved positions are reported in Table 7.5. From the Fermi edge the work

E_{SS}	$(1.13 \pm 0.1) \text{ eV}$
E_{FD}	$(1.54 \pm 0.1) \text{ eV}$
E_{IPS}	$(2.61 \pm 0.1) \text{ eV}$

Table 7.5: Energetic position of the SS, FD and IPS.

function can be evaluated and it is equal to 4.7 eV, which is comparable with the literature value. The separation between the Fermi edge and the SS is $(0.41 \pm 0.05) \text{ eV}$, which is comparable to the value reported in [19]. To test the setup, we collected the output power from Gemini scanning the delay time between the two pulses, as shown in Fig. 7.14(a). The photoemission intensity of the pump shows a periodic oscillation with a Gaussian envelope. We cannot observe the frequency since the acquisition step is higher than the frequency of the photon energy, but we have characterized the interferogram with the Gaussian envelope. The evaluated width is $(130 \pm 50) \text{ fs}$. Then, we collected a series of photoemitted intensities as a function of the energy changing the delay time. We choose to collect the spectrum at selected delay corresponding at the maximum of the emission to track the envelope. The amplitudes of the SS and IPS structures are inserted in Fig. 7.14. The curves are a Gaussian shape, and to evaluate the resulting curves we fit them with a Gaussian function. The

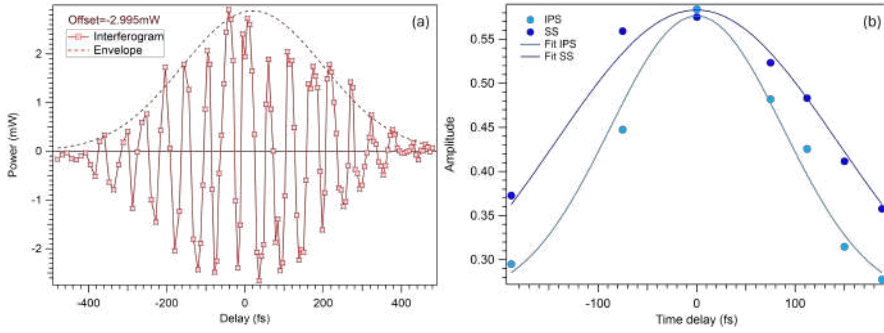


Figure 7.14: (a) Interferogram that describes the cross-correlation of the two pulses with their relative envelope. (b) Amplitude of the SS (blue markers) and IPS (light blue markers) peak as a function of the time delays.

extrapolated widths are (203 ± 50) fs and (124 ± 50) fs. for the SS and IPS, respectively. From the observation reported in Section 7.2, we can affirm that the decoherence and depopulation time are well below the cross-correlation between the two pulses, while the relaxation times in the SS state are longer than the IPS. In literature, is reported a pure dephasing time of 30 fs [190] and a total dephasing time of 17 fs [197].

7.4 Conclusion

In this chapter, we introduce the inter-tr-2PPE technique from both a theoretical and experimental point of view. To explore the effect of the decoherence and depopulation time on the interferometric pattern, we solved the OBE equation for a system of three levels that denote the photoemission process and an electric field composed of phase-locked pulses. In the perturbative regime, we observe that the shape of the interferogram does not change, while when we overcome the threshold for the perturbative regime, the width starts to decrease until the coherence is totally destroyed. We noted that the depopulation time of the intermediate state is the parameter that changes the interferogram shape more. T_2^{01} has a similar effect with a lower intensity. Eventually, T_2^{02} and T_2^{12} do not significantly affect the interferogram. From an experimental point of view, we have built the setup for the interferometric photoemission, and we collected some preliminary results. We collected the photoemission intensities for Cu(111). We found a difference in the width of the SS and IPS interferograms. Specifically, the IPS width is comparable with the cross-correlation of the two pulses, while the SS width is larger. Our idea is that the dephasing time for the IPS is much

lower than the cross-correlation, while the times of SS are comparable with them.

