



ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

DEPARTMENT OF PHYSICS AND ASTRONOMY "A. RIGHI"

SECOND CYCLE DEGREE

PHYSICS

Investigation of X-Ray-Induced Effects in Hybrid and Organic Semiconductors by UV-Vis Photocurrent Spectroscopy

Supervisor
Prof. Andrea Ciavatti

Co-supervisor
Dr. Camilla Bordoni

Defended by
Laura Solieri

Graduation Session 23-24 / July / 2026

Academic Year 2025/2026

To the reader whose eyes will drift on these lines:

*Let Curiosity drive you,
Welcome the Unexpected,
Take nothing for granted.*

*And, remember,
a bit of rigor
and a GOOD LOGBOOK
are your best lab allies.*

Laura Solieri

Abstract

Investigating how ionizing radiation interacts with condensed matter is essential for developing next-generation radiation sensors and radiation-hard electronics. Traditional ex-situ degradation studies cannot capture real-time transient electronic processes during exposure, while existing in-situ approaches are mostly limited to fixed-wavelength probes. This thesis addresses this gap through the design and implementation of a compact apparatus enabling continuous UV-Vis photocurrent spectroscopy under simultaneous steady-state X-ray irradiation.

The project also involved upgrading a standard UV-Vis photocurrent spectroscopy setup, validated on a BA_2PbI_4 thin-film photoconductor. From its photocurrent spectrum, the responsivity profile was derived, and the energy gap and binding energy were extracted using a truncated 3D Elliott fit. This system was then used to acquire photocurrent spectra and responsivity profiles for all other investigated materials, providing a benchmark for co-irradiation sweeps in the new setup.

Under X-rays, the low-dimensional $\text{PEA}_2\text{PbBr}_4$ thin film showed notable radiation hardness and transparency, with no electrical changes. Conversely, the $\text{PEA}_2\text{PbBr}_4$ single crystal exhibited a strong enhancement and broadening of its excitonic features. For the 3D vertical MAPbBr_3 single crystal, simultaneous X-ray exposure induced a marked increase in the excitonic peak accompanied by complete quenching of the continuum photocurrent, likely driven by enhanced exciton-phonon coupling due to radiation-induced bromine vacancies. Finally, the organic TIPS-PEN thin-film photoconductor displayed a fully reversible enhancement of its vibronic peaks within a 17-hour recovery window, along with a reproducible blueshift of the energy gap extracted from modified Tauc plots. The absence of continuum quenching in both TIPS-PEN and the $\text{PEA}_2\text{PbBr}_4$ single crystal suggests that X-ray-induced defects in these systems do not act as dominant recombination centres for excitons.

Contents

Abstract	ii
List of Abbreviations	v
List of Figures	vi
List of Tables	ix
Introduction	1
1 Theoretical Background	3
1.1 Inorganic-organic Hybrid Halide Perovskites	3
1.1.1 3D Hybrid Halide Perovskites	4
1.1.2 Low-dimensional Hybrid Halide Perovskites	5
1.2 Organic Semiconductors	7
1.3 Radiation-Matter Interaction	8
1.3.1 UV-Vis Irradiation	9
1.3.2 X-rays Irradiation	11
1.4 Photodetectors	12
1.4.1 Detectors for UV-Vis Photons	13
1.4.2 Detectors for X-rays Photons	14
2 Experimental Apparatus	16
2.1 UV-Vis Photocurrent Spectroscopy	16
2.1.1 Light Source	18
2.1.2 Monochromator	19
2.1.3 Chopper and Lock-in Amplifier	23
2.1.4 Detectors	25
2.1.5 Sample Bias	27
2.2 UV-Vis Spectroscopy Under X-ray Irradiation	29
2.2.1 X-rays Source	29
2.2.2 Optical Fibre	31
2.2.3 Operation	32

3	Setup and Calibration of the Photocurrent Measurement System	33
3.1	Focusing and Alignment	34
3.1.1	Focusing the Light Beam in ScienceTech-9055F	34
3.1.2	Aligning Mirrors and Verifying Gratings in SpectraPro-150	35
3.1.3	Directing The X-rays Beam	36
3.2	Acquisition Software	37
3.3	UV-Vis Sources Calibration	39
3.3.1	QTH Lamp	40
3.3.2	Xenon Lamp	42
3.4	Lock-in Noise Analysis	43
3.5	Samples Specifications	43
3.6	Data Analysis	47
4	Results and Discussion	50
4.1	BA_2PbI_4	51
4.2	$\text{PEA}_2\text{PbBr}_4$	53
4.3	MAPbBr_3	58
4.4	TIPS-PEN	62
	Conclusions	67
	Acknowledgements	69
A	Supplementary Graphs	71
B	Interpolation of SiPD Responsivity Curve	76
C	Alternatives to Tauc plots for TIPS-PEN	77
	Bibliography	79
	Index	85

List of Abbreviations

EMR	Electromagnetic Radiation
EQE	External Quantum Efficiency
GUI	Graphical User Interface
HOMO	Highest Occupied Molecular Orbital
IOHP	Inorganic-Organic Hybrid Perovskite
LoD	Limit of Detection
LUMO	Lowest Unoccupied Molecular Orbital
MQW	Multi-Quantum Well
OSC	Organic Semiconductor
PSD	Phase-Sensitive Detection
PYRO	Pyroelectric
QTH	Quartz-Tungsten-Halogen
RD	Ruddlesden-Popper
SiPD	Silicon Photodiode
VdW	Van der Waals
XRDET	X-rays Detector

List of Figures

1.1	Ideal perovskite cubic structure	4
1.2	Scheme of n-dimensional perovskites	5
1.3	Types of 2D hybrid perovskites	6
1.4	Scheme of σ - and π -bonds in a carbon-based chain	7
1.5	Diagram of the electromagnetic spectrum	8
1.6	Plot of optical processes in a typical semiconductor	9
1.7	Diagram of exciton states	10
1.8	Chart of ionizing radiation-matter interactions	12
1.9	Scheme of photoconductor geometries	13
2.1	Schematics of the standard setup	16
2.2	Optical layout outside the monochromator in the standard setup	17
2.3	QTH lamp scheme	18
2.4	Xenon arc lamp scheme	19
2.5	Typical spectra of QTH and of Xenon lamps	19
2.6	Basic monochromator scheme	20
2.7	Scheme of light interacting with a diffraction grating	20
2.8	Linespread graphs resulting from monochromator slits width choice	22
2.9	Functional diagram of SR830 lock-in amplifier	23
2.10	Responsivity curve of Si photodiode as a function of the wavelength	26
2.11	Responsivity curve of pyroelectric detector as a function of frequency	26
2.12	FEMTO DLPVA-100 voltage amplifier	27
2.13	Schematics of the electrical circuit in the standard setup	27
2.14	Scheme of sample connection modes	28
2.15	FEMTO transimpedance amplifiers	28
2.16	Schematics of the compact setup	29
2.17	Typical spectrum of a Molybdenum target X-ray tube	30
2.18	X-rays tube calibration	30
2.19	Monochromator-sample optical coupling in the compact setup	31
2.20	Effects of collimators on the lamp spectrum	32
3.1	Evolution of the benchmark photocurrent setup design	33
3.2	Picture of the compact setup	34
3.3	Scheme of multiple diffractions inside SP150 monochromator	35
3.4	Spectral analysis of SP-150 monochromator	36
3.5	Screenshot of SP150-SR830 Control main panel	37

3.6	Screenshot of SP150-SR830 Control manual/aux tab	38
3.7	Effective area of detection given the slit width	39
3.8	QTH raw spectra	40
3.9	QTH lamp flux	41
3.10	Powermeter verification of QTH lamp power density	41
3.11	Xenon lamp raw spectra	42
3.12	Xenon lamp flux	42
3.13	Lock-in noise analysis	43
3.14	Diagram of the 1-pixel interdigitated electrodes	44
3.15	Scheme of PEA2PbBr ₄ single-crystal structure	45
3.16	Scheme of MAPbBr ₃ sample structure	45
3.17	PEA2PbBr ₄ samples pictures	46
3.18	Picture of a TIPS-PEN sample	46
3.19	Data analysis flowchart	47
4.1	BA2PbI ₄ photocurrent spectrum	51
4.2	BA2PbI ₄ spectral response	52
4.3	Elliott fit on BA2PbI ₄	52
4.4	PEA2PbBr ₄ samples I-V characteristics	53
4.5	Comparison of PEA2PbBr ₄ samples photocurrent spectra	54
4.6	PEA2PbBr ₄ samples responsivity profiles	55
4.7	PEA2PbBr ₄ samples Elliott fit	55
4.8	Effects of X-rays on PEA2PbBr ₄ samples photocurrent spectra	56
4.9	Elliott fit on PEA2PbBr ₄ spectra acquired with the compact setup	57
4.10	MAPbBr ₃ I-V characteristics	58
4.11	MAPbBr ₃ photocurrent spectrum	59
4.12	MAPbBr ₃ spectral responsivity	60
4.13	MAPbBr ₃ Elliott fit	60
4.14	Effects of X-rays on MAPbBr ₃ spectrum	61
4.15	Elliott fit on MAPbBr ₃ spectra acquired with the compact setup	61
4.16	TIPS-PEN I-V characteristics	63
4.17	TIPS-PEN photocurrent spectrum	63
4.18	TIPS-PEN spectral responsivity	64
4.19	TIPS-PEN Tauc plot	64
4.20	TIPS-PEN X-rays spectra comparisons	65
4.21	Tauc fit on TIPS-PEN spectra acquired with the compact setup	66
A.1	Xenon lamp raw spectra in linear scale	71
A.2	BA2PbI ₄ raw photocurrent spectrum	71
A.3	PEA2PbBr ₄ samples raw photocurrent spectra	72
A.4	MAPbBr ₃ raw photocurrent spectrum	72

A.5	TIPS-PEN raw photocurrent spectrum	72
A.6	PEA2PbBr ₄ samples I-V characteristics (linear scale)	73
A.7	MAPbBr ₃ I-V characteristics (linear scale)	73
A.8	TIPS-PEN I-V characteristics (linear scale)	74
A.9	Effects of X-rays on PEA2PbBr ₄ samples photocurrent spectra (raw signal)	74
A.10	Effects of X-rays on MAPbBr ₃ photocurrent spectra (raw signal).	75
A.11	Effects of X-rays on TIPS-PEN photocurrent spectra (raw signal).	75
C.1	TIPS-PEN Spano fit	77
C.2	Spano fit on TIPS-PEN spectra acquired with the compact setup	78

List of Tables

2.1	Lock-in bandwidth and dwell time	25
3.1	Samples overview	44
4.1	Acquisition parameters and settings in the standard setup	50
4.2	Acquisition parameters and settings in the compact setup	50
4.3	BA2PbI4 Results	53
4.4	PEA2PbBr4 Results	58
4.5	MAPbBr3 Results	62
4.6	TIPS-PEN Results	66

Introduction

The primary objective of this thesis project is to study in-situ the effects of X-rays irradiation on organic and hybrid semiconductors. Traditionally, the macroscopic and microscopic degradation of optoelectronic properties under high-energy radiation is evaluated ex-situ, comparing device metrics before and after exposure. However, this static methodology cannot track real-time electronic processes—such as transient charge trapping, defect generation kinetics, and structural relaxation—occurring during active exposure. To capture these underlying physical phenomena, in-situ configurations are required. Existing configurations under X-ray irradiation are mostly limited to monitoring the total X-ray-induced current (radiocurrent) or performing optical analyses at fixed, single wavelengths. This thesis addresses this literature gap by designing and constructing an integrated apparatus for continuous UV-Vis photocurrent spectroscopy under simultaneous, steady-state X-ray irradiation, explicitly mapping the radiation-matter interaction. Instead of fixed-wavelength probes, this instrumentation sweeps the UV-Vis spectrum while the material is subjected to a calibrated, fixed X-ray dose.

To achieve this goal, the project was structured into two operational phases. The first phase involved the physical restoration, upgrade, and optimization of an existing, standard UV-Vis photocurrent apparatus. This stand-alone setup was utilized to establish reliable experimental protocols, extract baseline parameters, and acquire reference photocurrent spectra and spectral responsivity profiles. In the second phase, an innovative compact setup was designed, mechanically assembled and optimized to perform measurements inside an X-ray enclosure. To ensure robust instrumentation control and reliable data acquisition, a custom, two-threaded automation software featuring a Graphical User Interface (GUI) was developed in Python utilizing PyVISA, PyQt6, and GPIB communication protocols to handle automated wavelength sweeps. This combined apparatus was then deployed to probe the real-time modulation of photoelectrical properties across four different photoconductor samples.

The manuscript is structured into four main chapters and three appendices, organized as follows:

- **Chapter 1** provides a comprehensive theoretical background on Inorganic-Organic Hybrid Perovskites and Organic Semiconductors, on radiation-matter interactions under UV-Vis and X-ray photons, and on electromagnetic radiation detectors.
- **Chapter 2** details the architectural layout of the two experimental apparatuses used in this work. It describes the individual components comprising the standard UV-Vis photocurrent spectroscopy setup and outlines the design, X-ray source in-

tegration, and operational modes of the newly constructed co-irradiation compact setup.

- **Chapter 3** focuses on the hardware optimization, calibration routines, and mathematical methodologies developed for the setups. It covers the physical alignment of mirrors and gratings within the monochromators, the tracking of the X-ray beam, the logic of the custom Python acquisition software, the spectral flux calibration of the lamps, lock-in noise analysis, and the physical specifications of the analysed samples alongside the data analysis frameworks.
- **Chapter 4** presents and discusses the experimental results collected with both setups. It traces the baseline verification using the reference BA_2PbI_4 lateral photoconductor and compares the distinct photoelectrical and excitonic modifications observed under active X-ray exposure for the $\text{PEA}_2\text{PbBr}_4$, MAPbBr_3 , and TIPS-PEN samples.
- **Appendices A, B, and C** provide supplementary experimental graphs, the interpolation workflow for the Silicon Photodiode responsivity curve, and alternative analytical methods to the standard Tauc plots for interpreting the TIPS-PEN spectra.

The main achievements and physical insights derived from this work are summarized in the Conclusions.

1. Theoretical Background

Semiconductors are at the base of today's electronic technologies. Since the days of the first diodes, transistors and chips, material as silicon and germanium have played a fundamental role in the development and mass production of electronic devices.

Along with their doped forms and alloys, these materials are still widely employed, since they possess relatively good transport properties, their manufacturing methods are well-established and they are quite durable; yet, the poor sustainability of production processes, the sometimes problematic access to the raw material sources and the new requests for flexible, large area and even bio-compatible semiconductors have underlined the need to search for alternative materials.

In the last two decades, the research on two novel functional materials emerged [1]: inorganic-organic hybrid perovskites and organic semiconductors.

1.1 Inorganic-organic Hybrid Halide Perovskites

Perovskites are a class of materials with characteristic crystal structure ABX_3 , where A is a monovalent cation (metallic in the case of inorganic perovskites), B a divalent metallic cation and X an anion (typically an halogen, even if the name "perovskite" originally referred to $CaTiO_3$ [2]). The atoms involved are arranged in a cubic structure with the A cation at the centre and the BX_3 octahedra at the corners, as can be seen in Fig. 1.1.

The interatomic distances d and atomic sizes r must respect very tight criteria for this particular structure to exist in a stable form:

$$\begin{aligned} d_{BX} &= a/2 \\ d_{AX} &= \sqrt{a}/2 \\ \sim 0.75 < t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)} &\leq 1 \end{aligned} \tag{1.1}$$

where a is the unit cell length, and t is Goldschmidt's tolerance factor[2].

This factor can be easily altered by external agents such as light, oxygen, moisture and applied bias, leading to unwanted structural modifications. Other than from the structural point of view, stability is a central issue in perovskite research: material degradation can stem from processes such as ion migration, which is due to the weak bonds between the A -site cation and the BX_3 octahedra and can cause the formation and migration of vacancies, interstitials and anti-site defects ultimately leading to increased

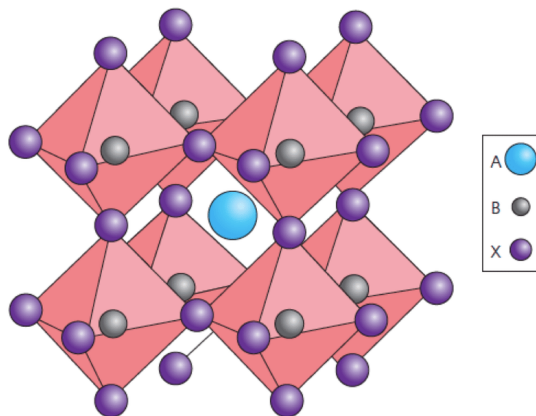


Figure 1.1: Ideal perovskite cubic structure. The monovalent cation sits at the centre, surrounded by eight octahedra with shared anions at the vertices and the divalent cation at their core. The image is adapted from [3].

hysteresis, slow photoconductive response and performance reduction[2]. These issues can partially be addressed by acting on the composition and dimensionality of the material – strategies which allow also to achieve tunable bandgaps, strong light absorption, high carrier mobility and increased resistance to defects, making them very versatile semiconductors.

The most used type of perovskite in optoelectronic application are metal halide perovskites but, in recent years, research has moved also in the direction of inorganic-organic hybrid perovskites (IOHPs, often referred to as just hybrid perovskites), which are obtained by replacing the monovalent metallic cations with organic ones.

1.1.1 3D Hybrid Halide Perovskites

This class of hybrid perovskites follows the ABX_3 crystal structure, in which A is an organic cation, such as methylammonium ($CH_3NH_3^+$, MA^+), while B is a metallic cation (typically Pb_2^+ , Sn_2^+) and X an halide anion (I^- , Br^- , Cl^-).

Pb -based IOHPs are by far the most employed, since lead yields the most stable configurations, however, its toxicity is encouraging research to substitute it¹.

The electronic properties of perovskites are primarily dependent on the metallic cation and on the halide atom, while the A -site cation contributes mainly indirectly, through its size [2]. The bandgap of IOHPs is generally direct [1] – which implies that no energy gets dissipated in phononic transitions during absorption and emission processes – and

¹Common replacements include Sn or Ge , which maintain the structure unaltered, Bi or Sb , for which the structure must change to $A_3B_2X_9$ or even double-atom configurations, in which lead is substituted by a monovalent and a trivalent metallic cation[4].

increases as the atomic weight of the halide anion decreases [2].

Along with energy gap tunability, 3D lead-based IOHPs exhibit excellent carrier mobility and lifetime – of the order of tens of $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and of few hundreds of ns, respectively – and high optical absorption, with absorption coefficients in the range $[10^3\text{-}10^5] \text{ cm}^{-1}$ near the band edge [5–7]. In high quality films and crystals, the carrier diffusion length can reach up to $10\mu\text{m}$ [7, 8]. All these properties have allowed IOHPs to obtain outstanding results in photovoltaics – with power conversions efficiencies above 20% – and to find applications also in LEDs, lasers and photodetectors [6].

1.1.2 Low-dimensional Hybrid Halide Perovskites

By increasing the size of the monovalent cation² and going through appropriate phase transitions, it is possible to engineer perovskite structures with lower dimensionality (2D, 1D, 0D). Fig. 1.2 shows a schematic diagram of IOHPs from the 0D to the 3D type. Low dimensional perovskites exist in several possible configurations and structures[2].

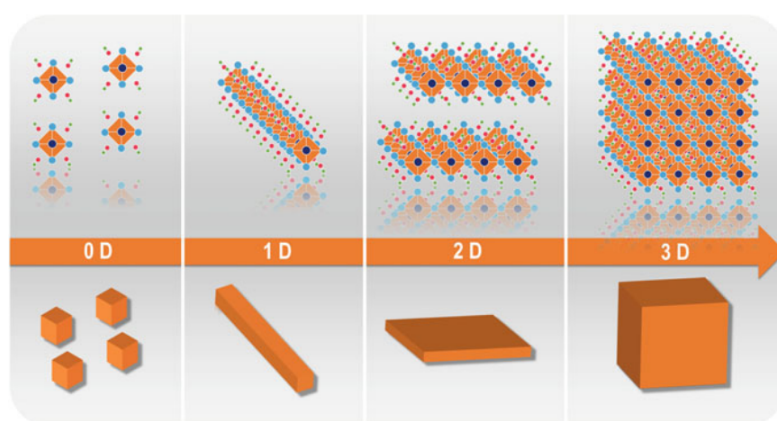


Figure 1.2: Scheme of n -dimensional perovskites. The image is adapted from [2].

In this work, the focus will be on 2D IOHPs of the Ruddlesden-Popper (RD) type [7, 9]. This class of 2D hybrid perovskites follows the formula A_2BX_4 , in which the monovalent organic cation is constituted by molecules such as butylammonium ($C_4H_9NH_3^+$, BA^+) or phenethylammonium ($C_6H_5CH_2CH_2NH_3^+$, PEA^+). The crystal comes in the form of alternating organic and inorganic layers, with covalent planar intra-layer bonds and only weak Van der Waals (VdW) forces established among adjacent layers (see Fig. 1.3a).

²It is interesting to notice that, as the size of the monovalent cation increases, it becomes also easier to incorporate in it several functional chemical groups, enhancing the material stability or granting it new properties [2].

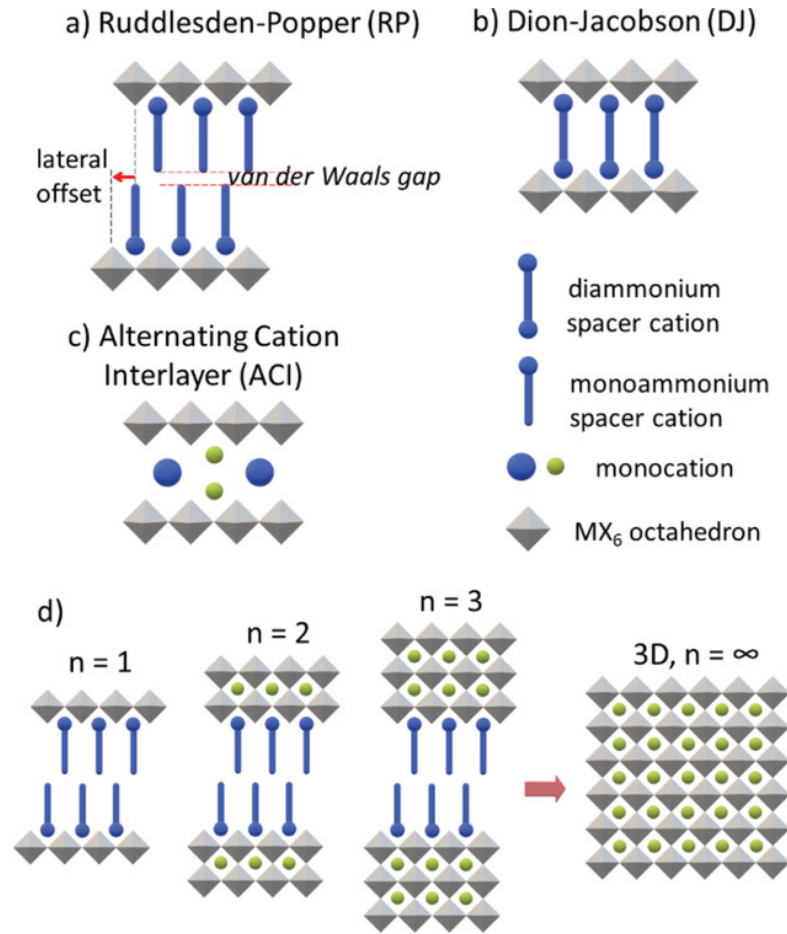


Figure 1.3: Types of 2D hybrid perovskites. Ruddlesden-Popper IOHPs are the most common 2D structure (a), followed by Dion-Jones (b) and Alternating-Cation-Interlayer ones (c). In (d) n -layered RP IOHPs are shown as compared to their 3D counterpart [10].

This arrangement gives naturally rise to a multi-quantum well (MQW) structure, which induces quantum confinement and dielectric confinement effects [11]. As a consequence, the material comes to display higher exciton binding energies than its 3D counterpart, resulting in a reduction of the charge carriers lifetime and diffusion length – down to half ns and few μm [7]. Moreover, the mobility is highly anisotropic, since charge transport is more favoured within the layers of metal halide octahedra (in-plane) than across the organic layers (out-of-plane)[10]. Despite their poorer electrical properties, 2D RP hybrid perovskites are widely studied since they offer increased structural flexibility and environmental stability [7].