Chapter 8

Conclusion and outlook

This thesis explores three main topics of exciton physics in layered semiconductors: formation, coherence, and exciton-phonon coupling. A comprehensive investigation of these processes is needed to unveil the underlying physical phenomena employed in ultrafast devices and to isolate the physical quantities that affect the exciton dynamics. This is the first milestone towards the possible optical manipulation of semiconductors. The experimental work tools used to follow the exciton formation, dynamics, and interactions are: broadband transient reflectance spectroscopy and time-resolved angle-resolved photoemission spectroscopy. The combined employment of these two techniques gives a unique complementary characterization of exciton physics. Low-dimensional materials are ideal platforms for the fundamental investigation of excitons. The reduction in dimensionality produces an enhancement in exciton binding energy and oscillator strength, making excitons more stable and observable at room temperature. It also produces longer dephasing and depopulation times and stronger interaction between excitons and the other degrees of freedom of the system with respect to the three-dimensional counterpart. Additionally, excitons dominate the absorption spectrum in low-dimensional material, as well as their relaxation pathways under photoexcitation. In this work, we choose to study bismuth tri-iodide, which is a layered semiconductor known as a potential substitute to lead-based solar cells. BiI_3 shows a unique rich excitonic landscape, where the lowest bright exciton has a binding energy of 140 meV [21]. In the following section, we recall the main results of our work.

Chapter 4 is focused on the investigation of exciton formation by tr-ARPES. The non-resonant pumping is employed to produce a population of quasi-free

carriers in the conduction band. The subsequent relaxation dynamics of the photoemitted intensity pass through three resonances assigned to free carrier, free exciton and trapped exciton. The combination of a careful analysis of the electron dispersion curves and a detailed simulation of the ARPES signal in the BSE @GW-DFT framework allows us to shed light on the formation of the exciton level. The lowest resonance is due to trapped excitons, which are long-lived states created by trapping processes in lattice deformations. These long-lived states are interesting for application in photovoltaics. In the momentum domain, we managed to track a change in concavity from an electron-like dispersion, typical for the electron in the conduction band, to a hole-like dispersion, which is expected by conservation laws in photoemission as discussed in Section 2.1.5. The exciton characterization is completed with the evaluation of the extension of the excitonic wave function[188, 43]. This provides insight into the formation process and proof of the power of a joint experimental-theoretical approach in determining and discerning the underlying excitonic mechanism. Moreover, the observation of exciton resonance creation is important as a starting point for an in-depth study of the role of the electronic structure and of the other degrees of freedom in the creation of the exciton and possible manipulation of its dynamics.

The core topic of Chapter 5 is the exciton coherence. As discussed in Section 1.3.1, the preparation of this state is fundamental in the observation of the exciton coherence. Since coherence is easily destroyed by scattering processes with the phonons and with quasi-free carriers, a systematic study of the effects of experimental parameters on the optical response of BiI_3 is needed to isolate the coherent state. The exciton-phonon coupling dominates the temperature-induced shift in the exciton resonance as described by Equation 1.18. In the equation the exciton-phonon interaction is encoded in the Bose-Einstein statistical factor, which is related to the Debye temperature. Through temperature-dependent static reflection dynamics, we isolate the Debye temperature of BiI_3 . The thermally activated phonon population is drastically reduced when the temperature is below the Debye temperature, neglecting the scattering with phonons. The pump photon energy determines the photoinduced population in the system. Specifically, the electronic population is suppressed by resonant pumping, reducing the channel of scattering with the other quasi-free carrier in the system. The control of these experimental conditions allows us to observe a counterintuitive response of BiI_3 in the first few hundreds of femtoseconds in the transient reflectance measurements. This demonstrates the possibility of observing the coherent state by choosing the proper environmental conditions and constitutes the first step toward the manipulation of this state. From the characterization of the counterintuitive state, we found that the spectral manifestation of the coherent state is a blueshift and an increase in the oscillator strength of the exciton. Our results are corroborated by *ab initio*

DFT calculation, providing univocal fingerprints of the coherent state. The decoherence time was measured by tracking the coherent to incoherent crossover. This demonstrates the importance in preparing the coherent state and gives an insight on how the environmental condition influences the manifestation of the coherent state and decoherence dynamics.