1.2 Organic Semiconductors

Carbon is at the base of organic semiconductors (OSCs). Its versatility derives from its capability to form stable bonds via orbital hybridization. In carbon-based rings and long chains, $2s$ - $2p$ hybrid orbitals (sp , sp^2 , sp^3) form σ -bonds whereas adjacent $2p$ orbitals not involved in the hybridization overlap creating π -bonds (Fig. 1.4).

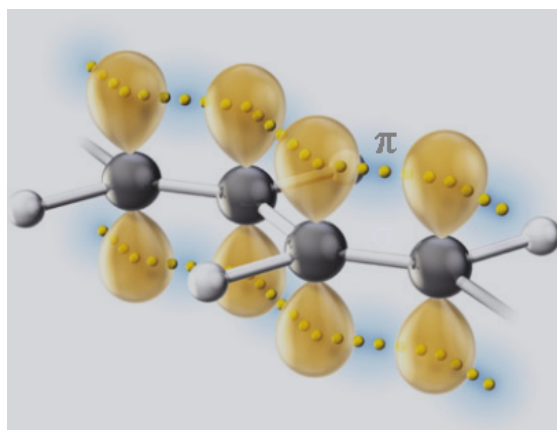


Figure 1.4: Scheme of σ - and π -bonds in a carbon-based chain. The image is adapted from [12].

Electrons in π -bonds are highly delocalized and can effectively contribute to charge transport. Moreover, when many organic molecules are gathered to form a crystal, it becomes possible to distinguish the equivalent of inorganic materials' conduction and valence band: the first created by the Lowest Unoccupied Molecular Orbitals (LUMOs) and the second by the Highest Occupied Molecular Orbitals (HOMOs) of the molecules[1, 12]. The energy gap of organic crystals lies in the range from 1 to 5 eV; they are normally undoped, and have no free charge carriers while at room temperature, resulting in a low dark current [13].

As in IOHPs, the bandgap is largely tunable via modification of the chemical composition. The organic compounds involved range from small molecules to aromatic structures, oligomers and polymers. This variability contributes to the difficulties to find comprehensive theories for transport properties in OSCs. The developed models include: hopping, band transport, polaron transport, multiple trapping and release and gaussian disorder [13].

Compared to their inorganic counterparts, OSCs exhibit lower electrical transport capabilities, with mobilities in the range of 10^{-6} to $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [13]. However, this class of semiconductors offers the possibility to develop lightweight, flexible and cost-effective devices; their growth does not require high temperatures and can be controlled by conventional wet chemistry methods[12–14].

Besides their lower performances, major challenges when working with organic mate-

rials are stability and degradation – as they are prone to degradation by oxygen, moisture, and UV light – and process reproducibility, since batch-to-batch variability and sensitivity to processing conditions impact device consistency[13].

1.3 Radiation-Matter Interaction

Either one's been dealing with material characterization or with shielding, harvesting or detection of radiation, it is fundamental to have some basics on the interaction between matter and electromagnetic radiation (Fig. 1.5).

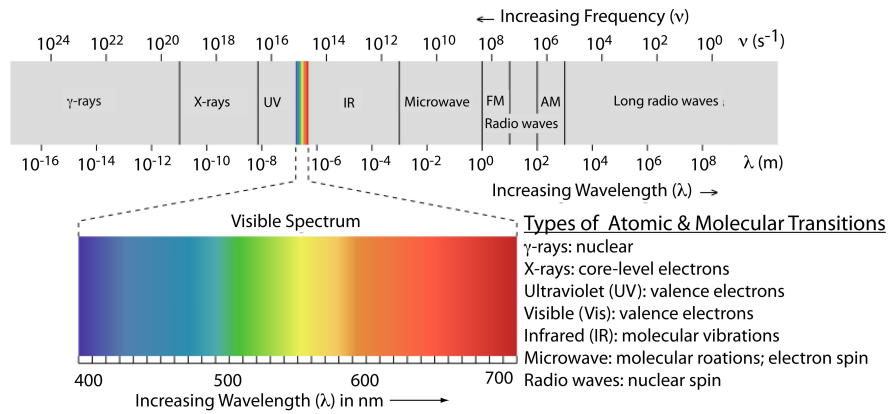


Figure 1.5: Diagram of the electromagnetic spectrum, alongside with a list of typical atomic and molecular transitions in matter for each spectrum range. The image is adapted from [15].

The effects of interaction between photons and matter vary dramatically with the type of material and with the energy of the photons, which depends on their wavelength λ (or, alternatively, frequency ν) as:

$$E_{ph} = h\nu = \frac{hc}{\lambda} \quad (1.2)$$

with h Planck constant and c light speed in vacuum.

When photons hit the surface of a material, they are always able to travel inside by a certain amount, which is referred to as penetration depth[16]. In Fig. 1.6, the main processes induced by electromagnetic radiation in a typical semiconductor material are presented. For the purpose of this thesis, the focus will be on UV-Vis and on X-rays photons.

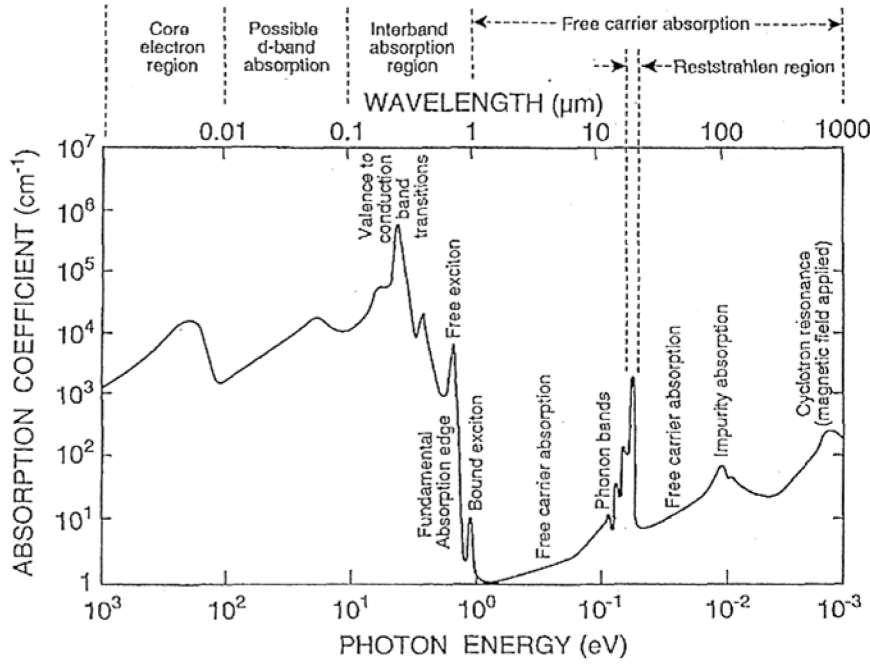


Figure 1.6: Graph of the absorption coefficient as a function of the impinging photon energy, featuring the main optical processes in a typical semiconductor [17].

1.3.1 UV-Vis Irradiation

On average, UV-Vis radiation can penetrate matter up to a distance of 50-300 nm.

The flux of photons at a given depth x is defined by Beer's law:

$$\Phi(x) = \Phi_0 e^{-\alpha(\lambda)x} \quad (1.3)$$

with $\alpha(\lambda)$ absorption coefficient of the material.

As shown in Fig. 1.6, α depends on the wavelength and, in the UV-Vis range, its behaviour is linked to three main features (listed below in order of increasing photons energy):

- bound excitons;
- free excitons;
- fundamental absorption edge.

Excitons are quasiparticles constituted by electron-hole pairs which have come to form hydrogen-like states due to mutual coulombic interaction [18, 19]. Excitons can travel in the lattice (free excitons) or be localized in trap states (bound excitons). Light promotes the formation of these electron-holes pairs, giving rise to the so-called excitonic peaks in

the absorption spectrum. These peaks are located near and below the band edge, since the additional energy levels provided by the excitons (Fig. 1.7) enable optical transitions also below E_g [19, 20].

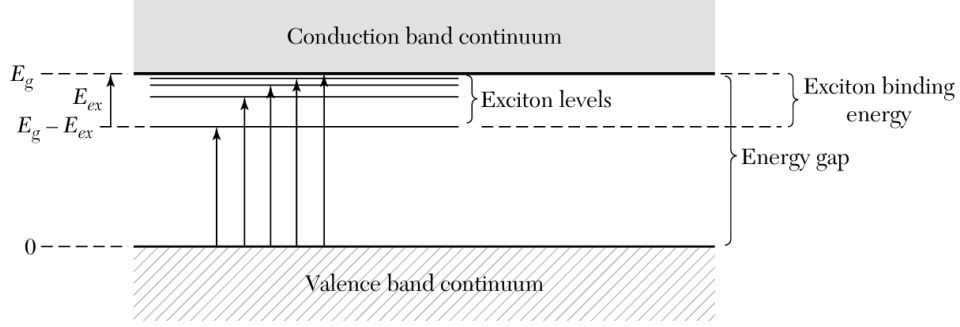


Figure 1.7: Diagram of exciton states. As n increases, the levels get closer to each other and rise towards the conduction band, ultimately merging into the continuum [19].

The fundamental absorption edge marks the transition between the region of transparency and opacity of the material to the incoming radiation: as soon as the photon energy becomes larger than the energy bandgap ($E_{ph} \geq E_g$) the light is absorbed and electrons consequently acquire enough energy to jump from the valence to the conduction band.

A simple way to obtain information on the material bandgap energy is to use Tauc plots, which are based on the assumption that the absorption coefficient can be expressed as

$$(\alpha \cdot E_{ph})^{1/\gamma} = B(E_{ph} - E_g) \quad (1.4)$$

where B is a constant while γ is a factor equal to $1/2$ in the case of direct-band transitions and to 2 for indirect-band transitions. The data are plotted so that Eq. (1.4) can be directly applied as a linear fit on the absorption edge. An estimate of the energy gap is obtained at the intersection between the x-axis and the fitting line [21].

For excitonic materials, the absorption curve in the UV-Vis range can be modelled through the Elliott formula [22–24], a more complete model, which is commonly used to fit the experimental data and extract, in addition to the energy gap, the exciton binding energy. This latter is defined as:

$$E_b = E_g - E_{opt} \quad (1.5)$$

where E_{opt} is the energy of the optical gap, i.e. the energy sufficient to generate an exciton, while E_g is the energy of the electronic gap, i.e. the energy necessary to separate the bound exciton state and get the electron to contribute to the current in the conduction band.

The basic structure of the Elliott formula is:

$$\alpha(E) = \alpha_{exciton}(E) + \alpha_{continuum}(E) \quad (1.6)$$

which, for 3D semiconductors, becomes:

$$\alpha(\omega) = \alpha_0^{3d} \frac{\hbar\omega}{E_0} \left[\sum_{n=1}^{\infty} \frac{4\pi}{n^3} \delta\left(\Delta + \frac{1}{n^2}\right) + \Theta(\Delta) \frac{\pi e^{\pi/\sqrt{\Delta}}}{\sinh(\pi/\sqrt{\Delta})} \right] \quad (1.7)$$

while, for 2D semiconductors:

$$\alpha(\omega) = \alpha_0^{2d} \frac{\hbar\omega}{E_0} \left[\sum_{n=0}^{\infty} \frac{4}{(n + 1/2)^3} \delta\left(\Delta + \frac{1}{(n + 1/2)^2}\right) + \Theta(\Delta) \frac{e^{\pi/\sqrt{\Delta}}}{\cosh(\pi/\sqrt{\Delta})} \right] \quad (1.8)$$

In Eq. (1.7) and Eq. (1.8), $\Delta = (\hbar\omega - E_g)/E_0$; the functions δ and Θ are respectively the Dirac Delta function and the Heaviside Step function while the fraction multiplying this latter takes the name of Coulomb enhancement factor. It is important to notice that the exciton ground state binding energy is $E_b = E_0$ for the 3D case and $E_b = 4E_0$ for the 2D case [20, 24].

Though appropriate for IOHPs, the Elliott formula cannot be used to model the absorption spectrum of organic semiconductors, since it is based off the Wannier-Mott excitons and OSCs instead are characterized by the smaller and more tightly-bound Frenkel excitons.

1.3.2 X-rays Irradiation

The intensity of transmitted radiation through a layer of thickness t follows a law similar to Beer's one:

$$I = I_0 e^{-\mu t} \quad (1.9)$$

being μ the linear attenuation coefficient, which increases with the atomic number of the elements involved and has units of cm^{-1} . In literature, it is more common however to find the mass attenuation coefficient, defined as $\mu_m = \mu/\rho_0$ [16]. As displayed in Fig. 1.8, depending on the energy of the X-rays, the attenuation has three main contributions: photoelectric absorption, Compton scattering and pair production processes [26, 27]. While visible and ultraviolet radiation have generally just enough energy to excite the electrons in the outer shells of the atoms, X-ray photons can easily affect also the core shells electrons.

This happens already at the least energetic part of the X-rays spectrum (soft to medium X-rays, with $E_{ph} < 50 \text{ keV}$), in which the photoelectric effect dominates: photons are absorbed and deeply bound electrons are ejected from the atoms as photoelectrons. This leaves the atoms in an unstable configuration, which leads outer shell electrons to fall back on the now unoccupied core states. As a consequence, X-rays radiation can be emitted during the de-excitation or, if the energy is transferred to other outer shell electrons, these can be in turn ejected as Auger electrons.

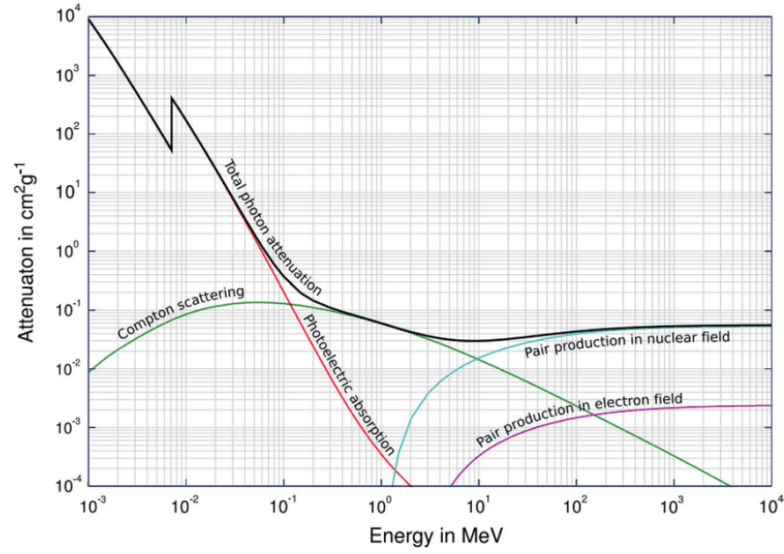


Figure 1.8: Mass attenuation coefficient as a function of photon energy for ionizing radiation-matter interactions, showing the main contribution to photon absorption and conversion processes [25].

In Compton scattering, ionizing radiation transfers energy to loosely bound outer shell electrons, which are ejected as Compton electrons while the photons continue to travel inside the material with enough energy to provoke further interactions. Compton scattering is dominant at lower atomic number or intermediate X-ray energies[27].

The amount of radiation absorbed by a material can be quantified through the absorbed dose, which is defined as the energy absorbed per unit mass:

$$\mathcal{D}_{abs} = \frac{dE_{abs}}{dM} \quad (1.10)$$

It is measured in Grays [Gy]³.

1.4 Photodetectors

Electromagnetic radiation (EMR) detectors are devices designed to convert an electromagnetic input signal into a readable output, the nature of which depends on the range to which the EMR belongs and on the physical phenomenon exploited for detection[28]. The following paragraphs will focus on photodetectors for the UV-Vis and the X-ray ranges.

³1Gy = 1J/kg.

1.4.1 Detectors for UV-Vis Photons

EMR detectors in this range are often referred to as photodetectors or optical detectors. They come into two main categories: thermal detectors (which are wavelength-independent) and photonic detectors. These latter can be further classified into photoemissive (when the energy of photons is higher than the work function of the detector material) or photovoltaic (when the energy of the photons is lower than the work function yet higher than the energy bandgap of the detector material)[28].

In this work, the samples under test are photoconductors, a type of photovoltaic detectors which is characterized by a very simple structure: a semiconductor with two electrodes. Photoconductors come either in lateral geometry or in vertical geometry (Fig. 1.9).

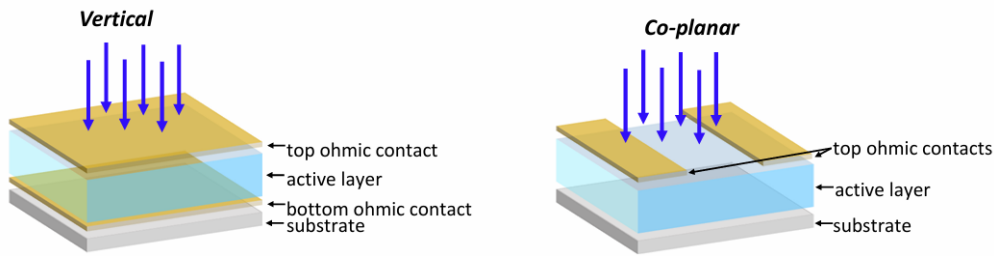


Figure 1.9: Scheme of photoconductor geometries. The blue arrows indicate the direction of impinging light. The image is adapted from [14].

The main difference between these two configurations is in the motion of charge carriers, which are collected with almost equal efficiency in a planar geometry and in function of their type and distance from the top contact in the vertical one.

The performance of a photodetector can be measured through several figures of merit[28, 29]. Among the most important there are the responsivity $\mathcal{R}$ and the External Quantum Efficiency (EQE). The plot of responsivity versus wavelength takes the name of spectral response and is a key graph in detector datasheets.

The responsivity is defined as:

$$\mathcal{R} = \frac{I_{out}}{P_{in}} \quad (1.11)$$

where I_{out} is the detector's output current and P_{in} the incident light power. Also known as optical power, this last quantity is linked to the photon flux Φ via the active area $\mathcal{A}$ of the detector:

$$P_{in} = \Phi E_{ph} \mathcal{A} \quad (1.12)$$

The EQE is usually reported as a percentage and is related to the responsivity in a simple way:

$$EQE = \mathcal{R} \cdot \frac{E_{ph}}{e} \quad (1.13)$$

where E_{ph} is the energy of the incident light and e is the elemental charge.

1.4.2 Detectors for X-rays Photons

X-rays detectors (XRDETs), are primarily divided into direct and indirect detectors. The first are composed of materials which are able to convert X-rays into an immediately readable (electrical) output, while the second are generally comprised of two stages: one converting X-rays to less energetic photons (scintillator) and the other converting these into the electrical output (UV-Vis photodetector). Of course, this additional passage reduces the efficiency, but both types of XRDETs are widely employed and actively researched.

The amplitude of response of a direct X-ray detector is quantified by its sensitivity S , which is proportional to the quantum efficiency, the generation of charges by the absorbed X-ray photons and the charge collection efficiency [14]. An operative definition of the sensitivity for a detector operating in current mode is:

$$S = \frac{1}{\mathcal{A}} \frac{\partial(I_{Xray} - I_{dark})}{\partial(DR)} \quad (1.14)$$

where $\mathcal{A}$ is the detector active area and DR the dose rate in $[\text{Gy s}^{-1}]$.

Other than the sensitivity, among the most important figures of merit of a XRDET, there are the dark current I_{dark} , the Limit of Detection (LoD), and the response time.

The dark current must be as low as possible to ensure a good signal-to-noise ratio; its value therefore affects also the LoD, i.e. the smallest detectable signal. The response time quantifies the speed of the detector, which however is often reported in terms of rise time and fall time. The first is typically defined by the time required by the signal to go from 10% to 90% of the full amplitude, while the second is defined as the time needed by the signal to relax from the 90% to the 10% of the full amplitude, when the radiation is switched off [14].

In searching for new solutions, a list of the requirements for an ideal radiation detector[30] has been defined:

1. high stopping power (large atomic number, interaction volume and density)
2. good purity and uniformity (defect-free or defect-controlled material, high quality electrodes)
3. high resistivity ($>1 \text{ M}\Omega \text{ cm}$) and low leakage current
4. high charge collection efficiency (low exciton ionization energy, high charge carriers mobility and lifetime)
5. stability (both of material and electrodes)

No material can still satisfy completely all these points, yet, IOHPs and OSCs are qualifying as promising materials for the development of XRDETs, of course according to their strengths and weaknesses. IOHPs have generally better optoelectronic properties but, as said, suffer from stability issues. OSCs have also lower stopping power, but are more eco-friendly and easy to grow and offer the possibility to realize biocompatible, flexible and large-area detectors⁴[14, 30].

⁴In dosimetry applications, the fact that they possess a tissue-equivalent density can be exploited to reduce the need for calibrations.

2. Experimental Apparatus

In this thesis project, two apparatuses were optimized and used: one performing stand-alone UV-Vis spectroscopy (standard or benchmark setup) and the other designed to allow UV-Vis spectroscopy under simultaneous X-rays irradiation (compact or portable setup).

2.1 UV-Vis Photocurrent Spectroscopy

Photocurrent spectroscopy is an experimental technique which allows to acquire the photocurrent spectrum of a material.

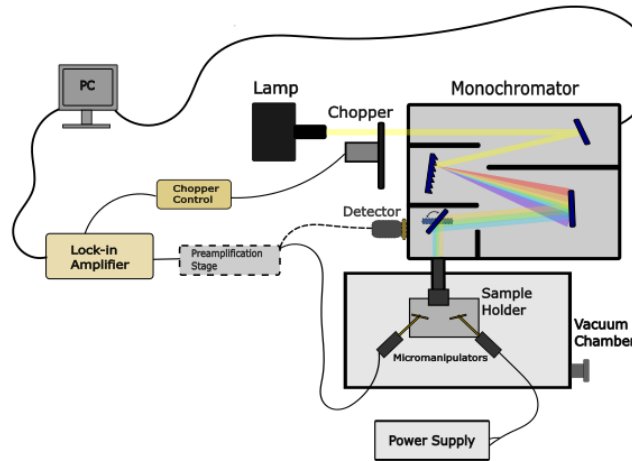


Figure 2.1: Schematics of the standard UV-Vis photocurrent spectroscopy setup. Inside the monochromator, a mirror can be set in two positions, allowing the light either to go through the lateral slit and shine on the sample in the vacuum box or to pass through the frontal slit and hit the detector. A pre-amplification stage may be present depending on the sample or detector characteristics.

The sample is placed under bias and shone with monochromatic light at different wavelengths. The photocurrent – i.e. the light-induced current – depends on the convolution of:

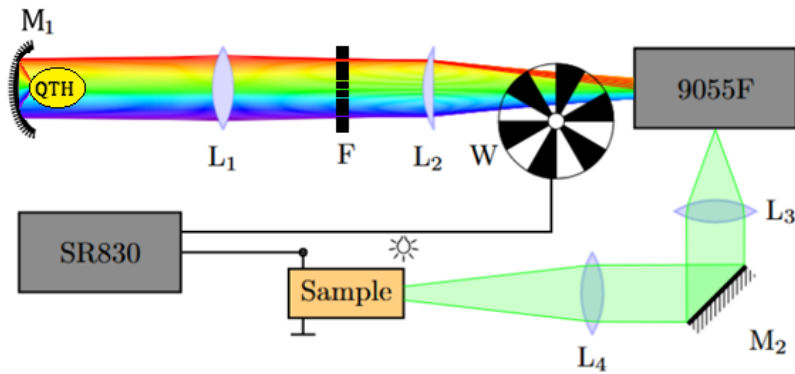


Figure 2.2: Scheme of the optical layout outside the monochromator in the standard setup. At the monochromator's entrance: the light from the QTH lamp is collected by a parabolic mirror (M_1), sent through a collimating lens (L_1), a 6-mountings filter wheel (F), a focusing lens (L_2) and the chopper wheel (W). At the monochromator's exit: the light is sent through a collimating lens (L_3), onto a right-angle turning mirror (M_2) which sends it downwards through a focusing lens (L_4) with 10 cm focal length onto the sample. The image is adapted from [31].

1. the absorption spectrum of the material, which dictates the generation of charge carriers;
2. charge transport and collection, which are affected by trap states and electrodes' interfaces.

From the acquired photocurrent spectrum it is possible to obtain information on the energy gap, the exciton binding energy and on the electrically active defect states of the sample.

The apparatus is generally comprised of:

- a UV-Vis broadband light source, paired with a monochromator;
- a power supply for sample bias;
- a chopper, modulating the signal;
- and lock-in amplifier, to acquire the sample response.

In Fig. 2.1, the scheme of the UV-Vis spectroscopy setup used in this thesis work is presented, while Fig. 2.2 details the optics outside the monochromator. Other than the basic components required for sample photocurrent acquisition, the apparatus allows also for alternative configurations, which simplify the acquisition of the pure lamp spectrum with a detector.