Chapter 6 explores the exciton-phonon coupling in a layered semiconductor. As discussed in Section 1.3.2, a common theoretical-experimental description of the manifestation of the exciton phonon coupling is not achieved yet. By means of transient reflectance spectroscopy in non-resonant pumping, we identify the fingerprints for the exciton-phonon coupling. In the phonon response, a node in the coherent phonon amplitude and the π -shift in its phase at the exciton energy are the fingerprints of the exciton-phonon coupling. First principle simulations corroborate our results, providing for the first time a common description of the spectroscopic manifestation in transient optical spectroscopy. These findings are also supported by successive work [157]. Under photoexcitation, exciton resonance shows a periodic modulation with the frequency of the A_g phonon frequency and a redshift. The periodic modulation of the excitonic resonance describes how the exciton-phonon coupling influences the exciton relaxation dynamics. With a joint experimental-theoretical effort, we managed to connect the amplitude of exciton oscillation in energy to the atomic displacement in real space, which is of the order of a few pm. The manifestation of the exciton-phonon coupling also depends on the photoinduced dynamical screening. In fact, the exciton-phonon coupling manifestation changes with the suppression of the electronic population produced by a quasi-resonant excitation. In this situation, the unscreened exciton-exciton interaction is dominant, resulting in a slight blueshift of the exciton population and a periodic modulation in the exciton oscillator strength. This provides a description of how the manifestation of the exciton-phonon coupling can be manipulated by tuning the experimental conditions.

Chapter 7 is a preliminary introduction to the interferometric time-resolved two-photon photoemission (inter-tr-2PPE). In the initial description of the inter-tr-2PPE, a Michelson interferometer is exploited to create a pair of pulses with a well-defined phase [138]. After the interaction of the pulses with the sample, the photoemitted intensity is collected. The resulting photoemitted intensity as a function of the delay time between the two pulses has an interferogram shape. To understand the physical information encoded in the interferogram, we simulate the interferometric pattern by solving the optical Bloch equations for a three-level system interacting with two identical pulses. With a systematic investigation of the effect of the depopulation and the dephasing time on the shape of the interferometric pattern, we identify the main contribution is due to the depopulation time of the intermediate level, while the decoherence time

produces little changes in the interferograms. On the other hand, we built an inter-tr-2PPE setup employing an optical interferometer combined with a time-of-flight analyzer. As a case study we choose to use a Cu(111) single crystal. We compared the envelope of the interferogram associated with the image potential state and the surface state with the envelope of the interferogram generated by two pulses. We find that IPS, being comparable with the envelope of the pulses, has decoherence and depopulation time much faster than the pulse duration; this observation is not valid for the Shockley state. This constitutes a starting point for development and the commissioning of an inter-tr-2PPE spectroscopy, that can be exploited to directly achieve exciton coherence in inorganic and organic semiconductors.

In conclusion, this thesis explores the effects of interaction on exciton formation and relaxation in a layered semiconductor. Furthermore, it explores how the environment modifies their spectroscopic signatures. The acquired knowledge acts as a starting point in the possible optical manipulation of the exciton processes by means of an appropriate tuning of the environmental condition. The exploration of the effect of the interaction on the exciton dynamics and coherence in layered material can continue in several directions. Firstly, the excitonic resonance can be modulated by changing the semiconductor, i.e. substituting the halogen (i.e. with Br) or the metal (i.e. with Sb) or doping it with other atoms to tune the optoelectronic properties of the materials. This would provide a better understanding of the role of the exciton characteristic in coupling and coherence. Moreover, our approach can be applied to explore the coupling between the degrees of freedom in more complicated materials, such as in organic-inorganic interfaces or in magnetic material where a further center of scattering with magnons is present. Eventually, the results reported in this thesis is the starting point for the commissioning of a inter-tr-2PPE setup to achieve directly the coherence in photoemission which compared to the all-optical techniques allows a direct access to the population of excited carriers in the momentum space.

Appendix A

ARPES setup

A.0.1 Setup for the evaluation of the top of the conduction band

The generation of 10.8 eV photon energy starts with the output of a Coherent Monaco laser system [131]. This is a Yb-based fiber laser and emits pulses with a central wavelength of 1035 nm, a pulse duration of 290 fs, and a repetition rate of 1 MHz. The beam of the probe path is frequency-doubled. Then, the fundamental and the doubled beams interact in a BBO crystal to generate the third harmonic of the fundamental light by sum frequency generation. The beam is then focused in a chamber filled with Xenon gas where, through a four-wave mixing third harmonic generation process, the ninth harmonic at 10.8 eV is generated. The ultra-violet light hits the sample at 30° with respect to the normal emission. The sample faces the analyzer slit, and the photoemitted electrons are acquired with a SPECS Phoibos 225 hemispherical analyzer. The sample is mounted on a six-degrees-of-freedom cryo-manipulator. The overall energy resolution is 26 meV. The parallel momentum is calculated using the conservation laws for the photoemission process [39, 168, 209, 13] as described in chapter 2.

A.0.2 Setup for the evaluation of the out-of-equilibrium photoemitted intensity

The tr-ARPES setup exploits a femtosecond pulsed RegA laser system with a 250 kHz repetition rate, 300 fs pulse duration, and 800 nm central emission

wavelength. The RegA output is divided by a beam splitter into two beams. The first branch, using a pump, is doubled before entering the photoemission chamber. Through a composite quarter-wave plate and polarizer optical element, the polarization and the beam intensity can be tuned. The second part of the beam is used as a probe. We used the fourth harmonic generation to have a final photon energy of 6.2 eV. The beam is compressed with a pair of ultra-violet-fused silica prisms. A delay stage is inserted in the pump path to manipulate the pump-probe time delays. The beams enter the ultra-high-vacuum chamber from a window kept at 35° respect to the normal of the sample. The sample faces the analyzer slit, and the photoemitted electrons are acquired with SPECS Phoibos 225 hemispherical analyzer. The instrumental response function, defined as the cross-correlation between the pump and the probe measured at the sample position, is limited by the temporal duration of the pump pulse and results in 200 fs. To evaluate the energy resolution, we fitted the edge of a polycrystalline gold collected at room temperature. The edge has a Fermi-Dirac shape. We fitted it with a convolution with the Gaussian response function that represents the instrumental response. The resulting energy resolution is 50 meV. In our experiment, the absorbed fluence is $6 \mu\text{J cm}^{-2}$, since the spot size is $150 \mu\text{ m}$. The pump and the probe beams are linearly polarized. The sample is kept at 130 K and cleaved *in situ*.

Appendix B

Static experimental techniques

Spectrophotometer

The spectrophotometer used is the PerkinElmer Lambda 950 (Fig. B.1).



Figure B.1: Image of the PerkinElmer Lambda 950 spectrophotometer.

A spectrophotometer measures the absorbance of a sample at various wavelengths. This device can probe the UV/VIS/NIR spectral ranges (175-3300 nm) with a maximum resolution of 0.05 nm. Generally, a spectrophotometer is composed of a spectrometer that produces light at any wavelength and a photometer to measure the intensity of the light. In the spectrometer, there are two radiation sources, a deuterium lamp and a halogen lamp, to cover all the working wavelengths. Two monochromators are also used to select

the impinging wavelength. The sample is set between the spectrometer and the photometer. The photometer measures the amount of light that passes through the sample and delivers a voltage signal to the display. If the absorption of light changes, the voltage signal also changes. The detector used in this instrument is a Peltier-controlled PbS. This device permits collecting R (or T) from the intensity of the incident light and the reflected (or transmitted) as described above. The optical absorption is calculated from the transmittance $A = -\log_{10}T$. The spectrophotometer is equipped also with an integrating sphere, that allows us to collect the reflected and scattered light, simultaneously. However, by removing part of the white coverage of the integrating sphere part, it is possible to decouple the two contributions to the reflectance.