2.1.1 Light Source

The two UV-Vis sources employed here are the Quartz-Tungsten-Halogen (QTH) lamp and the Xenon (Xe) arc lamp. Both are incoherent continuum sources, i.e. they emit over a broad range of wavelengths with relatively smooth variations of intensity. Lamps come along with their power supplies and a cooling fan which is fundamental to preserve their integrity during their operation.

QTH lamps (Fig. 2.3) are widely used since they can be regarded as graybodies in the visible range, and they are characterized by long life and constant efficiency[28]. Their emission is excellent in the Vis-IR range, but their flux decreases rapidly under the 400-350 nm.

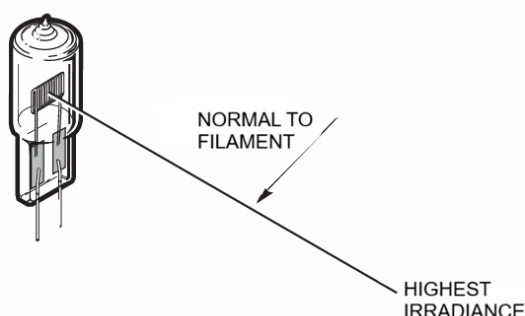


Figure 2.3: QTH lamp scheme. Emission in flat-filament lamps like this is not isotropically distributed. The image is adapted from [32].

The lamp is made of a quartz glass¹ envelope which contains a tungsten (W) filament and an halogen gas (typically iodine). When current passes through the filament, this becomes incandescent and starts evaporating and emitting light. The evaporated tungsten recombines with the gas, forming an halide compound which then, at sufficiently high temperatures, dissociates and reacts with the filament, depositing again tungsten onto it. This halogen cycle prevents the complete evaporation of the filament and keeps the bulb clean, ensuring a constant light output throughout the lamp life[28, 32].

With respect to QTH, Xe arc lamps show much higher spectral irradiance and are better UV emitters. They provide continuous emission over a wide range of wavelengths and the presence of the element characteristic lines makes them also suitable as line sources[28, 33]. The structure of a Xe short-arc² lamp features a quartz glass envelope which contains two metal electrodes surrounded by high-pressure xenon (Fig. 2.4). The light is generated by sending high-voltage pulses through the electrodes: the gas in between gets ionised, until arc discharge occurs. After this moment, a low voltage is

¹Also known as fused silica.

²There exist also long-arc lamps, in which the distance between the electrodes is greater, however, their efficiency is lower.



Figure 2.4: Image of a double-ended xenon short-arc lamp [33].

sufficient to maintain the arc[33].

Figure 2.5 shows the typical spectra of a QTH and of a Xe lamp.

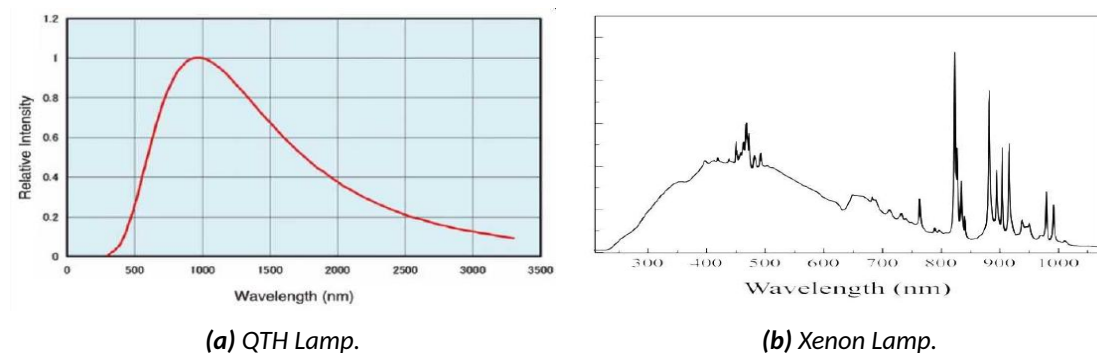


Figure 2.5: Typical spectra of QTH and of Xenon lamps [34]. The y-axis represents the intensity in arbitrary units.

The lamps used in this setup are a Philips 24V/150W QTH lamp and the THORLABS SLS400 Mercury-Xenon short-arc lamp; this latter is a Xe arc lamp, with added traces of mercury (Hg), which provides higher peaks at the blue and UV end of the spectrum.

2.1.2 Monochromator

The monochromator is an instrument designed to turn a beam of white light into a monochromatic one[35]. Its basic internal structure, schematized in Fig. 2.6, is very straightforward: mirrors help direct the beam from the entrance slit to the diffraction grating and from the latter into the exit slit.

The diffraction grating (Fig. 2.7) is an optical dispersive element with the surface characterized by reflecting grooves³ at a certain angle θ_B from its normal – the blaze angle.

The grating is mounted on a rotating turret: this is what allows to change the resulting wavelength, since it depends on the angle α of the incident light and on the angle

³This is true for reflection gratings, however, also transmission gratings exist.

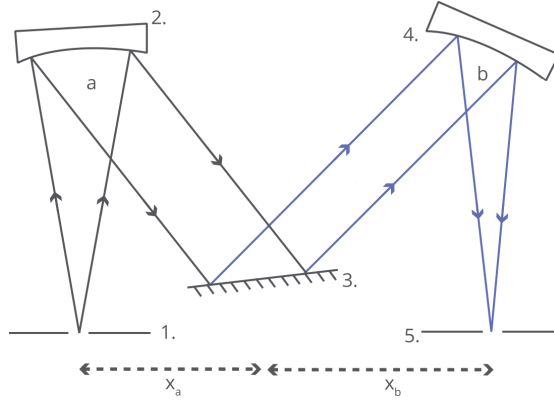


Figure 2.6: Basic monochromator scheme. This particular disposition takes the name of Czerny-Turner configuration: light enters from the entrance slit (1), is reflected off a concave mirror (2) onto the diffraction grating (3) and is focused through a second concave mirror (4) out of the exit slit (5). The image is adapted from [36].

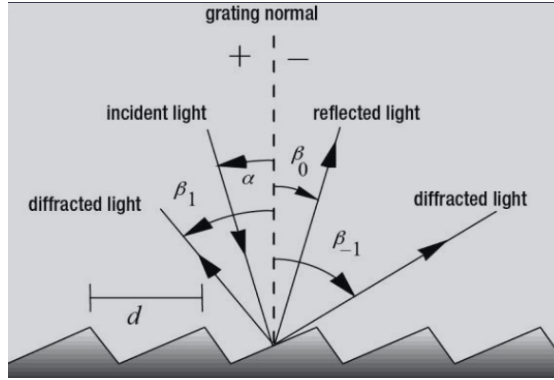


Figure 2.7: Scheme of light interacting with a diffraction grating. The beam arrives on the grooves at an angle α with respect to the grating normal and is diffracted at angles β_n , with n diffraction order. d is the groove spacing. The image is adapted from [35].

β of diffracted light according to the grating equation:

$$m\lambda = d(\sin \alpha + \sin \beta) \quad (2.1)$$

where m is the diffraction order and d is the groove spacing. According to Eq. (2.1), plane waves hitting the grating surface are diffracted in such a way that only those wavelets with the adequate wavelength survive and interfere constructively, while the other interfere destructively [35].

Given a set of values of λ , α and d , Eq. (2.1) is satisfied by several values of β , since there are several light paths differing by an integer multiple m of the set wavelength λ . This leads to the formation of the so-called higher-order diffractions, which however

have lower intensity than the principal ones[35].

The intensity of the diffracted light is maximum when the blaze condition is satisfied:

$$m\lambda = 2d\sin\theta_B \quad (2.2)$$

When, in addition, $\alpha - \beta = 0$, the grating is said to be in Littrow configuration and its efficiency is maximal.

The quality of the monochromatic beam exiting from a monochromator can be measured in terms of dispersion and resolution.

The first is usually reported as reciprocal linear dispersion D and can be intuitively interpreted as the range of wavelengths that is spread per unit length of the entrance slit image. It is defined as

$$D = \left(L \cdot \frac{\partial\beta(\lambda)}{\partial\lambda} \right)^{-1} \quad (2.3)$$

where L is the output focal length and $\frac{\partial\beta(\lambda)}{\partial\lambda}$ is the angular dispersion of the grating. The angular dispersion is defined as the spectral range $\Delta\beta$ per unit angle and can be derived by differentiating the grating equation, assuming the incidence angle α to be constant:

$$\begin{aligned} \beta(\lambda) &= \arcsin\left(\frac{m\lambda}{d} - \sin\alpha\right) \\ \frac{\partial\beta(\lambda)}{\partial\lambda} &= \frac{1}{\sqrt{1 - \left(\frac{m\lambda}{d} - \sin\alpha\right)^2}} \cdot \frac{m}{d} = \frac{1}{\sqrt{1 - \sin^2\beta}} \cdot \frac{m}{d} = \frac{1}{\cos\beta} \cdot \frac{m}{d} \end{aligned} \quad (2.4)$$

The limit of resolution⁴ $\Delta\lambda$ is instead the maximal precision up to which the instrument is able to separate two adjacent wavelengths. It depends on D and it is strictly tied to the resolving power R :

$$\begin{aligned} R &= \frac{\lambda}{\Delta\lambda} = \frac{\lambda}{w \cdot D} \\ w &= \max(w'_{in}, w_{out}) \end{aligned} \quad (2.5)$$

with w'_{in} width of the entrance slit as imaged onto the plane of the exit slit (defined by the system's magnification M as $w'_{in} = M \cdot w_{in}$) and w_{out} width of the exit slit.

The resolving power is one of the most important figures of merit for monochromators, since it allows to measure the instrument's ability to effectively resolve adjacent spectral lines at different wavelengths. Since $\Delta\lambda$ varies much less with the wavelength than λ itself does during a sweep, the spectra are usually more noisy at shorter wavelengths [35].

⁴Also known as spectral resolution or resolution.

The reason for which w in Eq. (2.5) is that of the largest slit can be intuitively comprehended by considering that the major source of spectral error comes from the slit which leads to the worst resolution.

During acquisitions, a good empirical rule is to keep $w_{in} = w_{out}$. More precisely, w_{out} should roughly match the dimensions w'_{in} of the entrance slit image, as detailed in Fig. 2.8:

- when $w_{out} < w'_{in}$, not all the dispersed lines can reach the exit slit, resulting in a reduction both of the spectral bandwidth and of the relative intensity, which fails to reach its maximum value;
- when $w_{out} = w'_{in}$, at exactly one point of the spectra all the diffracted lines are contained in the exit slit, resulting in a peak of relative intensity;
- when $w_{out} > w'_{in}$, the relative intensity stays at its maximum value across several points of the spectra but the spectral bandwidth is large and this means that more wavelengths than necessary are allowed past the exit slit.

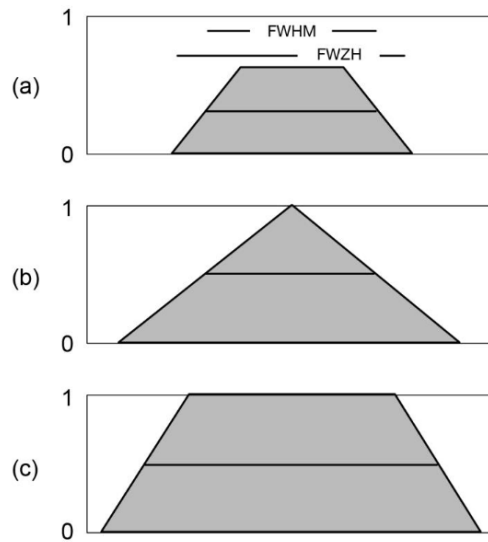


Figure 2.8: Linespread graphs showing the effects of relative size of exit slit width w_{out} and image width w'_{in} . In (a) $w_{out} < w'_{in}$, in (b) they are equal and in (c) $w_{out} > w'_{in}$. The y-axes represent the relative light intensity at the image plane while moving on the x-axes implies changing the selected wavelength (either by rotating the grating or by considering to move the exit slit across the image in the plane of dispersion). The image is adapted from [35].

Overall, the choice of the slit width always reduces to a trade-off between output intensity and output spectral resolution [28, 35]. Typical widths for photocurrent spectroscopy fall in the range of tens of micrometres to few millimetres, depending on the

sensitivity of the detectors measuring the output monochromated light or on the light response of the samples under analysis.

In the stand-alone UV-Vis photocurrent setup, the monochromator employed is the ScienceTech-9055F, which features a turret with two 1200 grooves/mm gratings of 3.3 nm/mm reported reciprocal linear dispersion and blaze wavelengths of 300 nm and 1000 nm respectively.

In the compact apparatus, the monochromator used is the Acton SpectraPro-150, which possesses a turret with a 1200 grooves/mm grating of 5 nm/mm nominal reciprocal linear dispersion and balze wavelength of 500 nm and a 600 grooves/mm grating of 10 nm/mm nominal reciprocal linear dispersion and balze wavelength of 1 μm .

2.1.3 Chopper and Lock-in Amplifier

The lock-in amplifier exploits a technique known as phase-sensitive detection (PSD) to lock onto the signal and distinguish it from the background noise by means of a specific reference frequency and phase[37, 38]. In Fig. 2.9, the functional diagram of a lock-in amplifier is shown.

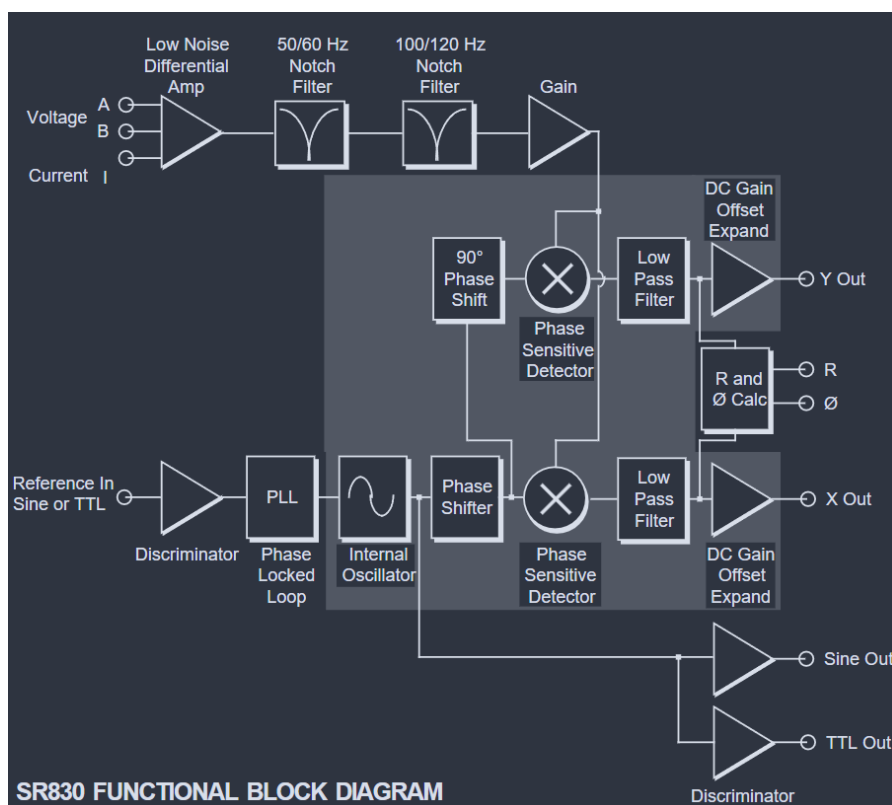


Figure 2.9: Functional diagram of SR830 lock-in amplifier. The image is adapted from [37].

The basic workflow of PSD involves three main steps[38]:

1. the input signal is split and separately multiplied with the reference signal (i.e. a pure sine wave whose frequency matches the reference one) and a 90° phase-shifted copy of it;
2. an adjustable low pass filter is applied onto the outcome of the multiplication, resulting in the two outputs X (in-phase component) and Y (quadrature component);
3. the amplitude R of the signal and the phase difference ϑ between the input and the reference signal are determined with a conversion from Cartesian into polar coordinates.

The reference frequency f_{REF} is provided by the chopper, a rotating wheel with alternated full sectors and holes which modulates the light arriving on the sample at a known frequency (reference frequency).

The lock-in amplifier is able to detect and magnify very small signals, down below fA and nV and the dynamic reserve allows to tune the expected signal-to-noise ratio to acquire the signal while avoiding sudden noise-related overloads[37]. The signal itself can be either a voltage (absolute or differential) or a current (internally amplified by the lock-in⁵).

The goodness of the acquisition depends mainly on the filter roll-off and on the time constant. The first controls the steepness of the filter while the second affects the integration time i.e. the width of the time window during which the signal is averaged. Together, these two parameters affect the bandwidth of the measurement and the dwell time, as reported in Table 2.1.

The more clear the signal, the more stable the detected phase. For the purpose of this work, the following additional settings were used:

- input type: AC;
- sync < 200 Hz enabled;
- 50 Hz and 100 Hz line filters active.

The lock-in amplifier used for both setups is the Stanford Research Systems 830, while the chopper controller unit is the Stanford Research Systems 540 for the standard apparatus and the Scitec Instruments 300CD for the compact apparatus.

⁵In the specific case of this setup, the gain was either a factor of 10^6 or 10^8

Time Constant	Parameter	Filter Roll-off			
		6 dB/oct	12 dB/oct	18 dB/oct	24 dB/oct
30 ms	BW [Hz]	8.33	4.76	3.70	3.33
	t_{dwell} [s]	0.15	0.21	0.27	0.30
100 ms	BW [Hz]	2.50	1.43	1.11	1.00
	t_{dwell} [s]	0.5	0.7	0.9	1.0
300 ms	BW [Hz]	0.83	0.48	0.37	0.33
	t_{dwell} [s]	1.5	2.1	2.7	3.0
1 s	BW [Hz]	0.25	0.14	0.11	0.10
	t_{dwell} [s]	5	7	9	10
3 s	BW [Hz]	0.083	0.050	0.040	0.030
	t_{dwell} [s]	15	21	27	30

Table 2.1: Frequency bandwidth BW and minimal dwell time t_{dwell} for different time constants and filter roll-off parameters. Data adapted from [31].

2.1.4 Detectors

In order to acquire the lamp spectrum, the light exiting from the monochromator is sent onto a photodetector.

In this work, the detectors used are a Silicon photodiode (SiPD) and a pyroelectric (PYRO) detector; both have a circular active area, with radius of 1.25 mm and of 0.5 mm respectively.

The SiPD is a photovoltaic detector. Light impinging on the p-n junction induces generation of excess carriers, which are swept out of the depletion region by the electrical field⁶ and collected at the electrodes.

It is characterized by a non-linear response in a well-defined wavelength range (190-1110 nm), as can be seen in Fig. 2.10, however, it is very sensitive and fast (0.15-2.5 μ s) in response[29].

The PYRO is a thermal detector made of a pyroelectric material – i.e. a material which possesses a natural electrical polarization and can generate a temporary voltage difference when heated or cooled[39]. Photons impinging on the sensor increase the material's temperature, inducing a slight modification of the crystalline structure and thus of the polarization.

The capability of a PYRO detector to return a strong signal depends on the chopping frequency of the impinging radiation: if the chopping frequency is slow compared to the thermal relaxation time of the crystal, the crystal remains close to thermal equilibrium and the current response is small[28]. In Fig. 2.11, the responsivity curve of the PYRO detector is reported as a function of the frequency at which the light impinging on it is

⁶Photodiodes are usually employed under reverse bias. When the voltage is zero, the device operates as a photoconductor, and its response is weaker and less linear with the photocurrent.

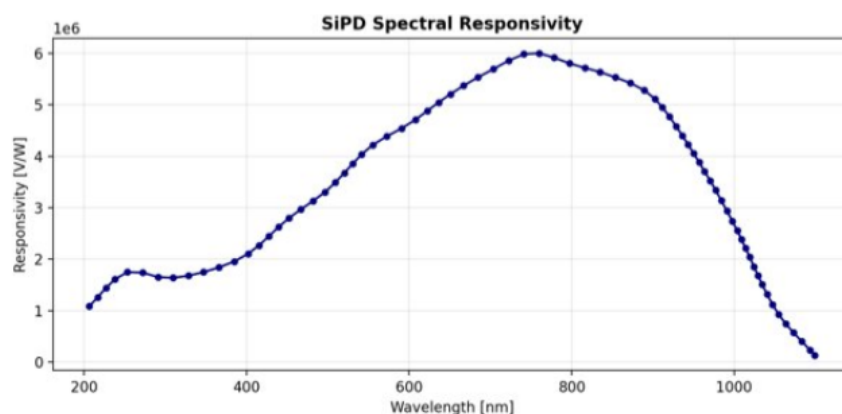


Figure 2.10: Responsivity curve of Si photodiode as a function of the wavelength. The peak resides at 760 nm, while at 1100 nm – in correspondence with silicon bandgap – the responsivity drops.

chopped.

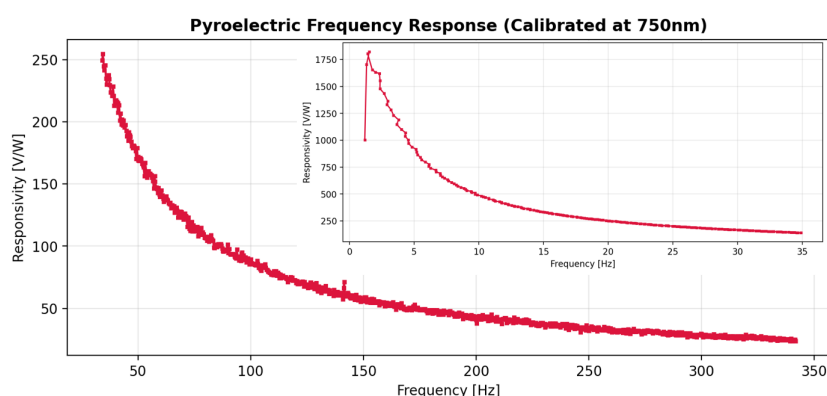


Figure 2.11: Responsivity curve of pyroelectric detector as a function of frequency. The main plot is taken at chopper controller's 400 Hz full scale while the small plot has been obtained at 40 Hz full scale.

This detector has also a lower responsivity than the SiPD, thus, its output needs to be amplified by a voltage amplifier before being given as input to the lock-in amplifier. For the acquisition, a FEMTO DLPVA-100 voltage amplifier (Fig. 2.12), with an amplification factor of 60 dB, was used. Despite these cons, the major advantage of the PYRO with respect to the SiPD is that, being a thermal detector, it is characterized by an almost-constant spectral response at fixed modulation frequency.

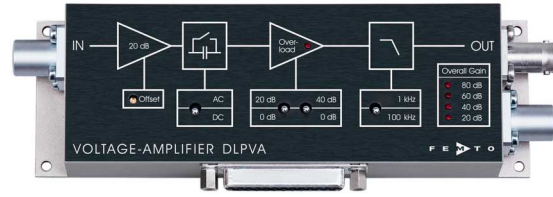


Figure 2.12: FEMTO DLPVA-100 voltage amplifier[40].

2.1.5 Sample Bias

To perform photocurrent spectroscopy, the light exiting the monochromator is sent through a focusing lens and then onto the sample, in such a way that the beam illuminates its active area.

The sample is connected on one electrode to the power supply and on the other to the lock-in input; the circuit is closed connecting virtually the grounds of the two instruments (Fig. 2.13).

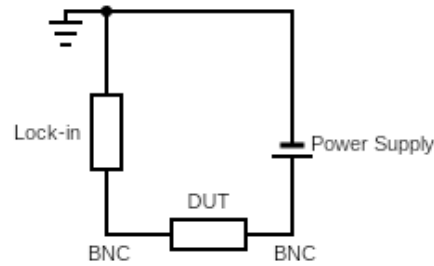


Figure 2.13: Schematics of the electrical circuit in the standard setup. The transimpedance amplifier can be inserted between the sample (indicated as the Device Under Test, DUT in the image) and the lock-in amplifier. The circuit is virtually closed by the sample itself.

The connection can be done either using micromanipulators or by placing the sample in a small box with BNC connectors for coaxial cables, as shown in Fig. 2.14. Depending on the sample material, the signal going to the lock-in could need a pre-amplification stage: if the photocurrent is high enough, the lock-in current input with internal gain 10^6 or 10^8 can suffice; otherwise, the lock-in voltage input ("A" mode) must be paired with a transimpedance amplifier.

Figure 2.15 shows the two amplifiers employed during the measurements.

In both setups, the bias is provided to the sample with an AimTTi CPX400SP power supply.