Fourier transform infrared spectroscopy

The FTIR spectroscopy is based on the Michelson interferometer principle. In this interferometer, the initial light source is divided into two branches using a beam splitter and then the two beams are reflected by two mirrors and recombined at the collector. One of the two mirrors is not fixed. Changing the difference in the path of the two beams an interferogram can be collected. The Fourier transformation of this interferogram retrieves the energy spectrum of the source. If the source is monochromatic the ft is usually a Gaussian located at the energy of the source and with a width that is related to the coherence length of the source. The spectrometer used is a Bruker Vertex V80, equipped with a tungsten lamp for the VIS/NIR generation (from 400 nm to 1666 nm) and a global lamp to cover the MIR/FIR region (from 1666 nm to 200 μm). The spectral resolution is up to 0.06 cm^{-1} . The setup works in two configurations: transmittance and reflectance. After the interaction of the light with the sample the light passes through an interferometer to reconstruct the interferometer path and the intensity is acquired with a photodetector (Si-based for VIS, Ingas for NIR, DLaTGS for MIR/FIR).

Raman spectroscopy

Raman spectroscopy is an optical technique based on the inelastic Raman scattering. It is used to determine the modes of molecular oscillations, such as vibrational and rotational modes.

The experimental setup is constituted by a continuous wave (CW) laser with energy $h\nu_i$ that, impinging on the surface of the sample, interacts with the atoms. The interaction between the light and the solid drives a transition from a vibrational state to a virtual or real state. Then, the electrons relax to a lower vibrational state, emitting light with energy $h\nu_e$. The result of light-

solid interaction is the scattering intensity, called Raman intensity, versus the Raman shift, which is proportional to the difference in the frequency between the incident photon and the emitted photon. The scheme for these types of transition is shown in Fig. B.2.

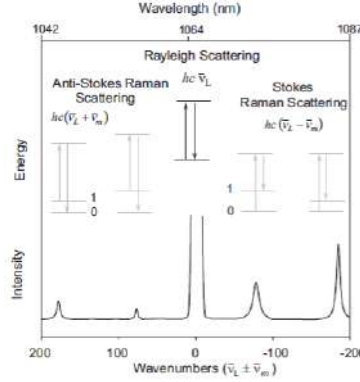


Figure B.2: Transition scheme for Raileigh, Stokes and Anti-Stokes scattering.

The interaction between the light and the sample results in polarization. To be detected, the Raman process has to change the polarization. The overall polarization has three contributions:

- the elastic one, called Rayleigh scattering, that is the most probable. The interaction with the sample leaves the frequency of the impinging light unchanged.
- the inelastic one, which could be divided into Stokes and anti-Stokes. The first corresponds to a decrease in the frequency of the emitting light. On the contrary, the latter corresponds to the enhancement of the frequency of the emitted light. Stoke peaks are usually more intense than the anti-Stokes since usually, the Raman process involves the ground state.

An example of the Raman spectra is shown in Fig. B.2. The central peak corresponds to the Rayleigh scattering. The Stokes and anti-Stokes peaks are symmetric to the zero, but they have different intensities. This is due to the different distributions of the population in the band, which follows the Boltzmann distribution. The interesting region of the Raman spectra is usually selected using either a Notch or an Edge filter.