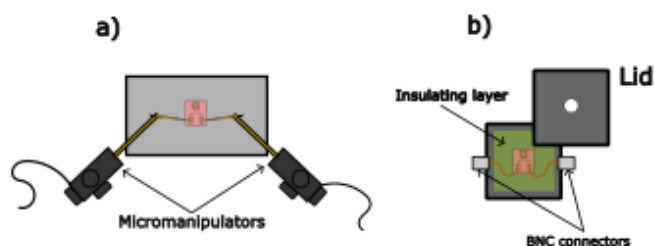


Figure 2.14: Scheme of sample connection modes. In (a), the conducting tips of the micromanipulators are directly touching the sample contacts. In (b), the sample is attached to the box bottom, over an insulating layer, and copper wires are soldered with tin to the BNC connectors and with silver paste to the sample electrodes.



(a) DLPCA-200



(b) DHPCA-100

Figure 2.15: FEMTO transimpedance amplifiers. The model in (a) is ideal in low-noise applications while the one in (b) is tailored for high-speed acquisitions. The images are adapted respectively from [41] and [42].

2.2 UV-Vis Spectroscopy Under X-ray Irradiation

This second setup allows to perform UV-Vis photocurrent spectroscopy under simultaneous X-rays irradiation.

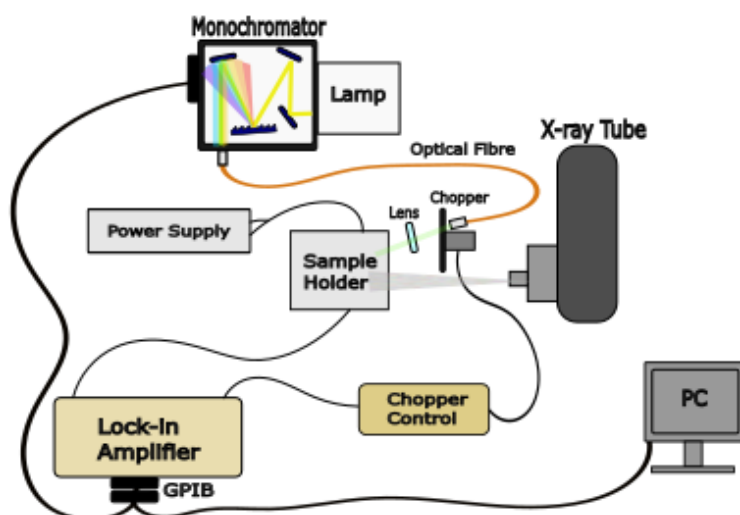


Figure 2.16: Schematics of the compact setup. The lamp-monochromator system, all the optics and the sample holder are enclosed with the X-ray tube in a lead-glass shielding cabinet. The monochromator and the lock-in amplifier are connected in parallel via GPIB to the computer.

The apparatus – schematized in Fig. 2.16 – is housed entirely within a lead-glass shielded enclosure, which provides the necessary attenuation against X-ray scattering produced by the irradiation source. For this reason, the monochromator-lamp system is configured as compact integrated unit, whose resulting output light is brought onto the samples through an optical fibre.

2.2.1 X-rays Source

X-rays are produced in a Coolidge X-ray tube with Molybdenum (Mo) target: a tungsten filament, heated by current flowing, emits electrons, which are accelerated by a high voltage (tens of kV) established between the cathode and the anode. The highly energetic electrons impinging onto the target Mo anode, decelerates and emits X-ray as Bremsstrahlung radiation and Mo characteristic lines (Fig. 2.17). The radiation is conveyed through Beryllium (Be) windows.

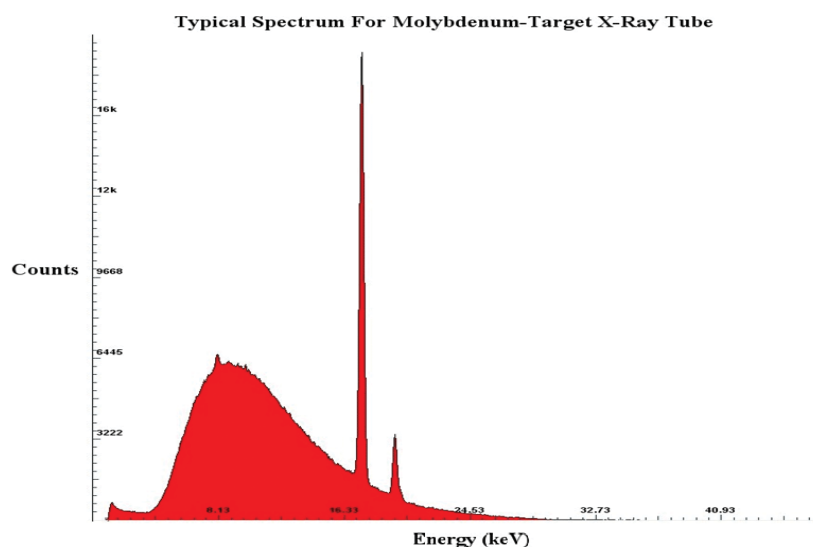


Figure 2.17: Typical spectrum of a Molybdenum target X-ray tube. The continuum is formed by the Bremsstrahlung radiation, while the sharp high-intensity peaks correspond to the characteristic lines of the Mo target. The image is adapted from [43].

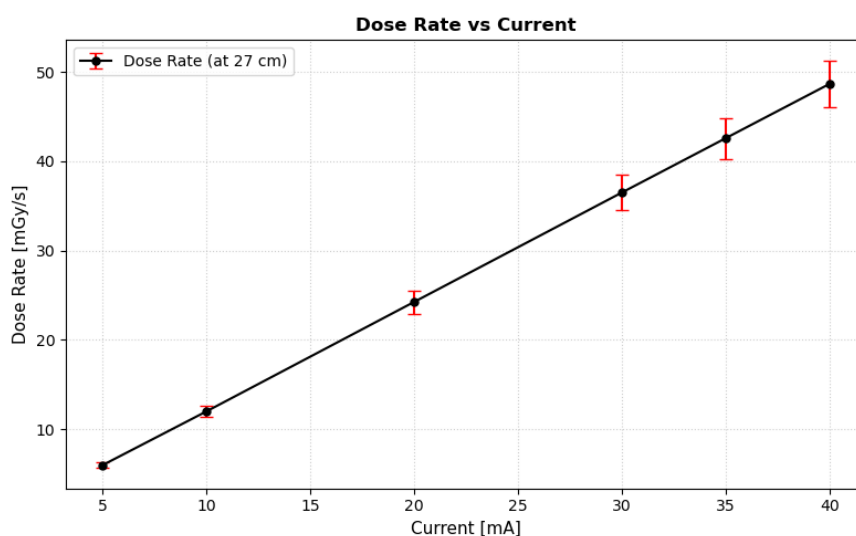


Figure 2.18: X-rays tube calibration at 35 kV and 27 ± 1 cm of distance. The relevant value for this study is 30 mA, which yields a dose rate of 36.5 ± 2.0 mG/s.

The beam intensity can be regulated by setting the cathodic voltage and the electronic current. In Fig. 2.18, the dose rates at a distance of 27 ± 1 cm from the tube are plotted as a function of the electronic current, with the cathodic voltage fixed at 35 kV.

The tube used in this setup is a PANalytical long fine focus Mo tube powered by a Spellmann DF6N03 high voltage power supply.

Safety systems include a X-ray shielding lead-glass enclosure, a manual enabling shutter, water-based cooling and the possibility to set a limit to the filament current⁷.

2.2.2 Optical Fibre

In this setup, the light exiting the monochromator slit is collected into a collimator and sent to the sample through an optical fibre. At the fibre's exit, the light is passed again through a collimator and then meets the chopper wheel, before being focused onto the sample with a lens (see Fig. 2.19).

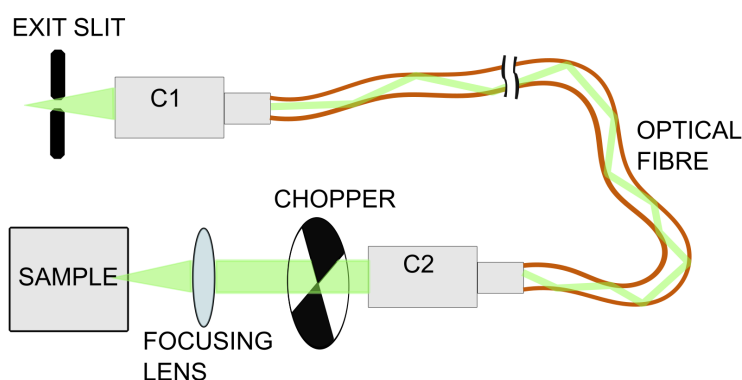


Figure 2.19: Scheme of the monochromator-sample optical coupling in the compact setup. Light from the monochromator exit slit is collected by the first collimator (C1), sent through the optical fibre and collimated again with the second collimator (C2), for then being modulated by the chopper and focused with a lens onto the sample.

The collimator is employed mainly to convey efficiently the light into the fibre, but it comes with a drawback: its internal coating limits the allowed optimal wavelengths (in this case, to the range 350-700 nm). This affects the intensity of the lamp photon flux, changing drastically the shape of the lamp spectrum outside of the optimal range: As can be seen in Fig. 2.20, the presence of collimators – even at lower lamp power – remarkably increases the intensity of the signal. The collimators used are THORLABS F950SMA-A multimode collimators while the optical fibre is the THORLABS M96L02 Step-Index Multimode Fiber-Optic Patch Cables with SMA ends.

⁷The filament current is of the order of the A while the electronic current is around tens of mA.

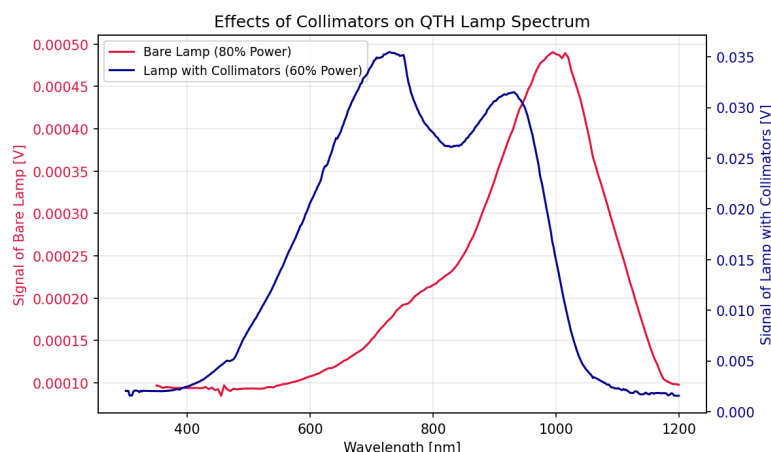


Figure 2.20: Effects of collimators on the raw lamp spectrum. At 700 nm, the internal coating induces a drop in the signal amplitude and, beyond, the shape is modified – according to the collimator manufacturers – in an untraced batch-dependent way.

2.2.3 Operation

The developed setup allows different acquisition modes, adjusting the chopper position and the instruments employed:

1. standard UV-Vis photocurrent spectroscopy: the chopper is inserted between the optical fibre output and the sample, while the X-ray tube is off;
2. photocurrent spectroscopy under constant X-ray excitation: UV-Vis source chopped and X-ray tube on. This allows to see the effects of ionising radiation on the photocurrent spectrum;
3. radiocurrent under constant UV-Vis irradiation: UV-Vis source constant and chopped X-ray tube on. This allows to see the effects of X-rays on the sample, a complementary study with respect to the previous;
4. X-ray induced current dynamics acquisition: UV-Vis source off and chopped X-ray tube on. This allows to collect radiocurrent (as a function of time). Both here and in the above configuration, the dose must be manually varied.

The experimental protocol followed in this thesis project involved just modes (1) – for validation of the newly-assembled setup and evaluation of the sample conditions – and (2).

3. Setup and Calibration of the Photocurrent Measurement System

In the following paragraphs, the main experimental challenges encountered during the upgrade of the standard UV-Vis photocurrent spectroscopy apparatus and the implementation of the compact UV-Vis one for measurements under X-rays irradiation, are presented. In the last section of this chapter, sample specifications are included as well. Fig. 3.1 shows the evolution of the standard setup: wooden supports have been replaced with an optical table plane, to which the chopper stand, the new lamp housing and the optical plane to which the monochromator is fixed have been carefully aligned and riveted. The vacuum chamber stands on newly made supports too, to match the new height requirements.

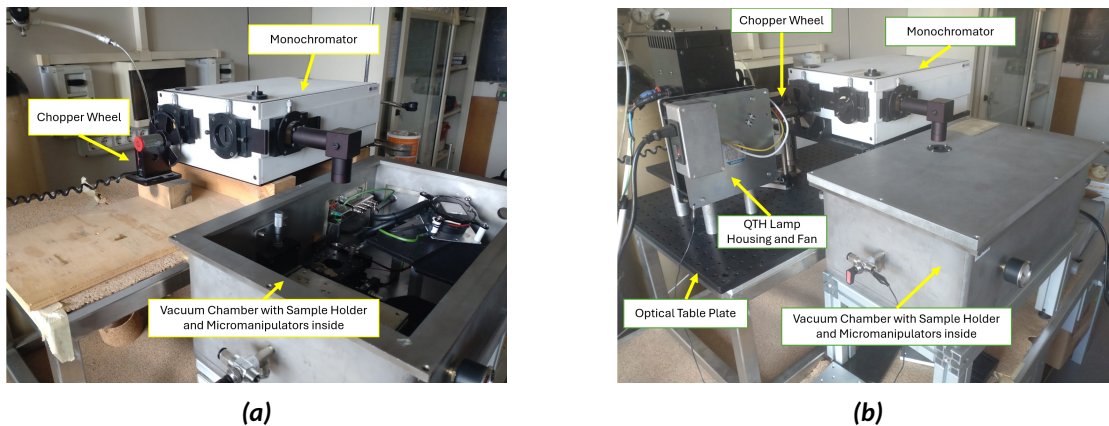


Figure 3.1: Evolution of the benchmark photocurrent setup design. Before (a) and after (b).

Fig. 3.2 shows instead the final configuration of the compact setup: the monochromator has been aligned and coupled with its QTH lamp on the entrance slit and with the collimator on the optical fibre's end on the exit slit. Custom supports and adapters have been developed to secure the collimators in place and an optical plate has been riveted to the slotted base plate whose rails the sample holder – a pantograph with a slotted plane – is constrained to as well. The chopper and collimating lens have been aligned and fixed to the optical plate. The X-ray tube cooling system has been repaired and a support for the mechanical piece acting as shutter-enabler has been fixed to the slotted base plate.

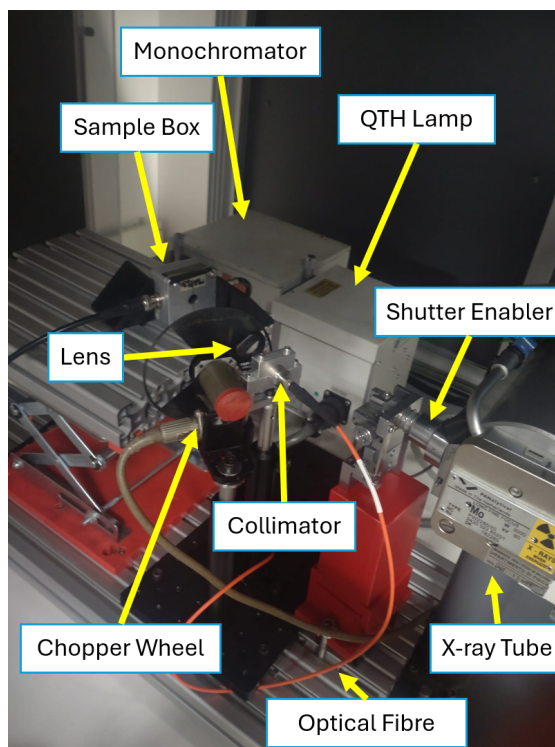


Figure 3.2: Picture of the compact setup.

3.1 Focusing and Alignment

In order to achieve a strong signal, alignment and focusing of the beam are vital steps.

3.1.1 Focusing the Light Beam in ScienceTech-9055F

In the UV-Vis spectroscopy setup, the QTH lamp housing hosts the lamp bulb, a parabolic mirror behind it and a tube with a plano-convex lens to focus the beam into the entrance slit of the monochromator on the exit hole. The focusing procedure involved:

- adjusting the three screws of the parabolic mirror to define the plane it laid upon;
- fixing the distance of the lens from the entrance slit to focus the lamp onto it;
- moving the whole lamp housing along the plane perpendicular to beam direction to centre the slit and having the beam focused on it.

The procedure involved a first rough correction of the major optical issues (e.g. the double-halo), then, the maximum of intensity was searched with the aid of the SiPD detector.

At the fixed wavelength of 640 nm and 80 Hz chopper frequency, this allowed to increase the signal read by the lock-in from 1.32 mV to 179 mV.

3.1.2 Aligning Mirrors and Verifying Gratings in SpectraPro-150

The alignment procedure in the combined UV-Vis and X-rays setup was more tricky. The monochromator itself needed optical tweaking, since the internal optics was not properly aligned and the beam did not travel correctly up to the exit slit.

To correct the internal optics, a monochromatic light source, 635 nm (red) laser, was used. Before acting on the monochromator, the laser itself needed to be aligned with respect to the optical table. This was achieved by directing the beam on a target which was progressively moved further and then again closer, until there was no more need of adjustment on any of the three axes.

With the grating positioned in full-reflection mode (initialized at zero), the plane of each monochromator's mirror was corrected by regulating the set and socket screws.

Once the mirrors were set, the grating behaviour was investigated: in fact, once the laser hit its surface, beams other than the principal one were clearly visible (Fig. 3.3) and, depending on the wavelength of the laser and on the grating position, they varied in number and direction, even causing multiple reflections inside the monochromator. By using a powermeter, it was confirmed their nature as higher-order harmonics.

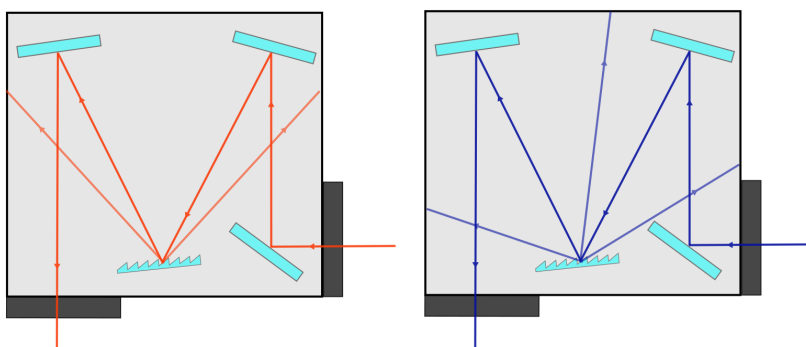


Figure 3.3: Scheme of multiple diffractions for the 635 nm (red) laser and the 405 nm (blue) laser inside the SP150 monochromator. The principal beam is the first order beam ($n=1$), which gets diffracted and sent exactly through the exit slit. The zero order beam ($n=0$) can be identified as the one for which the grating is behaving as a simple reflecting mirror, while higher order beams ($n>1$) appear as fainter lines. The blue laser shows a higher number of rays with respect to the red one, since it is more energetic, and therefore higher orders are populated.

To better verify whether these additional diffractions and reflections could be a problem for acquisitions with white-light sources, the laser was replaced with a QTH lamp and the beam exiting the monochromator was analysed at different wavelengths

through a spectrometer. The data collected, plotted in Fig. 3.4, demonstrated that the spectrum is actually clean in the useful acquisition range. Higher harmonic peaks ap-

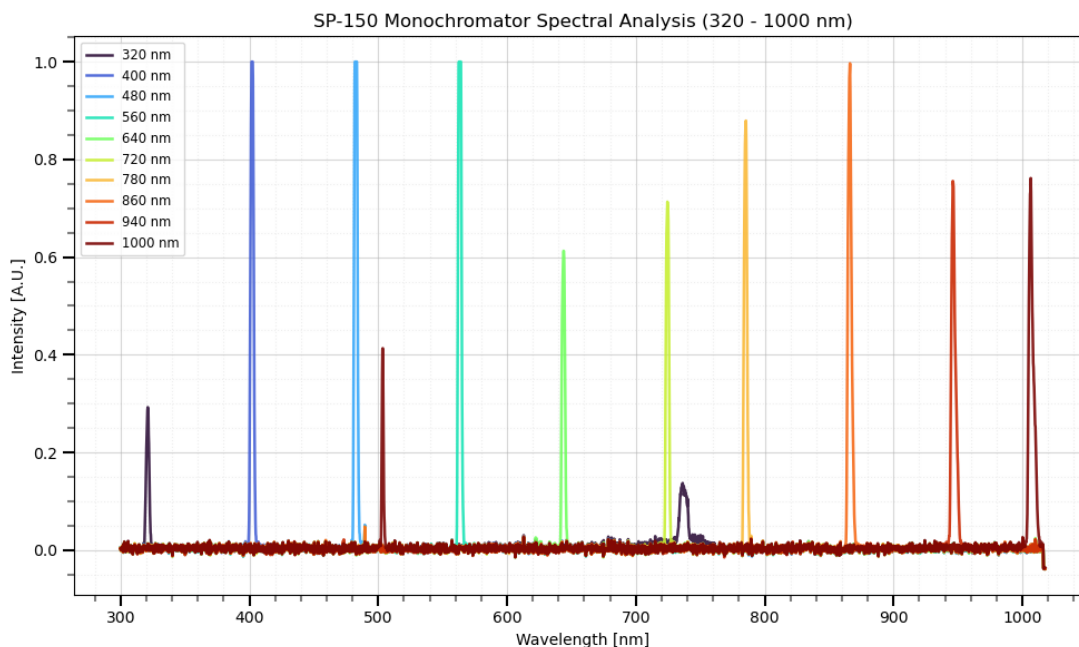


Figure 3.4: Spectral analysis of SP-150 monochromator. Each coloured line corresponds to a different spectral acquisition. The peaks correspond to the set wavelengths, exhibiting a minor redshift of 2-3 nm, which is consistent with the instrument's specified spectral resolution.

pear just when the monochromator is set at 320 nm and at 1000 nm, with secondary peaks visible at 735 nm and 505 nm respectively. The data were acquired with a THOR-LABS CCS200/M spectrometer through the OSA software.

3.1.3 Directing The X-rays Beam

Inside the Molibdenum tube, the X-rays are produced when the power supply provides enough energy. When the beam is active, the only way to prevent it from travelling is by closing the shutter.

The shutter mechanism is designed so that it can be remotely controlled when a shutter-enabler is active. The latter is a piece which comes with an aperture designed to lock itself into the shutter window and allowing the beam to pass through a narrower tube, acting thus also as collimator.

Attention must be paid to the positioning of this piece to avoid diffraction effects.

In order to proper position the sample with respect to the beam and to effectively position the other optical components (chopper, optical fibre and lens) out of the radiation

path, X-rays fluorescence paper and X-rays photosensitive paper were used.

3.2 Acquisition Software

In the earlier steps, the monochromator was controlled via a custom MATLAB software, which was designed to move the monochromator while acquiring data with a Digilent DAQ.

While this was sufficient for alignment and grating testing, for proper photocurrent spectra acquisitions there was the need to mirror the capabilities of the LabVIEW software that controlled the ScienceTech-9055F monochromator.

The SP-150 can communicate both via serial RS-232 cable and via GPIB cable. After several tests, it was established that the GPIB connection was more robust and reliable.

The code has been developed in Python using PyVISA for serial resources management and PyQt6 for the creation of a Graphical User Interface (GUI).