The exciting continuous wave with wavelength λ has a momentum $\mathbf{k}$ equal to $\frac{2\pi}{\lambda}$, to compare with the first Brillouin zone associated with the crystal $\frac{2\pi}{\lambda}$,

where a is the lattice constant. The momentum of the exciting light is much lower than the one of the first Brillouin zone, so it can excite only phonons in a very small range around the Γ point (at $k=0$). So, only phonons at the center zone can be detected via Raman spectroscopy.

The device used for the microRaman measurements reported in this thesis work is the Renishaw Raman inVia (Fig. B.3). In this device, the Raman spectroscopy is combined with an optical microscope allowing us to perform measurements with a spatial resolution up to $1\mu\text{m}$. So, it can also extract morphological information.



Figure B.3: Image of the Renishaw Raman inVia.

The light emitted by a He-Ne laser at a 632.8 nm wavelength goes through a series of lenses and then impinges on the sample. The spot of the impinging light spans from $1\text{-}300\mu\text{m}$, and the grid $2400\text{ a }1/\text{mm}$ with resolution 0.5 cm^{-1} is used. The refracted, reflected and diffused light is collected and sent to a cooled Peltier CCD. The light, before reaching the CCD, goes through an edge filter and a diffraction grid. The setup is also equipped with a microscope to capture the images of the sample surface. It mounts four objectives: 5x, 20x, 50x and 100x. The numerical aperture associated and the angle of the cone are:

In our measurements, to prevent sample damage, we used 0.5% of the He-Ne

Objective	Numerical Aperture	Angle($^{\circ}$)
5x	0.12	11.5
20x	0.4	29
50x	0.75	97.2
100x	0.9	128.3

laser intensity.

The intensity of the laser on the sample is calculated as the ratio between the laser peak power (Watt) and the effective focal spot area (cm^2):

$$I = \frac{\text{laser peak power(W)}}{\text{effective focal spot area}(\text{cm}^2)} \tag{B.1}$$

The mean power of the He-Ne laser is 10 mW. The dimension(d_e) of the minimum focal spot is described by the following equation:

$$d_e = \frac{1.22 \cdot \lambda}{NA} \quad (B.2)$$

In our measurements, we used a 50x objective, so the effective focal spot area is:

$$A = \frac{\pi \cdot d_e^2}{4} = 8.31 \cdot 10^{-9} \text{cm}^2 \quad (B.3)$$

The resulting intensity is:

$$I = \frac{P}{A} = 1.2 \cdot 10^6 \frac{\text{W}}{\text{cm}^2} \quad (B.4)$$

Then the 0.5% of the total intensity is:

$$I(0.5\%) = 6 \cdot 10^3 \frac{\text{W}}{\text{cm}^2} \quad (B.5)$$

Appendix C

Characterization of the sample

In this section, we show the Raman spectra to have information on the frequency of the vibrational active modes. The new sample has never been cleaved, and it has been assembled just before the measurements.

Fig. C.1 (a) and (b) show the Raman spectra in the first few 300 cm^{-1} and at larger Raman shifts, respectively. The spectrum shows a sharp feature at $(114.72 \pm 0.06)\text{ cm}^{-1}$ Raman shift and a weak peak at $(228.6 \pm 0.3)\text{ cm}^{-1}$ Raman shift. The position of the first peak is in agreement with the literature [179, 158]. The peak at 114 cm^{-1} corresponds to the longitudinal optical phonon mode at Γ point of the Brillouin zone. This is assigned to the A_g vibrational

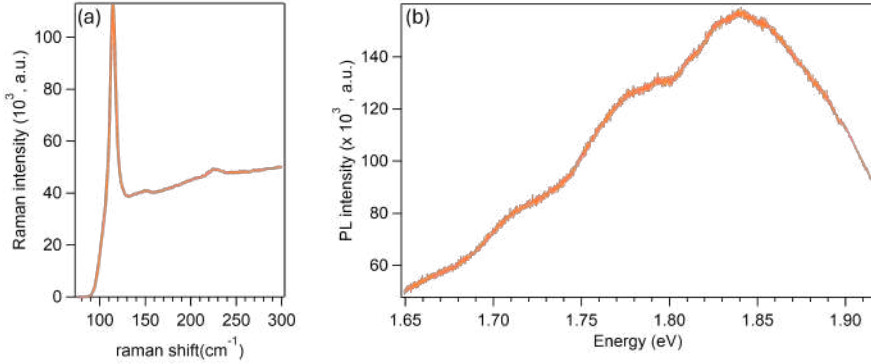


Figure C.1: (a) Raman spectrum of BiI_3 . (b) Photoluminescence of BiI_3 .

mode, which corresponds to a highly symmetric compression or stretching of the Bi-I bounds. We can assign the second peak to a second-order structure. In the long-range spectra in Fig. C.1(b), a broad band centred at 1250 cm^{-1} Raman shift is also present. This band could be ascribed to a luminescence process. In the following, we calculate the energy position of this band. The energy position of the peaks depends on the exciting source. In this case the source is a He-Ne laser emitting at a wavelength of 632.8 nm. The Raman shift (rs) is the difference between the wavenumber of the incident light (n_0) and the wavenumber of the emitted beam $\bar{\nu}$:

$$rs = n_0 - \bar{\nu} \quad (\text{C.1})$$

In the case of the He-Ne laser, the wavenumber is 15802.78 cm^{-1} . So, to calculate the wavenumber associated with the emitted beam $\bar{\nu}$, we use the following equation:

$$\bar{\nu} = n_0 - rs = (15802.78 - 1250) \text{ cm}^{-1} = 14552.78 \text{ cm}^{-1} \quad (\text{C.2})$$

So the resulting energy E is:

$$E = c \cdot h \cdot \bar{\nu} = 1.24 \cdot 10^{-4} \bar{\nu} = 1.8 \text{ eV} \quad (\text{C.3})$$

The resulting value is 1.80 eV, comparable to the direct band-gap, whose value is 1.96 eV.

Appendix D

The GEMINI interferometer

The GEMINI interferometer is an optical device that, by exploiting the interference between two replicas of the broadband input pulse, allows the detection of the differential reflectivity at fixed delay with a single photodiode. The GEMINI is based on the Translating Wedge based Identical pulses eNcoding System (TWINS) scheme presented in the work of Brida et al. ([16]).

TWINS is a simple optical device that generates two delayed, phase-locked collinear replicas of an input pulse. This device is inspired by the operating way of a Babinet-Soleil compensator. It is useful because it can work with a broad range of wavelengths (from UV and mid-IR) and with sub-10 fs pulses. This device exploits the properties of the birefringent media, where the ordinary and extraordinary components of the light travel with different group velocities (v_{go} e v_{ge}), accumulating a relative delay proportional to the propagation length. Our GEMINI device uses two pairs of wedges, as shown in the scheme in Fig. D.1.

The input pulse is polarized at 45° with respect to the x-axis before entering the GEMINI. The system frame is chosen, so the z-axis has the same direction of wave propagation, and it is shown in Figure D.1. The pulse then propagates along three building blocks made by the birefringent crystal BBO. Eventually, it passes through the final polarizer at 45° to ensure a final output with a linear polarization. We will briefly describe the three building blocks of the GEMINI. The first block (block A) is composed of a simple plate with the optical axis aligned along the y-direction and with a fixed thickness, d_a . The propagation of the light pulse across this plate generates two replicas of the initial pulse. The first is polarized along the x-axis, and the second is polarized along the y-direction. They experience a different refractive index as a result of

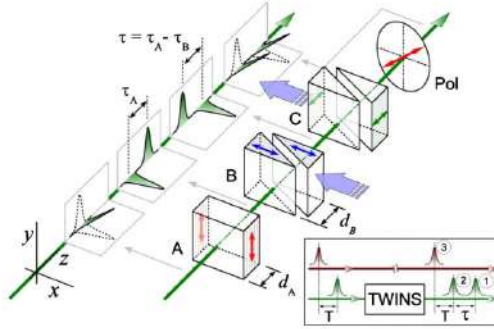


Figure D.1: Scheme of the TWINS system for the generation of phase-locked pulses([16]).