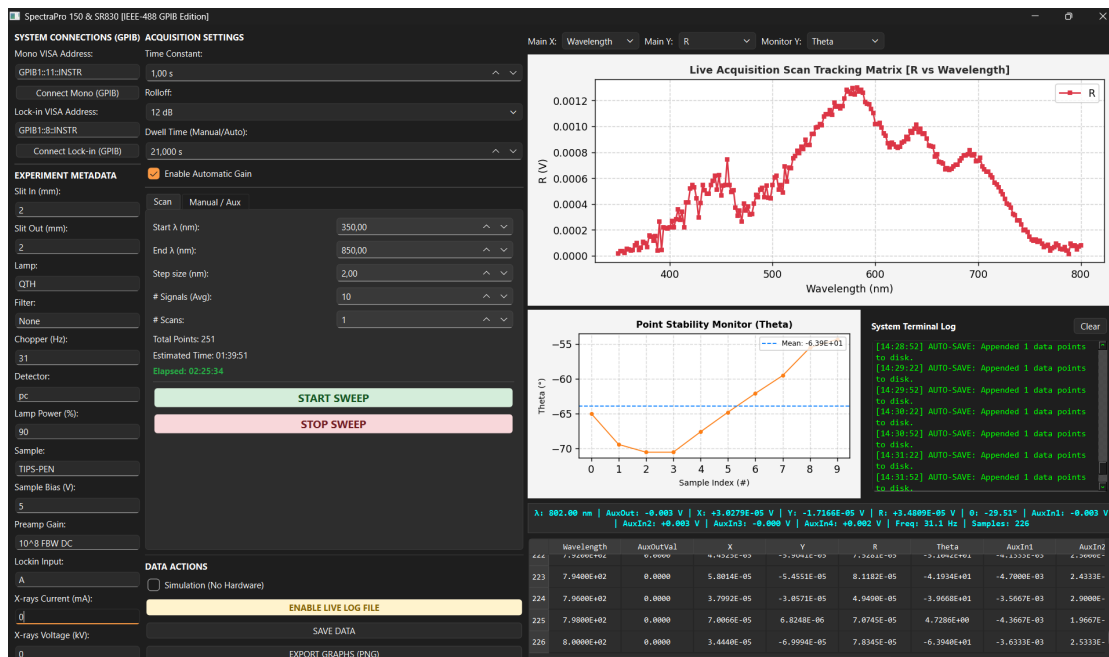


Figure 3.5: Screenshot of SP150-SR830 Control main panel. The leftmost column contains connection buttons and metadata fields. The central column allows to control the run mode and set the lock-in parameters. The rightmost column is dedicated to data visualization and log monitoring.

From left to right, the GUI is structured in three main columns, as depicted in Fig. 3.5:

- instruments connection and experiment metadata tracking;

- acquisition handling (time-affecting parameters, control mode, data saving);
- data visualization.

The central column has two tabs: Scan and Manual/Aux (Fig. 3.6). While Scan tab is responsible for the standard wavelength sweeps, in the Manual/Aux tab it is possible to send raw commands to the monochromator or to start lock-in Aux channels sweeps.

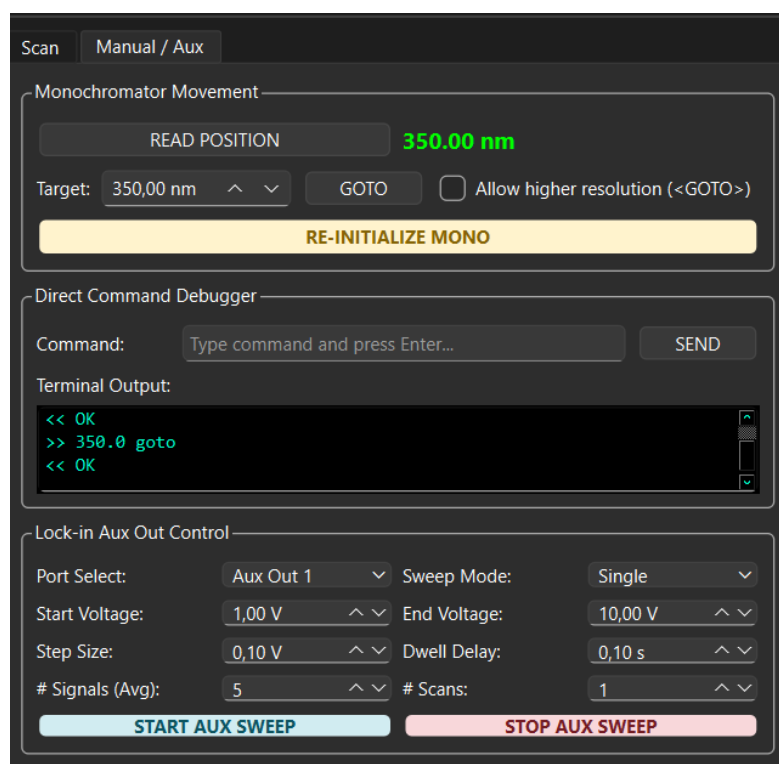


Figure 3.6: Screenshot of SP150-SR830 Control manual/aux tab. While the Scan tab allows to perform a standard wavelength sweep, this tab is designed to send basic serial commands to the monochromator and to control lock-in Aux channel sweeps.

The software is constructed to handle two threads, one allowing for live display of lock-in readings and the other managing the monochromator movement and the signal averaging.

The software was written exploiting generative AI models under strict human supervision and, after extensive testing, it is also available on GitHub at the link https://github.com/Sollau/Instrument_Controls.git.

3.3 UV-Vis Sources Calibration

Source calibration involves the acquisition of the spectrum of the lamp used for the measurement, with the final goal to correct the sample data, since their raw signal amplitude is convoluted with the lamp emission spectra.

The parameter to measure is the lamp spectral photon flux¹ Φ , which is obtained by dividing the raw lamp signal S_{raw} by the responsivity of the detector R_{det} used to acquire it:

$$\Phi(E) = \frac{S_{raw}(E)}{R_{det}(E) \cdot E_{ph} \cdot \mathcal{A}_{eff}} \quad (3.1)$$

in the formula, E_{ph} is the energy of the photons and $\mathcal{A}_{eff}$ is the effective active area of the detector. The latter depends also on the slit width d , and can be evaluated as follows:

$$\begin{aligned} \theta &= 2 \arctan \left(\frac{d}{2R} \right) \\ \mathcal{A}_{eff} &= \frac{2dR}{\sqrt{1 + \left(\frac{d}{2R} \right)^2}} + R^2 (\theta - \sin \theta) \end{aligned} \quad (3.2)$$

with R detector radius and θ being the angle indicated in Fig. 3.7.

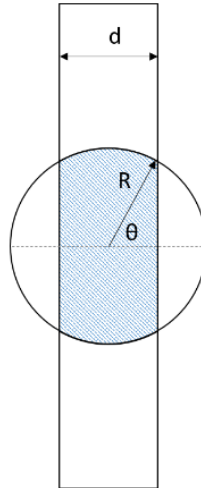


Figure 3.7: Effective area of detection given the slit width. This scheme applies whenever the slit width d is smaller than the detector diameter $2R$. The image is adapted from [31].

¹The photon flux is measured in units of photons per second per square centimetre ($ph\ s^{-1}cm^{-2}$).

Once the photon flux coming from the lamp is known, the actual photocurrent spectrum I_{PC} is obtained by dividing the raw signal I_{raw} for the photon flux.

$$I_{PC} = \frac{I_{raw}}{\Phi} \quad (3.3)$$

For better visualization, the photocurrent is then rescaled between 0 and 1 by dividing it by its maximum.

3.3.1 QTH Lamp

The spectrum of the QTH lamp used in the benchmark setup has been collected both with the SiPD and with the PYRO detector. The raw spectra can be observed in Fig. 3.8.

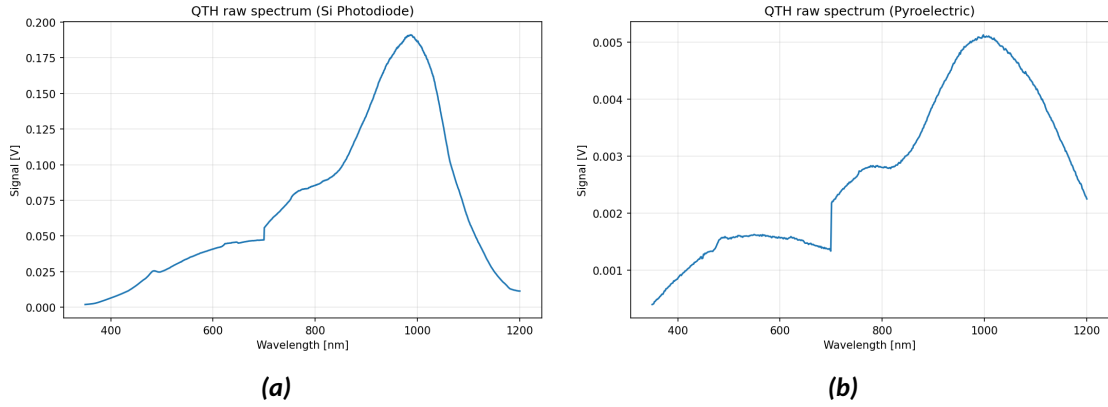


Figure 3.8: QTH raw spectra. At 700 nm, the grating change introduces a step and, beyond, modifies the intensity of the diffracted light, increasing the curve slope. In both cases, the lamp is operated at 23 V and 5.9 A. In (a) the QTH lamp spectrum acquired with SiPD detector at 0.4 mm slit width. The lock-in time constant was set to 100 ms. In (b) the QTH lamp spectrum acquired with PYRO detector at 0.5 mm slit width and lock-in time constant at 1 s. A 60 dB voltage amplification stage is added.

Following Eq. (3.1), the photon flux has been computed. In Fig. 3.9, the evaluated photon flux is shown for both detectors in logarithmic and in linear scale. It has to be noticed that, since the SiPD detector has a limited spectral range (190-1110 nm), inferior to the lamp spectrum acquisition window, mathematical artifacts appear in the flux curves. In this region, starting from ~900 nm, the SiPD detector is not reliable and the PYRO calibration must be used. Figures 3.9b and 3.10 display also alternative plotting strategies beyond this critical wavelength, which are further explained in Appendix B.

The computed flux is of the order of $10^{13} ph/(s \cdot cm^2)$. Due to the wavelength-independent responsivity of the pyroelectric detector, data collected with this latter

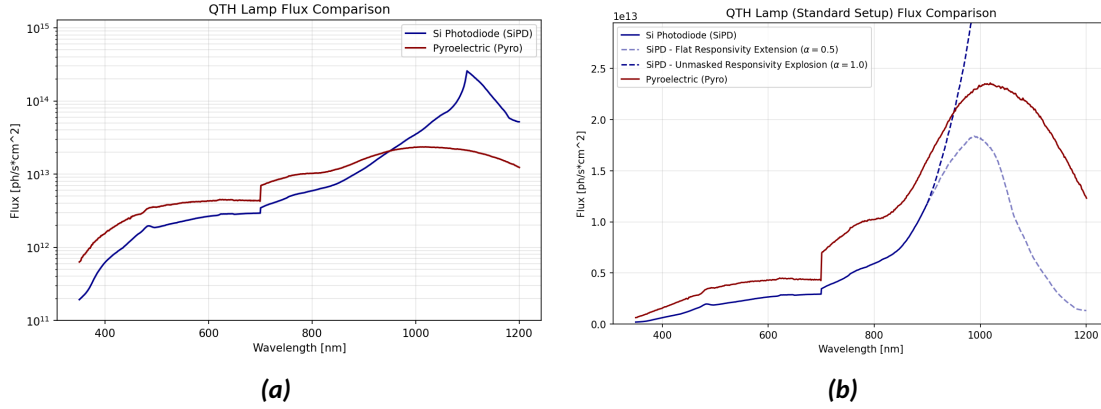


Figure 3.9: Comparison of QTH lamp flux obtained with SiPD and PYRO detectors. (a) Flux in logarithmic scale; the cusp at 1110 nm is a mathematical artifact due to the interpolation over the rapidly-falling SiPD responsivity. (b) Flux in linear scale; beyond 900 nm, the division by the responsivity curve is stopped, causing the flux to diverge (opaque dashed line) due to the detector responsivity drop. The semitransparent dashed curve shows the flux computed by keeping the responsivity constant at its 900 nm value.

are more reliable, and this has been also verified with a THORLABS PM400 Optical Powermeter. The procedure involved manual recording of the lamp power at discrete wavelengths. For each point, the instrument returned both the raw detected power and the value normalized by its SiPD sensor. For the purpose of the comparison Fig. 3.10, the data have been divided by the sensor active area, while the lamp flux has been converted to power density by multiplying for the photon energy.

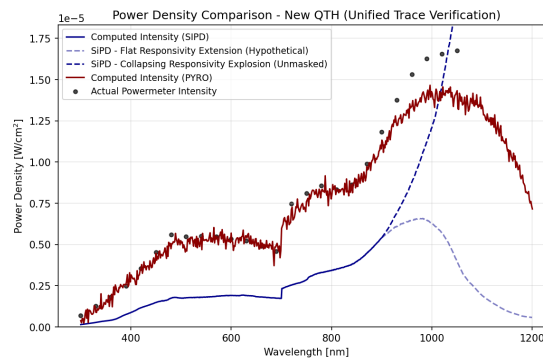


Figure 3.10: Powermeter verification of QTH lamp power density.

It has to be noticed that the spectra in Fig. 3.10 are slightly different from those in Figs. 3.8 and 3.9 since the lamp filament broke and therefore the lamp was substituted.

3.3.2 Xenon Lamp

The xenon lamp was used as an alternative to the QTH for the acquisition of the $\text{PEA}_2\text{PbBr}_4$ samples photocurrent spectra, where high UV photon flux, not achievable with QTH, is needed. The result of the Xe lamp calibration are reported below: Fig. 3.11 shows the raw spectra collected with the two detectors, while in Fig. 3.12 a comparison of the flux computed with respect to each detector is reported.

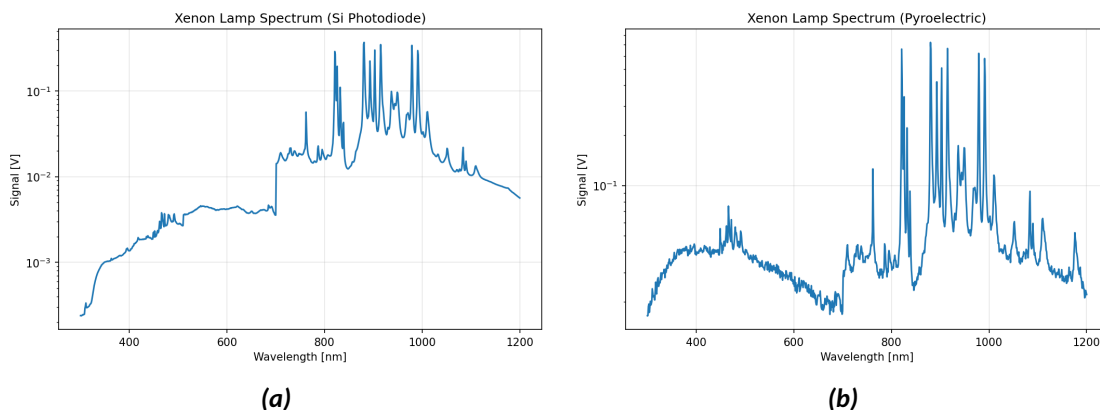


Figure 3.11: Xenon lamp raw spectra: (a) spectrum obtained with the SiPD detector at a 1.5 mm slit width; (b) spectrum obtained with the PYRO detector at a 0.2 mm slit width. In both cases, the lock-in time constant was set to 300 ms.

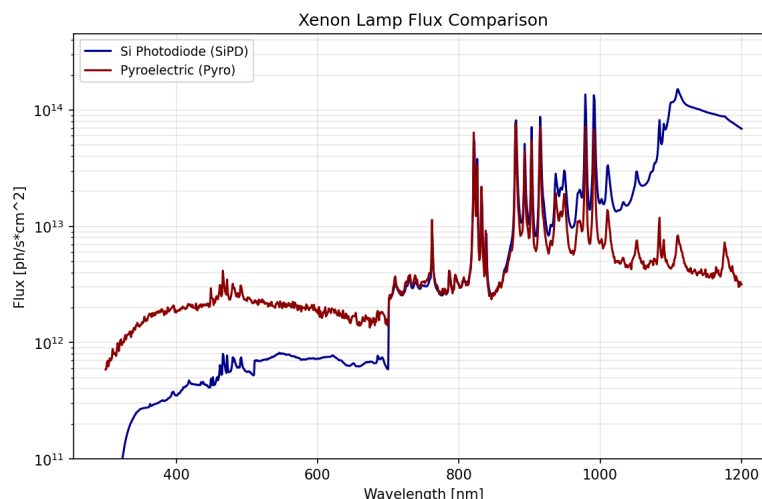


Figure 3.12: Xenon lamp flux. Even if no mathematical artifacts appear in this plot for the SiPD-computed flux, the non-linear spectral response of this detector clearly affects the flux calculation.

The choice of plotting the data exclusively in logarithmic scale for this lamp stems from the fact that, due to the high intensity of Hg and Xe characteristic spectral lines, they are spread over almost two orders of magnitude.

In the UV-Vis spectral range, the intensity of the lamp photon flux is comparable in order of magnitude with that of a QTH lamp.

3.4 Lock-in Noise Analysis

In order to assess the amount of noise affecting the lock-in measurements, the most common configurations in which the lock-in has been used during the acquisitions have been probed.

The lock-in input was left unconnected and floating, while its AUX exit drove the chopper in a sweep from 0 to 10 V (which corresponded to the 0 to 343 Hz range). The results are displayed in Fig. 3.13.

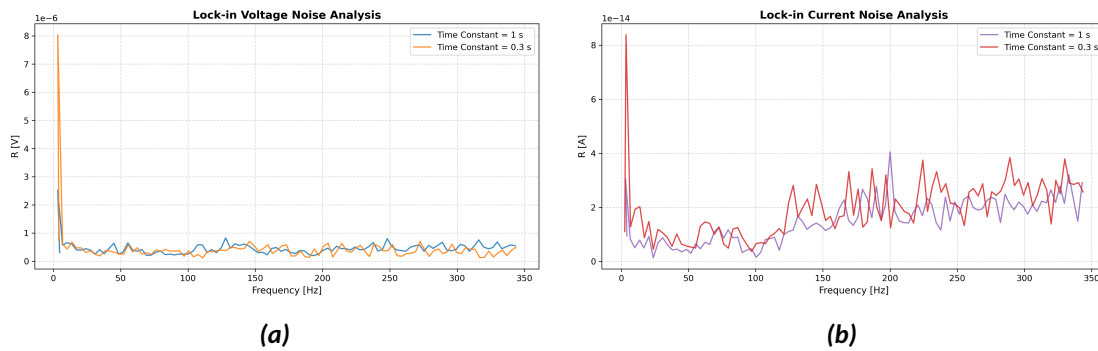


Figure 3.13: Lock-in noise analysis on two different input modes: (a) voltage noise analyses at 0.3 s and 1 s time constants; (b) current (10^8 input) noise analyses at 0.3 s and 1 s time constants. The parameters for both graphs are: 12 dB/oct roll-off, 50 Hz and 100 Hz line filters active, high reserve, ground, sync <200 Hz active, and AC coupling.

Apart from the spike near 0 Hz, the voltage noise is essentially constant. The current noise analysis has instead more interesting features: at 50 and 100 Hz, where the line filters are active, the noise is visibly suppressed; then, looking at the general trend of the noise, a subtle increase of its average value can be noticed towards the higher frequencies.

3.5 Samples Specifications

In Table 3.1 the samples employed for this study are presented.

Sample	Type	Contacts Geometry	Morphology
BA ₂ PbI ₄	2D Perovskite	co-planar	thin film
PEA ₂ PbBr ₄ -sc	2D Perovskite	co-planar	single-crystal
PEA ₂ PbBr ₄ -film	2D Perovskite	co-planar	thin film
MAPbBr ₃	3D Perovskite	top-bottom	single-crystal
TIPS-PEN	Organic Semiconductor	co-planar	thin film

Table 3.1: Samples overview. The full chemical names, in order from the top row, are: butylammonium lead iodide, phenethylammonium lead bromide(single-crystal and thin film), Methylammonium lead bromide and triisopropylsilylethynyl pentacene.

Despite the differences in material, morphology and contacts geometry, all samples are photoconductors.

Thin film samples are all characterized by the same interdigitated electrodes geometry (Fig. 3.14). The electrodes are made of a 30nm-thick gold (Au) layer plus an adhesion chromium (Cr) layer and are patterned via photolithography onto the substrates. The substrates used are Kapton (PEA₂PbBr₄-film), glass (BA₂PbI₄) and PEN (TIPS-PEN). The semiconductor film is deposited onto the electrodes via bar-coating (PEA₂PbBr₄-film), spin-coating (BA₂PbI₄) or drop-casting (TIPS-PEN).

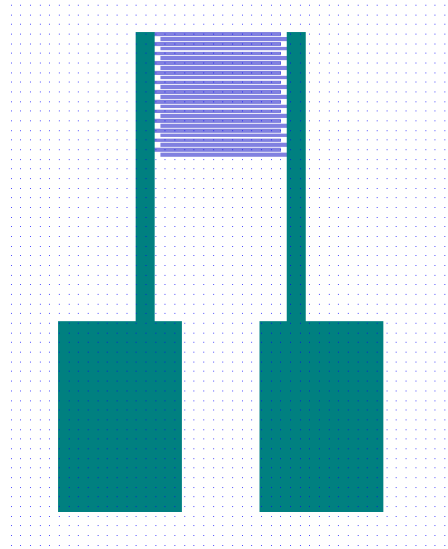


Figure 3.14: Diagram of the 1-pixel interdigitated electrodes. The channel width is $30\mu\text{m}$ while the channel length can be obtained as $L = (n - 1) \cdot l$, where n is the number of fingers of the interdigitated (here 26) and l is the length of the channel long side (here 2 mm), for a total of 50mm . This geometry is common to samples BA₂PbI₄, PEA₂PbBr₄-film and TIPS-PEN.

Both single-crystal samples feature a dielectric substrate layer (mica) on which cop-

per (Cu) contact pads are positioned with silver (Ag) paste.

The electrodes are deposited directly onto the sample surface via thermal evaporation with shadow mask.

Sample MAPbBr_3 has Cr electrodes, which are connected to the Cu pads with Ag paste (bottom electrode) and with an Au wire fixed with Ag paste (top electrode).

Sample $\text{PEA}_2\text{PbBr}_4\text{-sc}$ is instead secured onto the mica substrate via Ag paste; Au wires (always fixed with Ag paste on both ends) connect its Au/Cr electrodes to the Cu pads. In Figs. 3.15 and 3.16 the respective structures are shown.

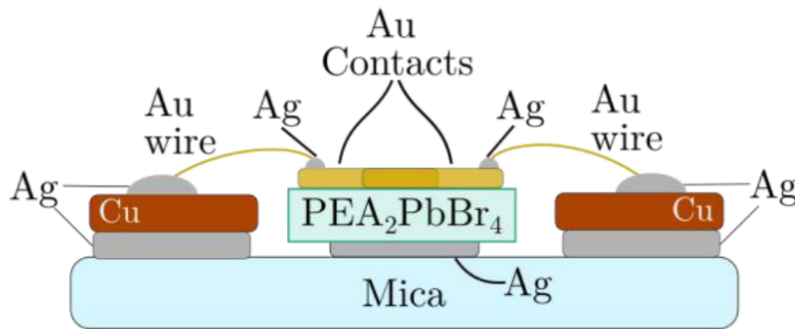


Figure 3.15: Scheme of $\text{PEA}_2\text{PbBr}_4$ single-crystal structure. The image is adapted from [44].

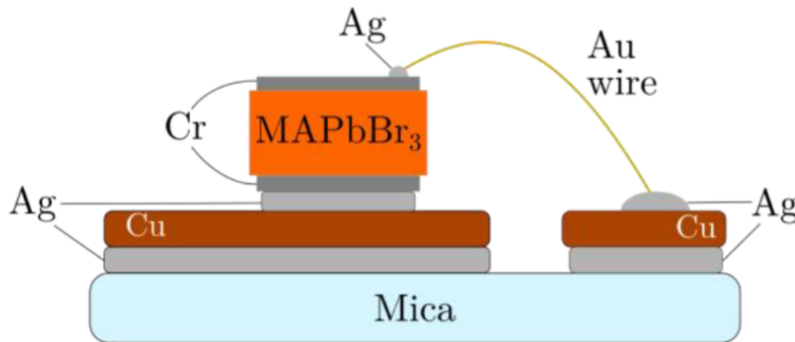
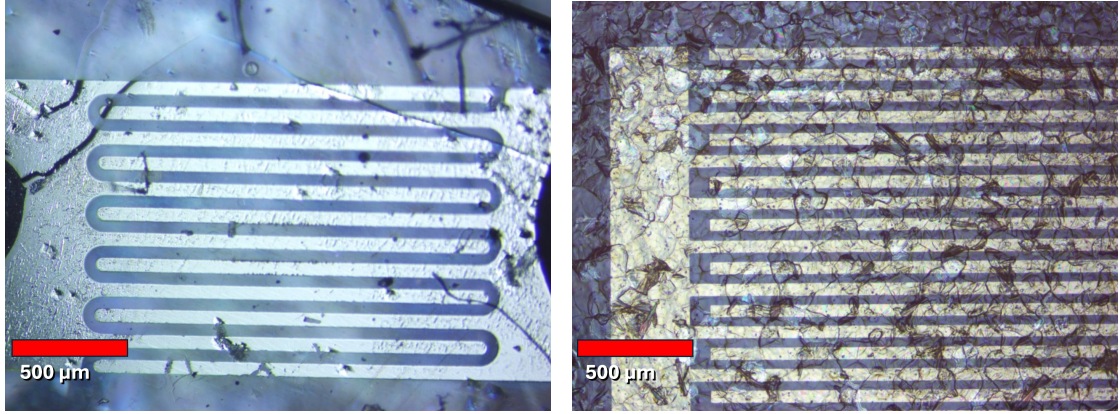


Figure 3.16: Scheme of MAPbBr_3 sample structure. The crystal has dimensions of $5 \times 5 \times 2 \text{ mm}$. The image is adapted from [44].

Of the samples under analysis, the two single crystals, $\text{PEA}_2\text{PbBr}_4\text{-sc}$ and MAPbBr_3 are the oldest (dating to 2022 and 2023 respectively), while the others were fabricated within the time period of this thesis project. Sample BA_2PbI_4 , used only as a first test for the validation of the benchmark photocurrent setup, degraded after few days outside of the glovebox.

In Figs. 3.17 and 3.18, optical microscope pictures of the $\text{PEA}_2\text{PbBr}_4$ and TIPS-PEN samples – taken to verify the channel condition and to highlight the difference between single-crystal and thin film morphologies – are reported.



(a) Detail of $\text{PEA}_2\text{PbBr}_4$ single-crystal sample. The channel has dimensions of $50\mu\text{m} \times 18.23\text{mm}$. Although old, the sample is still in good conditions.

(b) Detail of $\text{PEA}_2\text{PbBr}_4$ thin film sample. The channel has dimensions of $30\mu\text{m} \times 50\text{mm}$, thus greater than $\text{PEA}_2\text{PbBr}_4\text{-sc}$ sample.

Figure 3.17: $\text{PEA}_2\text{PbBr}_4$ samples pictures. The poly-crystalline nature of the thin film is neatly distinguishable.

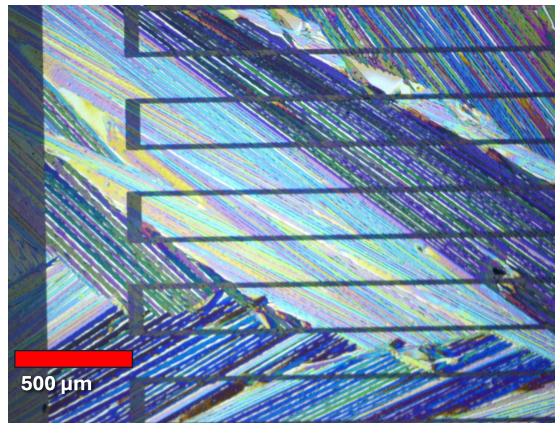


Figure 3.18: Picture of a TIPS-PEN sample. The sample in this image is not the same as the one on which the final measurements were performed, since it degraded and was substituted; however, it provides a clear example of TIPS-PEN film structure.

The $\text{PEA}_2\text{PbBr}_4\text{-sc}$ has a smooth surface with large uniform grain domains, while sample $\text{PEA}_2\text{PbBr}_4\text{-film}$ shows a dense disordered network of small grains. TIPS-PEN displays highly anisotropic, large crystalline domains with elongated needle-like morphology.

3.6 Data Analysis

In Fig. 3.19 the procedure to go from raw data to the extraction of the relevant parameters and figures of merit is shown.

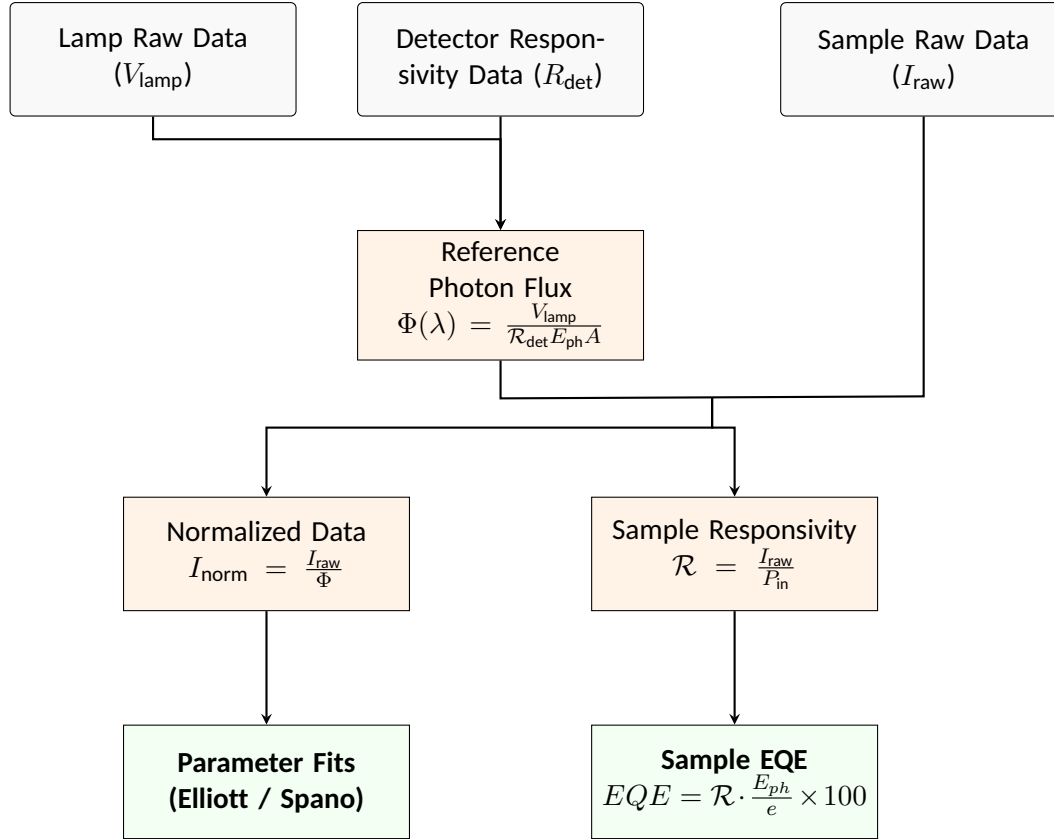


Figure 3.19: Data analysis flowchart. The procedure involves three fundamental steps: flux calculation, correction of sample raw data by flux normalization, extraction of the fit parameters and figures of merit.

When the sample raw data are corrected for the lamp flux, the unit of measure obtained is a photocurrent per flux [$A/(ph\ cm^{-2}s^{-1})$]. For improved visual clarity, in the graphs, this quantity is expressed as arbitrary units and rescaled between 0 and 1. When comparing in the same graph the photocurrent spectra of different samples or acquisitions, the normalization can be performed in two ways:

- if the relative magnitude of the spectra is relevant for the comparison, the scaling is performed globally after plotting, i.e. by dividing the spectra by the maximum value among all the datasets;

- if only the shape is relevant for the comparison, the scaling is performed individually on the two dataset (each one divided by a relevant common feature, such as the maximum of the excitonic peak) and then the profiles are plotted together.

The calculation of the responsivity involves dividing for the optical power instead that for the lamp flux. The formula used in this passage differs from Eq. (1.12) for an additional multiplicative term $r_w = w_{sample}/w_{lamp}$ which accounts for the different slit widths used to acquire the lamp and the sample spectra:

$$P_{in} = \Phi E_{ph} \mathcal{A}_{ch} r_w \quad (3.4)$$

where $\mathcal{A}_{ch}$ is the channel area of the sample. It is important to keep in mind that the responsivity is not an intrinsic property of the material as it is also influenced by the device morphology and architecture. Nonetheless, it is still a valuable parameter when coming to the evaluation of the system performance under the given experimental conditions.

The actual fitting formula employed in the data analysis differ from the theoretical ones in Chapter 1. In particular, to account for non-ideal effects (disorder, thermal effects, non-parabolicity of the bands, collection efficiency, experimental noise...), a truncated 3D Elliott model [45, 46] was implemented both for the 3D and the 2D IOHP samples:

$$\alpha_{total}(E) = \alpha(E) \cdot \eta_c(E) + y_0 \quad (3.5)$$

Where the modified 3D Elliott absorption coefficient $\alpha(E)$ is defined as:

$$\alpha(E) = A\sqrt{E_b} [a_x \cdot 2E_b \cdot g(E - (E_g - E_b), \Gamma) + \int_{E_g}^{\infty} g(E - E', \Gamma) \frac{1 + b_{np}(E' - E_g)}{1 - \exp\left(-2\pi\sqrt{\frac{E_b}{E' - E_g}}\right)} dE'] \quad (3.6)$$

Here, $g(\Delta E, \Gamma)$ represents the Gaussian broadening function capturing inhomogeneous disorder:

$$g(\Delta E, \Gamma) = \frac{1}{\Gamma\sqrt{2\pi}} \exp\left(-\frac{1}{2} \left(\frac{\Delta E}{\Gamma}\right)^2\right) \quad (3.7)$$

The term $\eta_c(E)$ is the asymmetric carrier extraction efficiency filter, accounting for high-energy transport losses:

$$\eta_c(E) = \begin{cases} \exp\left(-\frac{E - E_g}{\tau}\right) & \text{for } E > E_g \\ 1.0 & \text{for } E \leq E_g \end{cases} \quad (3.8)$$

In the above equations, E_g is the material bandgap energy, E_b the exciton binding energy, Γ the Gaussian broadening parameter representing inhomogeneous disorder, b_{np} the linear non-parabolicity coefficient, a_x the scaling factor for the discrete ground-state excitonic contribution, A the global amplitude scaling factor, τ the carrier collection decay constant, and y_0 the experimental baseline offset.

The Tauc plot is modified too, according to the strategies proposed by Makula et al. [21]: instead of following the procedure described in Chapter 1, the code calculates the first derivative of the smoothed spectrum, identifies the point of maximum slope, fits a straight line tangent to it and extrapolates its intercept.

4. Results and Discussion

In the following sections, the experimental results are presented and compared to the established literature values, when available.

Apart from BA_2PbI_4 , which underwent just the UV-Vis photocurrent measurement with the standard setup, each sample was characterized electrically collecting an I-V curve in dark and under 375 nm light¹ before having its photocurrent spectra recorded in the standard apparatus, and then in the compact one (both with and without X-rays irradiation). Linear I-V plots and raw sample spectra are left out from this chapter, but can be found in Appendix A.

The parameters of each acquisition are summarized in Tables 4.1 and 4.2.

Acquisition Parameters For Standard Setup							
Sample	Sample Bias [V]	Lock-in input	Lock-in tau [s]	Chopper Freq [Hz]	Preamp Gain [V/A]	Lamp	Slit in/out [mm]
BA_2PbI_4	5	I, 10^6	0.3	42	-	QTH	1
$\text{PEA}_2\text{PbBr}_4\text{-sc}$	20	A	0.3	62	10^9	Xe	1
$\text{PEA}_2\text{PbBr}_4\text{-film}$	20	A	1	62	10^9	Xe	1
MAPbBr_3	10	I, 10^6	0.3	67	-	QTH	1
TIPS-PEN	5	I, 10^6	1	31	-	QTH (new)	1

Table 4.1: Acquisition parameters and settings in the standard setup.

Acquisition Parameters For Compact Setup							
Sample	Sample Bias [V]	Lock-in input	Lock-in tau [s]	Chopper Freq [Hz]	Preamp Gain [V/A]	Lamp Power [%]	Slit in/out [mm]
$\text{PEA}_2\text{PbBr}_4\text{-sc}$	20	A	0.3	62	10^8	80	1
$\text{PEA}_2\text{PbBr}_4\text{-film}$	20	A	1	62	10^8	90	2
MAPbBr_3	10	I, 10^6	0.3	67	-	80	1
TIPS-PEN	5	I, 10^8	1	31	-	90	2

Table 4.2: Acquisition parameters and settings in the compact setup. When performing sweeps under X-rays irradiation, the tube settings were at 30 mA electronic current and 35 kV cathodic voltage for all the samples.

¹The source was a UV LED with a calibrated power density of $316 \mu\text{W}/\text{cm}^2$ at 3 cm from the sample.

4.1 BA_2PbI_4

For sample BA_2PbI_4 , a forward-backwards sweep was executed in the standard UV-Vis photocurrent spectroscopy apparatus. The return scan yielded a higher signal in correspondence of the peaks: this hysteresis effect is likely due to the fact that the carriers excited by the first scan filled trap states leading to a higher collection efficiency on the return scan.

Fig. 4.1 shows the corrected and normalized photocurrent spectra of BA_2PbI_4 . Two distinct peaks are visible: one at ~ 520 nm, corresponding to the excitonic peak, and another at ~ 490 nm, marking the fundamental absorption edge and the start of the continuum.

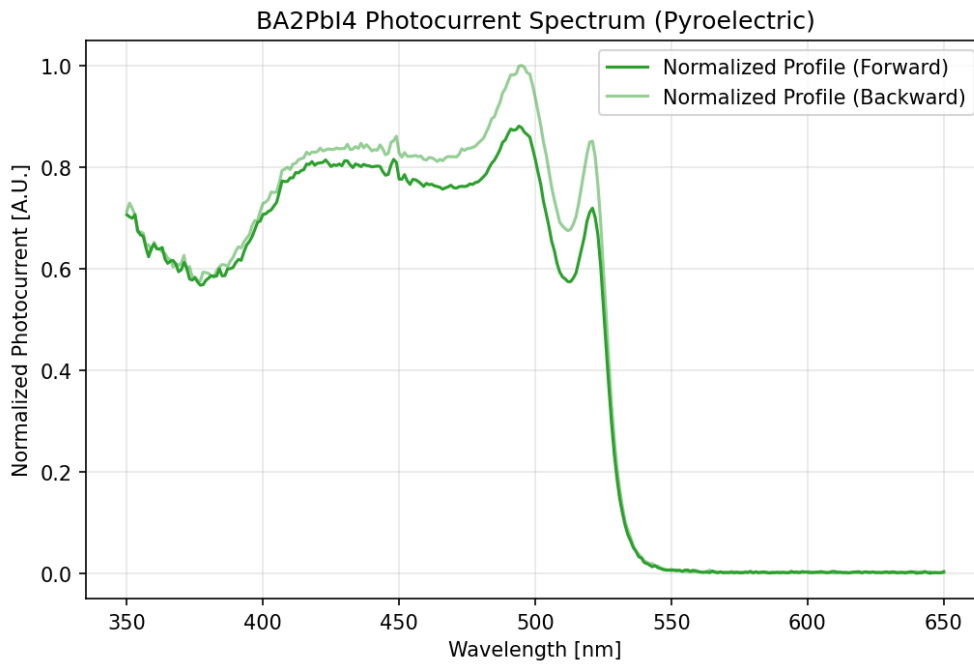


Figure 4.1: BA_2PbI_4 photocurrent spectrum, corrected for the QTH lamp flux and normalized. Both forward and backward scan, collected at 5 V bias, are shown.

The responsivity, computed on the forward scan, is 3.5 ± 0.1 mA/W at the 490 nm peak, which falls within the expected literature range [11]. Fig. 4.2 shows the spectral response of the sample.

The Elliott fit performed on BA_2PbI_4 yielded an energy gap of 2.43 ± 0.01 eV and an exciton binding energy of 48 ± 5 eV. The energy bandgap is in good agreement with known literature values [47], whereas the binding energy is far lower than the commonly acknowledged values of 200-300 meV [11, 47, 48].

The fit is plot in Fig. 4.3.

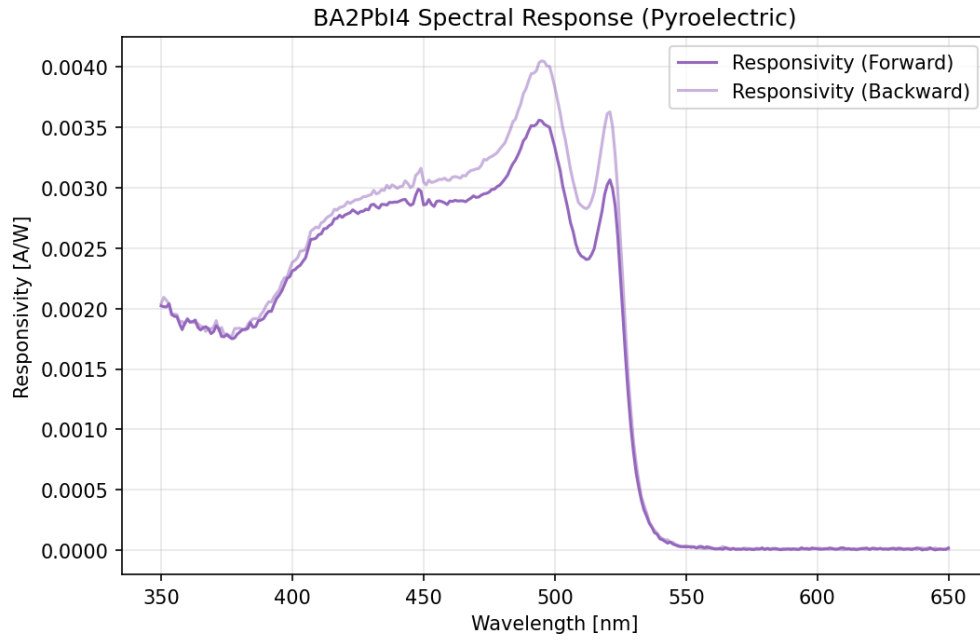


Figure 4.2: BA_2PbI_4 spectral response. Both forward and backward scan are shown.

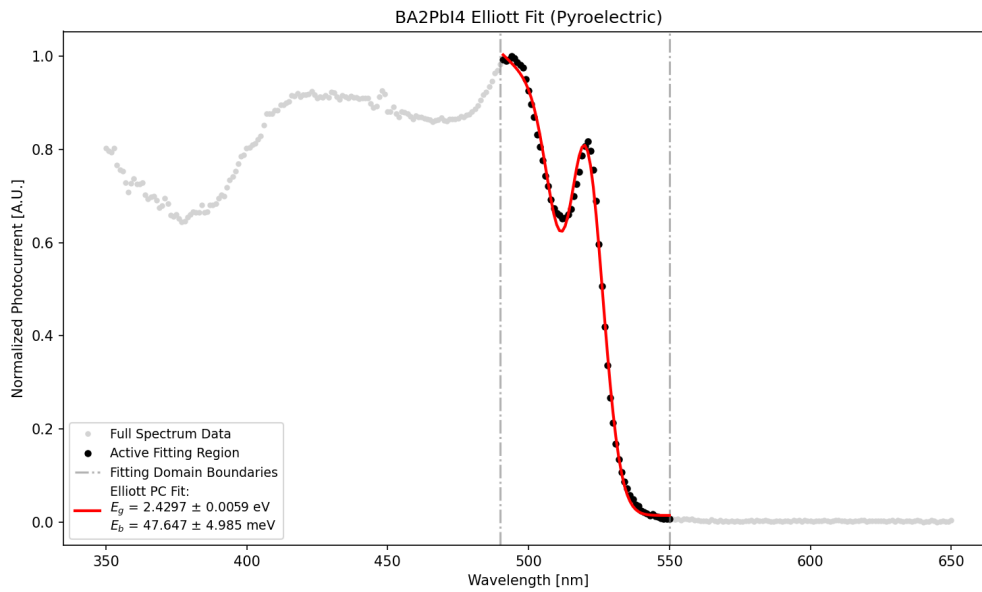


Figure 4.3: Truncated 3D Elliott fit applied on BA_2PbI_4 photocurrent spectrum. The model is applied in the window 490-550 nm to the forward trace.

Table 4.3 summarized the extracted parameters for the BA_2PbI_4 sample.

Extracted Parameters	
Responsivity	$3.5 \pm 0.1 \text{ mA/W}$
EQE	$0.89 \pm 0.03 \%$
Energy Gap	$2.43 \pm 0.01 \text{ eV}$
Binding Energy	$48 \pm 5 \text{ meV}$

Table 4.3: BA_2PbI_4 extracted figures of merit. The values of responsivity and EQE are evaluated at 5 V bias in correspondence of the 490 nm peak. All the parameters are computed on the forward scan.

4.2 $\text{PEA}_2\text{PbBr}_4$

The I-V curves of the two $\text{PEA}_2\text{PbBr}_4$ samples are plotted in Fig. 4.4. It is important to notice that, even if the voltage range is the same, the results are not directly comparable, since the two samples have different channel dimensions. For example, at 20 V applied bias, the resulting electric field is 4000 V/cm for the single-crystal and 6667 V/cm for the film². Comparing the values of the currents at 4000 V/cm electric field, I_{dark} ranges from 8 to 20 pA for $\text{PEA}_2\text{PbBr}_4$ -sc and of from 0.7 to 1 pA for $\text{PEA}_2\text{PbBr}_4$ -film; while I_{light} is 0.6 nA for the single-crystal and 30 nA for the film.

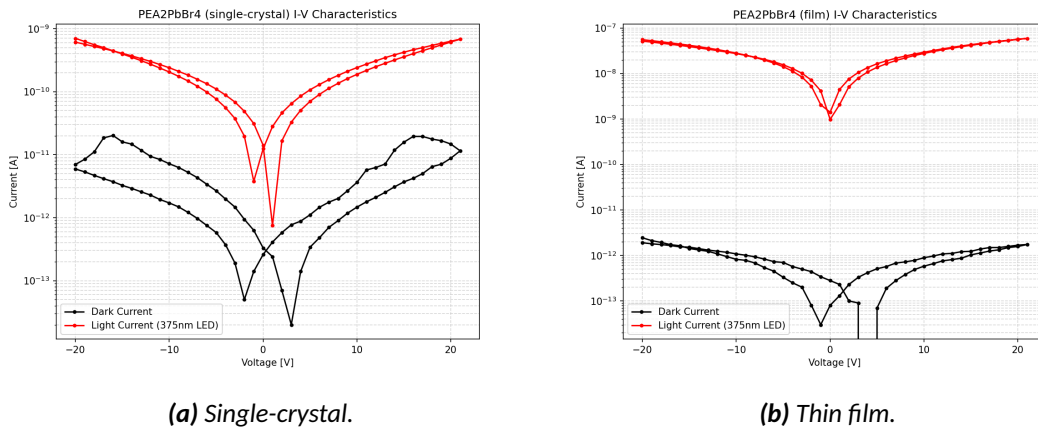


Figure 4.4: $\text{PEA}_2\text{PbBr}_4$ samples I-V characteristics. Light current is acquired under a 375 nm LED for a total power of $2.88 \mu\text{W}$ on the single-crystal (a) and of $4.74 \mu\text{W}$ on the thin film sample (b). The power is computed onto the channel areas.

The unexpected lower photocurrent response in $\text{PEA}_2\text{PbBr}_4$ -sc can be explained due to ageing-related degradation of that sample – which, indeed, shows also more hys-

²The electric field is computed as $E = V/d$, where d is the distance between adjacent fingers of the interdigitated.

teresis. A comparison with the I-V curve dating back to its creation [49] shows that the current at 10 V decreased from 40 nA to 0.2 nA, a difference which cannot be traced back to the different 375 nm LED used.

Besides this reduction in magnitude, the shape of the I-V curve has remained almost unaltered across the years. The sample has still a linear behaviour in the $[-10, 10]$ V range, and exhibits a small rectifying trend towards the -20 V and 20 V limits.

Sample $\text{PEA}_2\text{PbBr}_4$ -film demonstrates a pure ohmic behaviour throughout the full $[-20, 20]$ V range. Its I-V characteristics is in line with results obtained for similar samples [50].

The I-V characteristics confirmed that a bias of 20 V was suitable for the photocurrent spectroscopy measurements.

Figure 4.5 shows a comparison of the corrected spectra of the two $\text{PEA}_2\text{PbBr}_4$ samples. Since the experimental conditions were different, the relative intensities are not relevant and the normalization has been performed separately before plotting.