the different polarization. This results in a different group velocity, producing a delay between the two pulses proportional to the thickness of the plate. Then, the two replicas enter block B. Block B is composed of two wedges with a variable thickness, d_B , and the optical axis is aligned along the x-axis. After propagation across these two blocks, the relative delay (τ) between the two orthogonally polarized pulse replicas is:

$$\tau = (d_A - d_B) \delta_{eo} \quad (\text{D.1})$$

where δ_{eo} is the group velocity mismatch defined by:

$$\delta_{eo} = \frac{1}{v_{ge}} - \frac{1}{v_{go}} \quad (\text{D.2})$$

where v_{ge} e v_{go} are the group velocities of the extraordinary and ordinary polarized light. The delay (τ) can be controlled by fine-tuning the two wedges, i.e. changing the thickness that enters in the beam path. If its thickness is changed by an amount of Δd_B , then the delay is changed by $\Delta\tau = \Delta d_B \delta_{eo}$. Eventually, the beam enters the last block: block C. Block C is composed of a pair of wedges cut at the same angle as block B, with the optical axis aligned to the z-axis so that both replicas see the ordinary refractive index. The wedge of block C moves in the opposite direction of the one in block B. This ensures that the propagating beam passes through a fixed amount of BBO. This has two main assets:

- to maintain constant the absolute arrival time of one of the two replicas,

- to compensate for the first order for group delay dispersion (GDD) introduced by the varying thickness of block B, enabling the device to handle broadband pulses.

The changing in the wedge thickness only affects pulse 1 in the sequence, introducing a maximum GDD of $(GVD_e - GVD_o) \Delta d_B$ where GVD_e e GVD_o are the group velocity dispersions of the extraordinary and the ordinary polarization. The two replica pulses remain phase-locked and acquire a delay-dependent phase difference:

$$\Delta\phi = \omega_0 (\delta_{gpo} - \delta_{gpe}) \frac{\Delta\tau}{\delta_{eo}} \quad (\text{D.3})$$

ω_0 is the carrier frequency, $\delta_{gp} = \frac{1}{v_g} - \frac{1}{v_p}$ where v_p is the group velocity at the carrier frequency, δ_{eo} is the group velocity mismatch. The interferogram, resulting from the interference between the two replicas, represents the light transmitted through Gemini as a function of the position of the wedge in fixed delay τ . In conclusion, this device generates a pair of phase-locked pulses that can be used in the detection line in standard pump and probe experiments or can be a fundamental building block of more complex techniques such as two-dimensional electronic spectroscopy or interferometric time-resolved two-photon photoemission.

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List of publications

S. Mor, V. Gosetti, A. Molina-Sánchez, D. Sangalli, S. Achilli, V. F. Agekyan, P. Franceschini, C. Giannetti, L. Sangaletti, S. Pagliara Photoinduced modulation of the excitonic resonance via coupling with coherent phonons in a layered semiconductor *Phys. Rev. Research* **3**, 043175 (2021).

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V. Gosetti, J. Cervantes-Villanueva, S. Mor, D. Sangalli, A. Molina-Sánchez, W. Bronsch, F. Cilento, V. F. Agekyan, S. Pagliara Unveiling the exciton formation in time, energy and momentum domain in layered van der Waals semiconductors. *submitted*

FACOLTÀ DI SCIENZE MATEMATICHE, FISICHE E NATURALI
DIPARTIMENTO DI MATEMATICA E FISICA

Via della Garzetta 48
I-25133 Brescia
valentina.gosetti@unicatt.it



FACULTY OF ENGINEERING SCIENCE
DEPARTMENT OF MATERIAL ENGINEERING

Kasteelpark Arenberg 44
B-3001 Leuven
valentina.gosetti@kuleuven.be