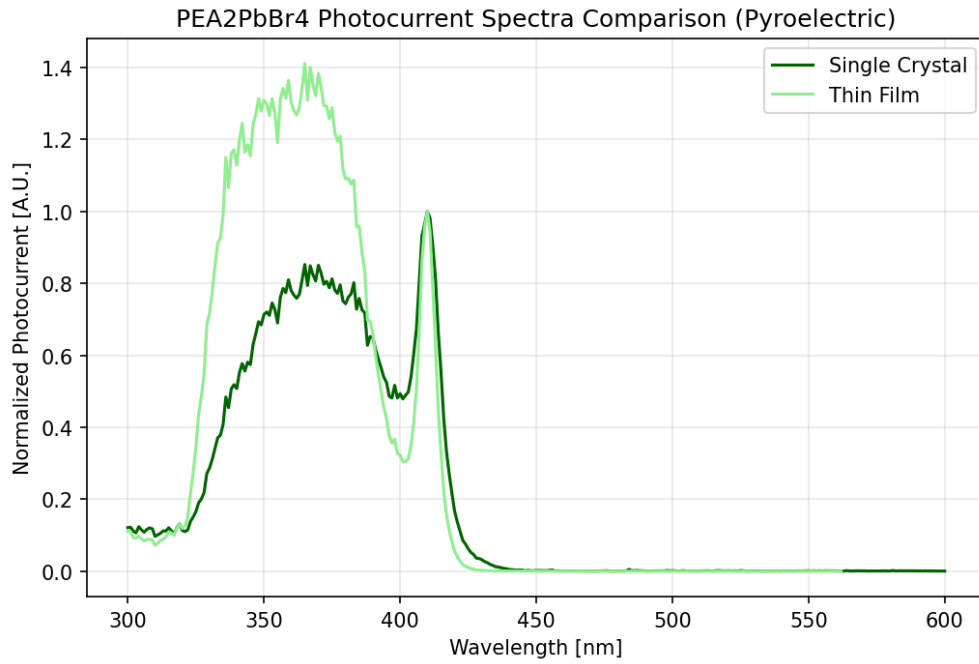


Figure 4.5: Comparison of $\text{PEA}_2\text{PbBr}_4$ samples photocurrent spectra, corrected for the Xe lamp flux and separately normalized for the height of the excitonic peak before being plotted together.

Both samples display a first peak at 410 nm (excitonic) and a hump peaked around 375 nm (the continuum). While in the film the continuum signal dominates, in $\text{PEA}_2\text{PbBr}_4$ -sc the continuum hump is reduced in intensity with respect to the excitonic peak. This is due to the fact that the absorption coefficient at those wavelengths is lower and therefore carriers are generated more deeply into the crystal, leading to increased re-

combination probability in their path towards the surface electrodes. In $\text{PEA}_2\text{PbBr}_4$ -film, the sample is instead thin enough that all the generated carriers are subject to the electric field produced at the surface electrodes, increasing thus the charge collection efficiency.

The shapes of the spectra are consistent with those in literature [50–52].

The spectral responses of the two $\text{PEA}_2\text{PbBr}_4$ samples are shown in Fig. 4.6. The responsivity of sample $\text{PEA}_2\text{PbBr}_4$ -sc is 0.80 ± 0.01 mA/W at the excitonic peak against the 53 ± 1 mA/W at peak of sample $\text{PEA}_2\text{PbBr}_4$ -film.

The single-crystal sample performed worse than the film: similar studies report that the single-crystal can have a responsivity of 12 mA/W, a value even 20 times higher than their film equivalents [52].

As suggested by the I-V curves, the reason of the discrepancy must be searched in the sample conditions. The truncated 3D Elliott fit has been performed on both samples

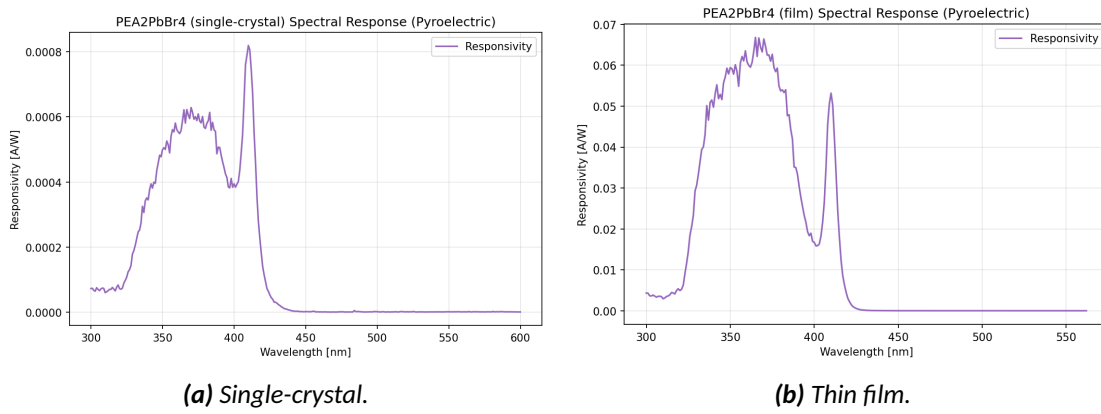


Figure 4.6: $\text{PEA}_2\text{PbBr}_4$ samples responsivity profiles.

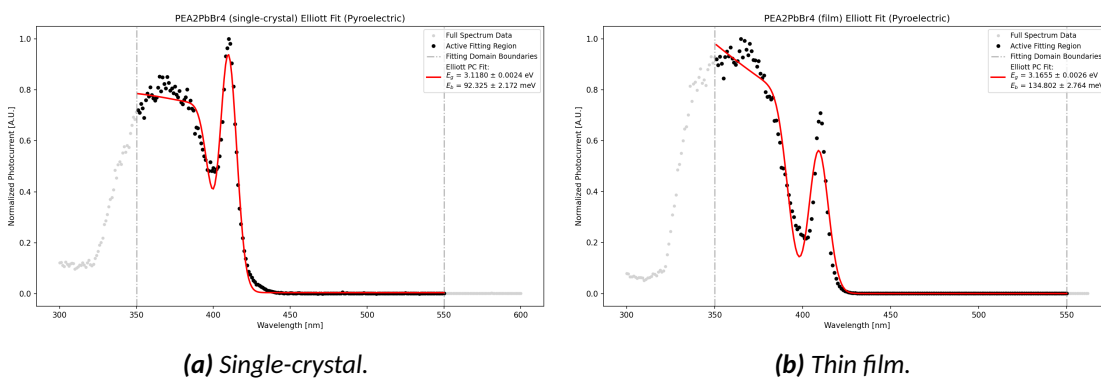


Figure 4.7: Truncated 3D Elliott fit applied on the two $\text{PEA}_2\text{PbBr}_4$ samples. In both cases, the fit window is 350 to 550 nm.

using the same fitting window Fig. 4.7. For PEA₂PbBr₄-sc, E_g is 3.12 ± 0.01 eV and E_b is 92 ± 2 meV. These values are close to those obtained by Ciavatti et al., who computed an energy gap of 3.08 ± 0.2 and a lower binding energy of ~ 60 meV [52].

The fit on the film yielded higher values than the single-crystal, with an energy bandgap of 3.17 ± 0.01 eV and an exciton binding energy of 135 ± 3 meV. These values are higher than those previously reported for analogous PEA₂PbBr₄ polycrystalline thin films[50] but the different deposition technique may have impacted on the material charge transport properties, affecting the photocurrent and ultimately the parameters that can be extracted from the fit.

Effects of X-rays on the photocurrent spectra of PEA₂PbBr₄ samples

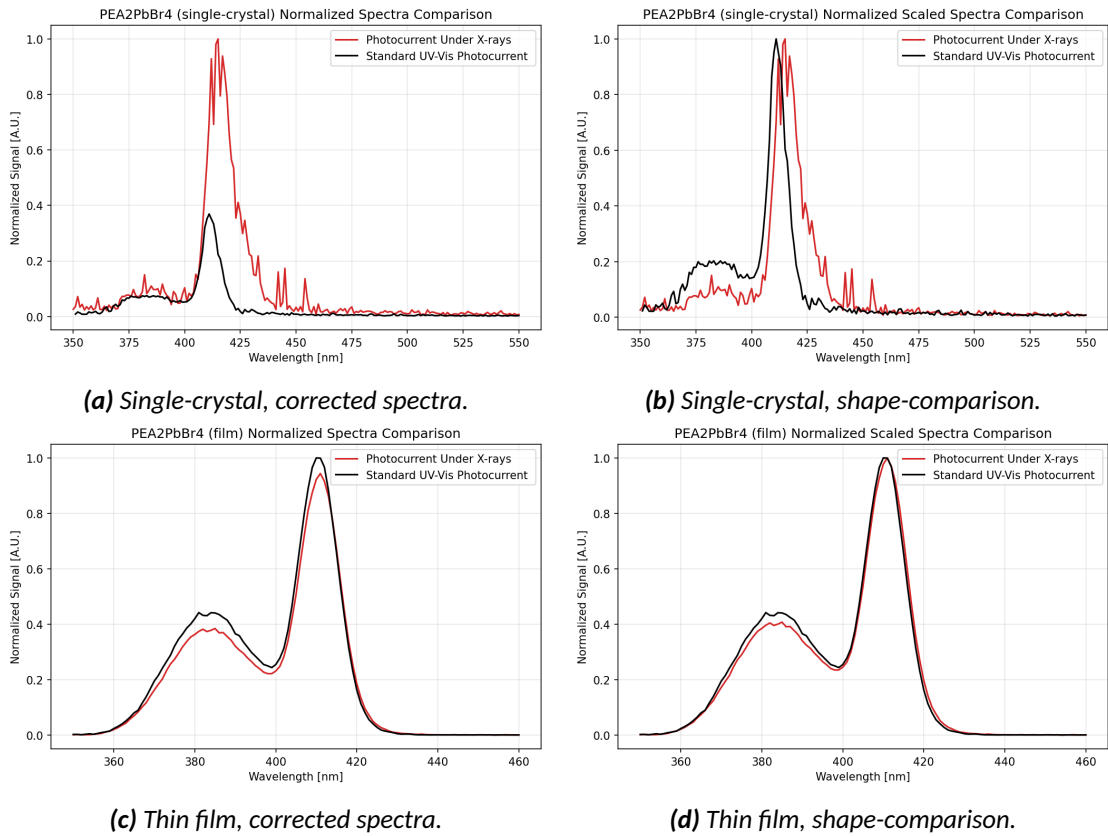


Figure 4.8: Effects of X-rays on PEA₂PbBr₄ samples photocurrent spectra collected with the compact setup.

In Fig. 4.8 the photocurrent spectra obtained with the compact setup, with and without X-ray irradiation, are displayed.

The plots include standard UV-Vis photocurrent spectra and the same photocurrent

spectra taken with simultaneous X-rays irradiation. To better appreciate the effects of X-rays on the photocurrent spectra shape, the corrected normalized images have been put directly next to the normalized and singularly-scaled ones.

The film shows almost no reaction to the X-rays: at the same beam settings of the single-crystal (30 mA, 35 kV) the curve was perfectly superimposing while at lower X-ray beam energy settings (20 mA, 20 kV) the photocurrent under X-rays is slightly lower than the standard one, as can be seen in Figs. 4.8c and 4.8d. This can be attributed to radiation transparency of the thin film structure and to the radiation hardness of the material.

On the contrary, sample $\text{PEA}_2\text{PbBr}_4$ -sc underwent a massive excitonic peak enhancement under x-rays: the signal strength roughly tripled and the peak broadened towards longer wavelengths with an increase of $\sim 30\%$ of its FWHM (Figs. 4.8a and 4.8b).

In Fig. 4.9 the effects of X-rays irradiation on the photocurrent spectra of the two samples are quantified by means of the truncated 3D Elliott fit. The extracted parameters confirm that, while $\text{PEA}_2\text{PbBr}_4$ -film remains unaltered, in the $\text{PEA}_2\text{PbBr}_4$ -sc the energy bandgap transitions from 3.09 ± 0.01 eV to 3.16 ± 0.04 eV and the exciton binding energy jumps from 80 ± 13 meV to 180 ± 40 meV.

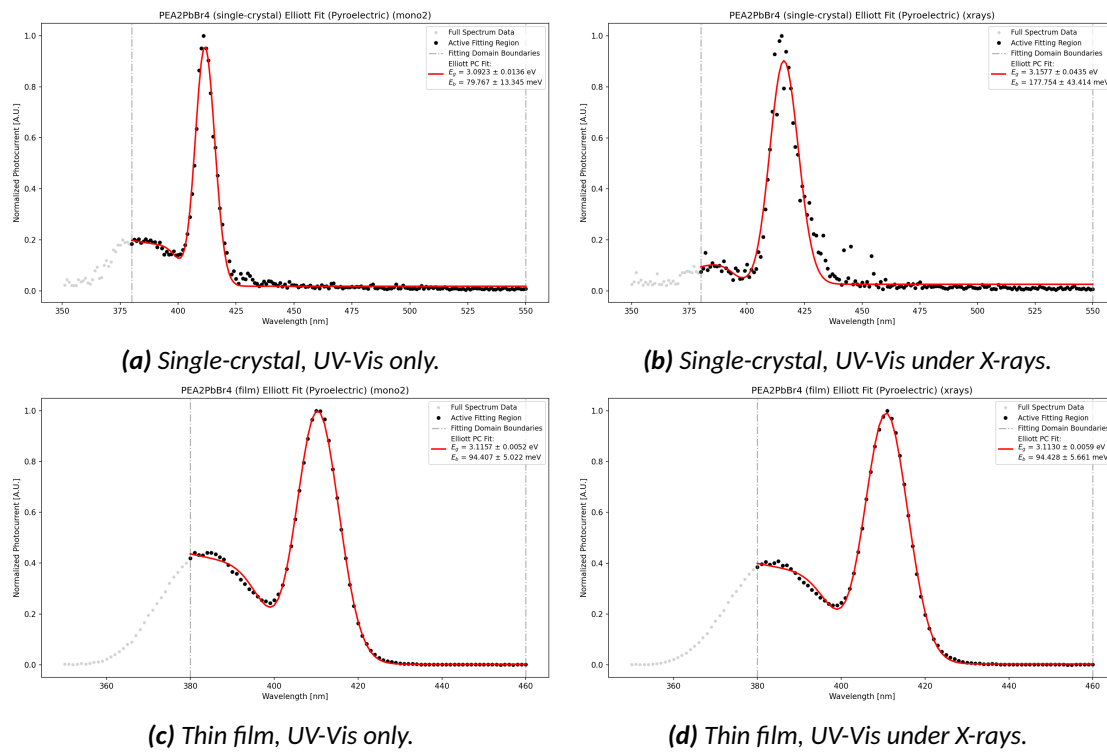


Figure 4.9: Truncated 3D Elliott fit applied on the $\text{PEA}_2\text{PbBr}_4$ samples spectra acquired with the compact setup.

Table 4.4, displays the figures of merit and fit parameters extracted from the mea-

surements on the two samples.

Parameter	Material	Standard	Compact	Compact, under X-ray
Responsivity	SC	0.80 ± 0.01 mA/W	–	–
	Film	53 ± 1 mA/W	–	–
EQE	SC	0.24 ± 0.01 %	–	–
	Film	16.0 ± 0.3 %	–	–
E_g (eV)	SC	3.12 ± 0.01	3.09 ± 0.01	3.16 ± 0.04
	Film	3.17 ± 0.01	3.12 ± 0.01	3.11 ± 0.01
E_b (meV)	SC	92 ± 2	80 ± 13	180 ± 40
	Film	135 ± 5	94 ± 5	94 ± 6

Table 4.4: $\text{PEA}_2\text{PbBr}_4$ extracted figures of merit. The responsivity and EQE are computed at 20 V bias in correspondence of the 410 nm peak.

4.3 MAPbBr₃

The electrical characterization of sample MAPbBr₃ has demonstrated that, despite its age, it still possesses good properties: at -10 V, the dark current is comprised between 10 and 20 nA, while the light current rises up by two orders of magnitude, ranging from 0.7 to 1 μA (Fig. 4.10).

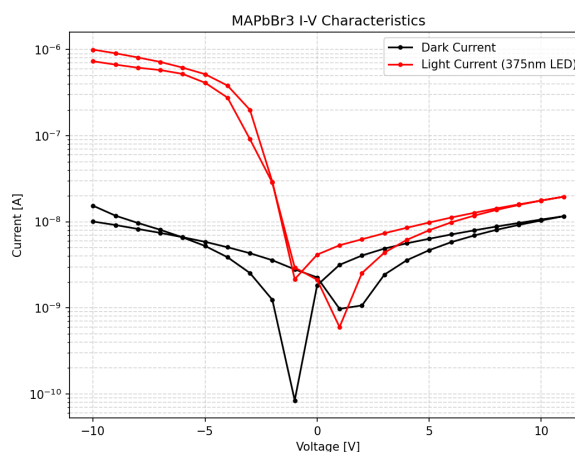


Figure 4.10: MAPbBr₃ I-V characteristics. Light current is acquired under a 375 nm LED for a total power of 63.2 μW . The vertical geometry leads to an asymmetric charge collection between the two electrodes.

The I-V curve of sample MAPbBr₃ shows a clear asymmetry, which comes from the vertical photoconductor geometry: light impinging on the top electrode makes it so that one type of charge carrier is driven by the bias immediately towards it while the other type of carrier has to travel all the way through the bulk till the bottom electrode, resulting in lower collection efficiency.

The shape of the curve, is coherent with the one reported by Armaroli et al. [45], where a MAPbBr₃ sample coming from the same batch was studied. While the LED used is again different (375 nm versus the 475 nm one used by Armaroli et al.), the light current is still around 1 μ A whereas the dark current is lower by one order of magnitude with respect to the reference. Overall, the sample shows similar photoelectrical behaviour as a pristine sample from the same batch. In Fig. 4.11 the corrected photocurrent spectrum of MAPbBr₃ is shown. The excitonic peak is located at 550 nm.

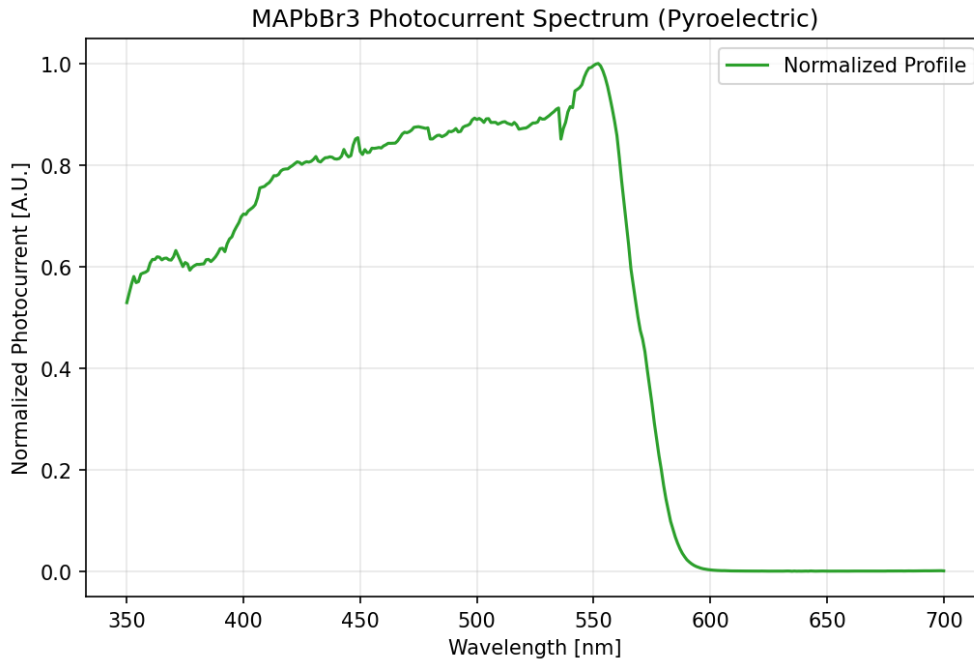


Figure 4.11: MAPbBr₃ photocurrent spectrum, corrected for the QTH lamp flux and normalized.

Figure 4.12 shows the spectral response of MAPbBr₃ sample. The computed responsivity of 2.2 ± 0.1 mA/W at peak falls within the expected range of [0.04, 5.3] mA/W associated to samples coming from the same batch under 20 V/cm electrical field [44].

Fig. 4.13 displays the result of the truncated 3D Elliott fit performed onto the corrected and normalized photocurrent spectrum.

The energy gap and exciton binding energy of MAPbBr₃ are 2.27 ± 0.01 eV and 46 ± 3 meV, respectively. These values are in good agreement with those of 2.30 ± 0.01 eV and 39

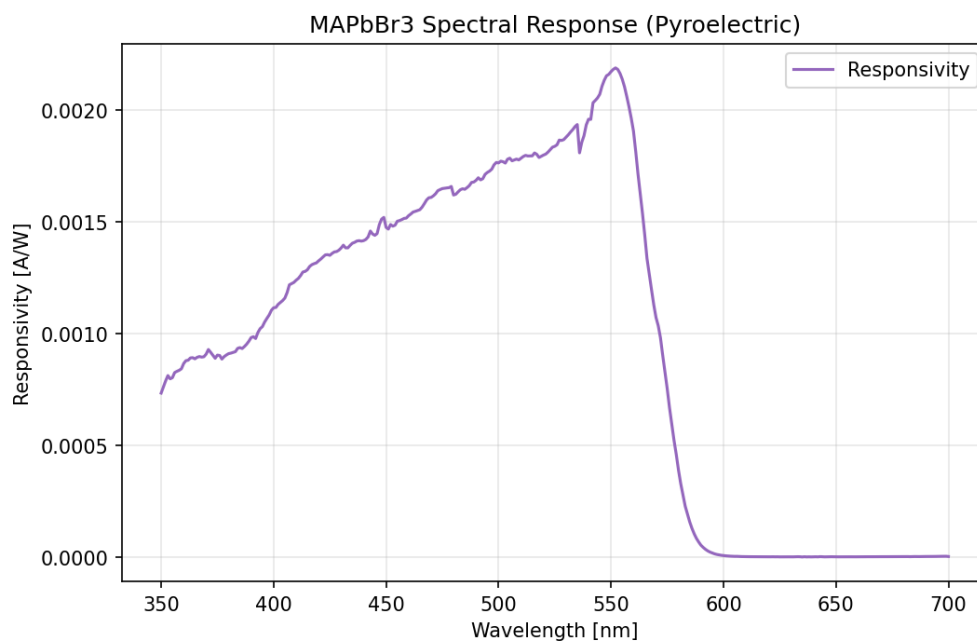


Figure 4.12: MAPbBr₃ spectral responsivity.

± 1 meV found by Armaroli et al. [45].

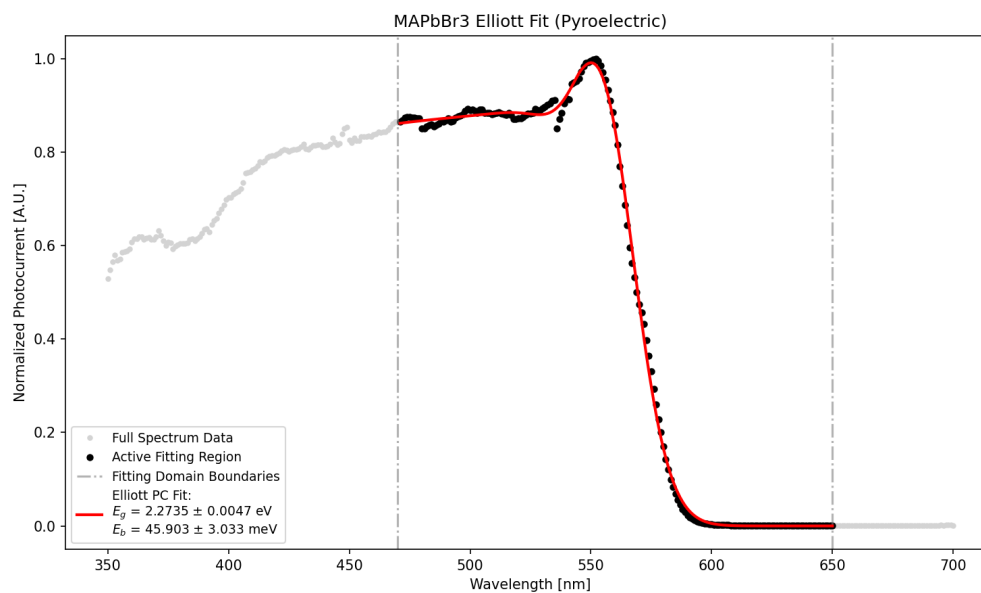
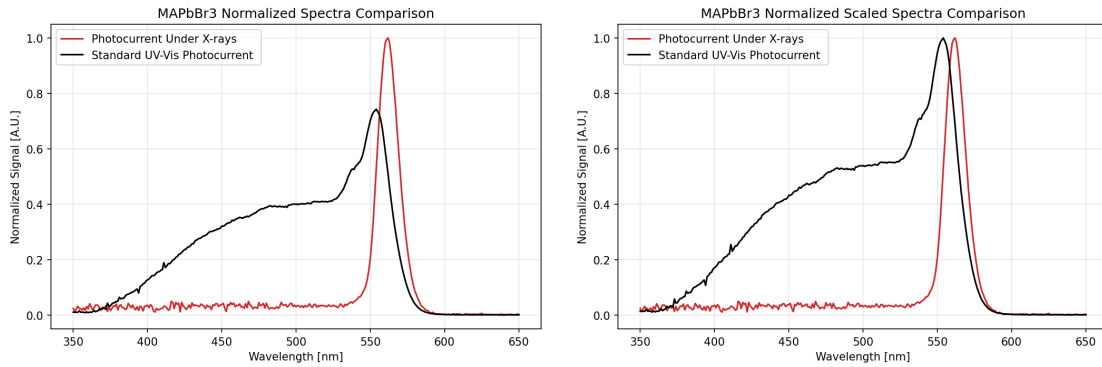


Figure 4.13: MAPbBr₃ Elliott fit. The fitting window goes from 470 to 650 nm.

Effects of X-rays on the photocurrent spectrum

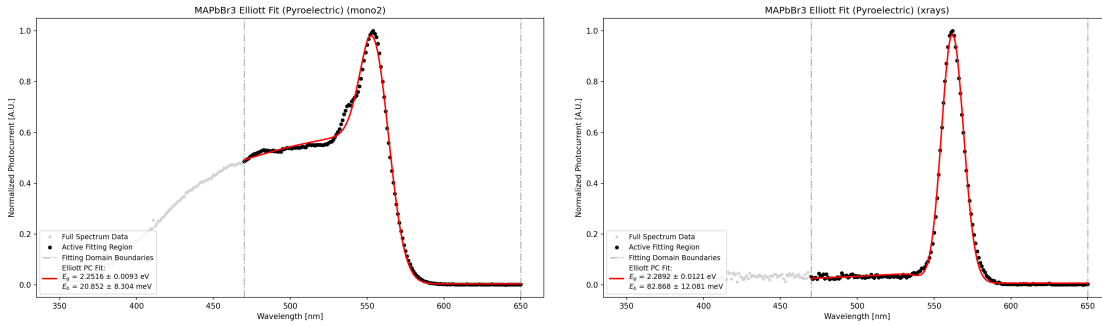
The effects of X-rays on MAPbBr₃ UV-Vis photocurrent spectrum can be observed in Fig. 4.14. Even more clearly than in PEA₂PbBr₄ single-crystal, the X-rays enhance the excitonic peak – which increased in strength by ~30% and, remaining quite sharp, moved by 8 nm towards longer wavelengths – moreover, the effect is paired with a complete quenching of the photocurrent in the continuum region and the overall shape of the spectrum changes dramatically.



(a) Effects of X-rays on MAPbBr₃ corrected UV-Vis photocurrent spectrum.

(b) Effects of X-rays on MAPbBr₃ normalized spectrum.

Figure 4.14: Effects of X-rays on MAPbBr₃ photocurrent spectrum.



(a) Elliott fit on MAPbBr₃ UV-Vis photocurrent spectra acquired with the compact setup.

(b) Elliott fit on MAPbBr₃ UV-Vis photocurrent spectra acquired under X-rays.

Figure 4.15: Elliott fit on MAPbBr₃ spectra acquired with the compact setup. The fitting window goes from 470 to 650 nm.

Fig. 4.15 displays the results of the truncated 3D Elliott fit onto the spectra acquired in the compact setup.

E_g shifts from 2.25 ± 0.01 eV to 2.29 ± 0.01 eV and the binding energy increases as well,

transitioning from 21 ± 8 meV to 80 ± 12 meV.

This increase of the binding energy under X-rays has been observed also by Armaroli et al., who suggest that the excitonic peak observed under standard UV-Vis photocurrent spectroscopy is likely formed by free excitons weakly coupled to phonons, while the peak emerging at lower energies under X-rays is probably formed by bound excitons strongly coupled with phonons. The effect is reversible in the timespan of 1 week, possibly for the filling of bromine vacancies by water and oxygen [45].

Table 4.5 summarizes the extracted figures of merit and fit parameters across the measurements on MAPbBr₃ sample.

Parameter	Standard	Compact	Compact, under X-ray
Responsivity	2.2 ± 0.1 mA/W	-	-
EQE	0.50 ± 0.02 %	-	-
Energy Gap	2.27 ± 0.01 eV	2.25 ± 0.01 eV	2.29 ± 0.01 eV
Binding Energy	46 ± 3 meV	21 ± 8 meV	80 ± 12 meV

Table 4.5: MAPbBr₃ extracted figures of merit. The responsivity and EQE are evaluated at 10 V bias in correspondence of the 550 nm peak.

4.4 TIPS-PEN

The I-V characteristics of TIPS-PEN can be observed in Fig. 4.16. The voltage range is more limited with respect to that used for the other samples, since this organic semiconductor is more susceptible to damage from high bias. Sample TIPS-PEN displays a slight rectifying behaviour in the $[-5, 5]$ V range. The ratio between light and dark current is of the order of 10^2 , comparable with literature values [53].

The photocurrent spectrum of sample TIPS-PEN (Fig. 4.17) features three distinct vibronic peaks at roughly 580, 640 and 690 nm. The peak at 450 nm is instead a higher-energy transition, which is not relevant for the purposes of the determination of the energy bandgap.

For sample TIPS-PEN, the responsivity value in the 550-700 nm range is comprised between 0.1 and 0.2 mA/W. Though a direct comparison with the exact sample morphology was not found, data from Wei et al. suggest that there is a strong dependence of the responsivity on the applied bias, illumination and channel length. At 5 V and $8.2 \mu\text{W}/\text{cm}^2$ a device with 200 μm channel length shows a responsivity of 230 mA/W (under 532 nm light) [53]. In the present work, the power at that wavelength is about $5 \mu\text{W}/\text{cm}^2$, which would lower the expected responsivity to 160 mA/W, as for the impact of the channel length, its increase induces an exponential decay in the value of $\mathcal{R}$, but the study performed by Wei et al. does not include data for interdigitated electrodes

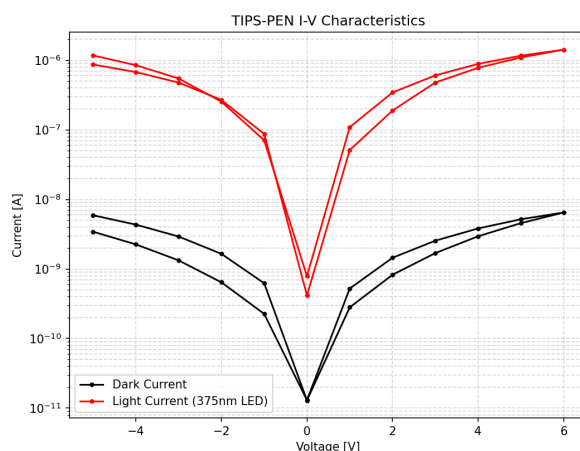


Figure 4.16: TIPS-PEN I-V characteristics. Light current is acquired under a 375 nm LED for a total power of $4.74 \mu W$. The vertical geometry leads to an asymmetric charge collection between the two electrodes.

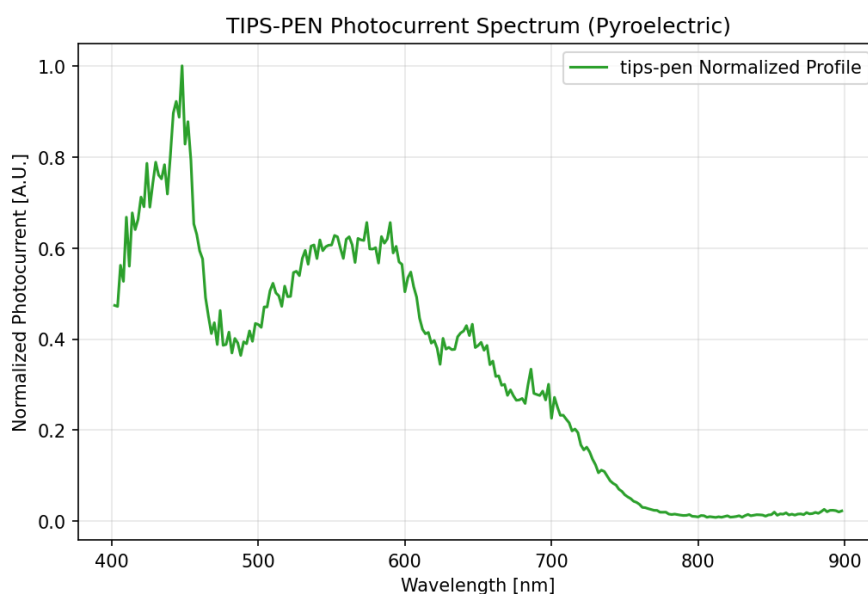


Figure 4.17: TIPS-PEN photocurrent spectrum, corrected for the new QTH lamp flux and normalized.

geometries, where charge collection is dominated by the fringes of the electric field.

The spectrum has been analysed with a Tauc plot in the range 660-750 nm (Fig. 4.19). The Tauc fit yielded an energy gap of 1.64 ± 0.01 eV, which is consistent with the average

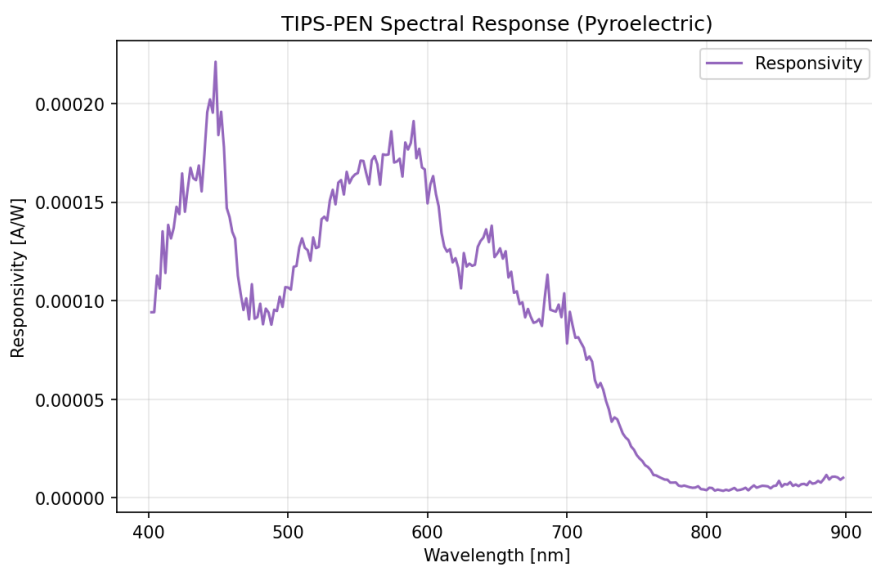


Figure 4.18: TIPS-PEN spectral responsivity.

literature values [54, 55].

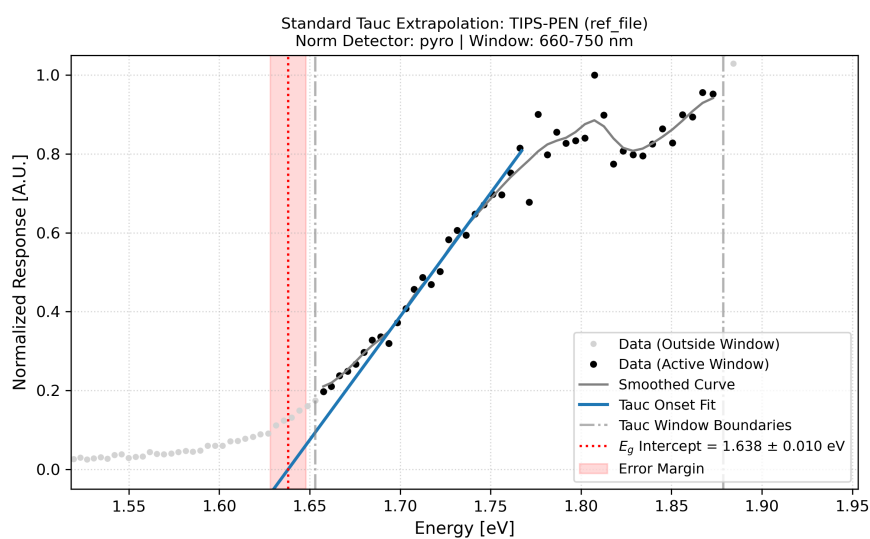
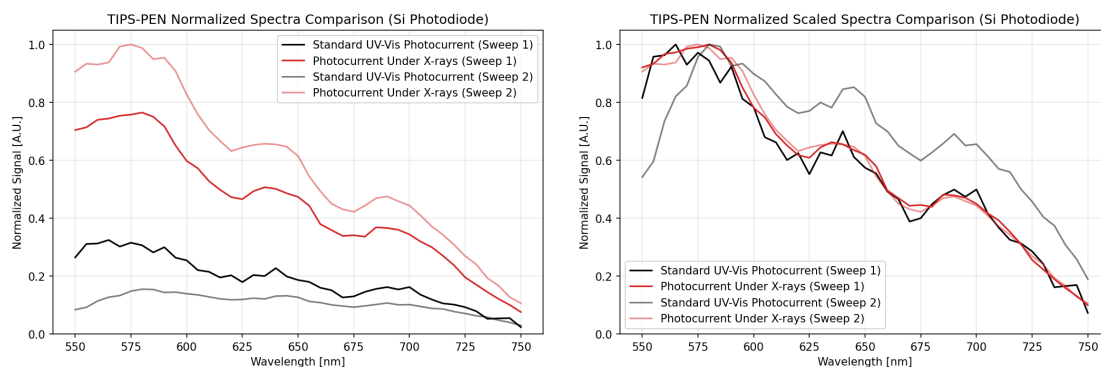


Figure 4.19: TIPS-PEN Tauc plot. The fitting window covers the wavelengths between 660 and 750 nm.

Effects of X-rays on the photocurrent spectra of TIPS-PEN

The TIPS-PEN was irradiated under X-rays several times. As for samples $\text{PEA}_2\text{PbBr}_4\text{-sc}$ and MAPbBr_3 , the effect of the radiation on the photocurrent was concentrated on the peaks of the spectrum outside of the UV range; therefore, in Fig. 4.20, only the region of the vibronic peaks is shown.

In Fig. 4.21 the results of the Tauc fits performed on each sweep trace are reported.



(a) Effects of X-rays on TIPS-PEN corrected UV-Vis spectra.

(b) Effects of X-rays on TIPS-PEN normalized UV-Vis spectra.

Figure 4.20: TIPS-PEN X-rays spectra comparisons across multiple sweeps. Between the end of the first sweep under X-rays and the start of the second sweep under just UV-Vis light, 17 hours had passed. Before the start of each sweep under X-rays, the sample was irradiated for at least 5-10 minutes, to give it enough time for all the trap states to activate.

In TIPS-PEN the effect of X-rays is more similar to that observed in sample $\text{PEA}_2\text{PbBr}_4\text{-sc}$. The spectrum is affected only exclusively in the range from 500 to 800 nm, where the 0-0 transition and the vibronic peaks are located. The increase in the signal strength is variable, yet consistent in time: after 17 hours from the first sweep under X-rays, the sample had already fully recovered and was able to respond as well to another irradiation Fig. 4.20. The Tauc fits yielded consistently higher energy bandgaps on the spectra acquired under X-rays irradiation, with a transition from 1.61 ± 0.01 to 1.63 ± 0.01 in the first sweep and from 1.61 ± 0.01 to 1.62 ± 0.01 in the second sweep.

Table 4.6 displays the extracted parameters for the TIPS-PEN sample.

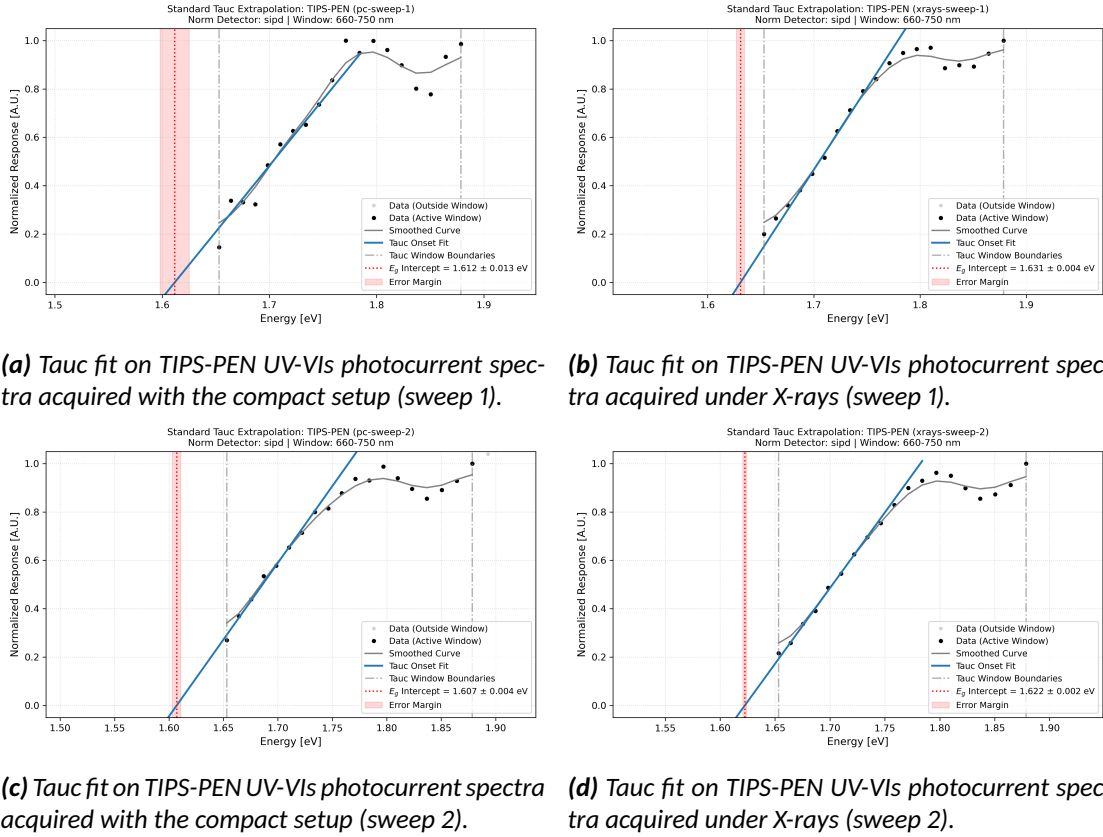


Figure 4.21: Tauc fit on TIPS-PEN spectra acquired with the compact setup. The fitting window is the same for every image, spanning from 660 to 750 nm.

Parameters	Standard	Compact	Compact, under X-ray
Responsivity	0.19 ± 0.05 mA/W	-	-
EQE	0.04 ± 0.01 %	-	-
Energy Gap	1.64 ± 0.01 eV	1.61 ± 0.01 eV	1.63 ± 0.01 eV

Table 4.6: TIPS-PEN extracted figures of merit. For the energy gap values computed on data collected with the compact setup (with and without X-rays irradiation) an average has been performed on the fit parameters obtained from the two sweeps. The responsivity and EQE have been evaluated at 5 V bias in correspondence of the 575 nm peak.

Conclusions

In this thesis project, the effects of X-rays on the photocurrent spectra of Inorganic-Organic Hybrid Perovskites and Organic Semiconductors have been analysed by means of a custom setup.

The work involved the restoration and upgrade of a standard UV-Vis photocurrent apparatus and the implementation of an innovative compact setup for performing UV-Vis photocurrent spectroscopy under simultaneous X-rays irradiation.

The standard setup was validated through the acquisition of the photocurrent spectrum of a thin film BA_2PbI_4 lateral photoconductor, which, upon fitting with a truncated 3D Elliott formula, yielded an energy gap of 2.43 ± 0.01 eV and an exciton binding energy of 48 ± 5 meV. The responsivity was also computed, resulting in 3.5 ± 0.1 mA/W at 5 V in correspondence of the 490 nm peak.

The standard setup was then used to validate the compact setup.

Photocurrent spectra of $\text{PEA}_2\text{PbBr}_4$ single-crystal and thin film lateral photoconductors were acquired and fitted with the truncated 3D Elliott model, yielding average energy gaps of 3.10 ± 0.01 eV and 3.14 ± 0.04 eV respectively and average exciton binding energies of 86 ± 13 meV and 114 ± 20 meV respectively. The responsivity at the 410 nm peak for these samples was 0.80 ± 0.01 mA/W at 4000 V/cm electric field for the single-crystal and 53 ± 1 mA/W at 6667 V/cm electric field for the thin film. Under X-rays, the thin film sample showed no reaction, due to radiation transparency of the thin film structure and to the radiation hardness of the material, while in the single-crystal an enhancement and broadening towards longer wavelengths of the excitonic peak was observed, with a shift of the energy gap to 3.16 ± 0.04 eV and of the binding energy to 180 ± 40 meV.

Photocurrent spectra of a MAPbBr_3 single-crystal vertical photoconductor were collected too with both setups, and fit with a truncated 3D Elliott model on the data from the standard UV-Vis photocurrent setup yielded an energy gap of 2.27 ± 0.01 eV and exciton binding energy of 46 ± 3 meV, while the computed responsivity at the 550 nm peak under 10 V bias was evaluated as 2.2 ± 0.1 mA/W. Under X-rays, the sample displayed as well an increase in the strength of the excitonic peak, which appeared shifted towards longer wavelengths, but the effect was paired with a complete quenching of the photocurrent in the continuum. The Elliott fit performed on the data from the compact setup demonstrated a shift of the energy bandgap from 2.25 ± 0.01 eV to 2.29 ± 0.01 eV and an increase of the binding energy from 21 ± 8 meV to 80 ± 12 meV. This can be explained in terms of exciton coupling with phonons, as a consequence of the formation of bromine vacancies under irradiation.

The last sample analysed with the two apparatuses was a TIPS-PEN thin film lateral pho-

toconductor. From the photocurrent spectra, by means of a Tauc plot it was possible to extract an energy gap of 1.64 ± 0.01 eV. The responsivity at 5 V bias was computed to be 0.19 ± 0.05 mA/W at the 575 nm vibronic peak. Under X-rays, the peaks were also in this case enhanced. The effect was fully reversible in about 17 hours. A shift of the energy gap by 2 eV towards higher energy was observed consistently across repeated sweeps.

The absence of continuum quenching in TIPS-PEN and PEA₂PbBr₄-sc suggests that X-ray induced defects are not acting as effective recombination centres for excitons.

Acknowledgements

I wish to thank my supervisor Prof. Andrea Ciavatti and my co-supervisor Camilla Bordoni, for the support and the guidance during these months.

Special thanks go to Federico De Santis, for the realization of the custom components needed in the upgrade and implementation of the two setups, for the long hours spent talking between the endless acquisitions.

I thank Prof. Laura Basiricò, for leading me to this thesis project, and Prof. Daniela Cavalcoli, for the academic career advices.

I sincerely thank Prof. Tobias Cramer, whose suggestions were fundamental for the troubleshooting of signal detection and instrument communication.

My thanks go to all the "Semiconductor Physics" group, to Francesca, Giulia, Elisabetta and to all the PhDs and colleagues, for their presence and help with equipment and samples in the department labs.

I particularly thank Inês and Richard, for the invaluable breaks during the most frustrating lab days; Sara and Nicholas, who were there on the longest days before the run for the train; Jakob, Niccolò and Alessia with whom I shared a fantastic bouldering day.

I thank Benedick Andrade, Huthaifa Alkasaji, Michele Solari and all the MANO course friends. For the support, for the funny moments, for the shared trips and adventures. Our paths in the next years may part, but I still hope we will still meet, let it be skiing in Pesariis, philosophically chatting while walking in a park in Bologna, having a cup of tea and deep conversations night-time after a good Dungeons and Dragons session.

I thank Irene Ballantini and Francesca di Masi, for their patience and understanding across this last year dense of surprises and changes.

I wish now to make amend for not having written the Acknowledgements in my Bachelor thesis. It's surely a long list of deep thanks, warm smiles and embraces.

To Lorenzo Van Zutphen and Ilaria Mingazzini, fantastic holidays companions and who remained there through a difficult period.

To Camilla Benedetti, Veronica Mungai, Simone Naglieri and all the "Fisicati" group, with whom I shared the first university years.

To Sara Patelli, Matteo Grilli, Andrea Talamazzini, Filippo Campanini, Matteo Innocenti, Lorenzo Cazzoli, Matteo Donigaglia, Davide Gresta, Niccolò Giuliani, Martino Garelli, Carlo Lovecchio, Gaia Bernazzani and all the "Campagnona" group; companions of endless parties, games, study and adventures, both in Approdo and in some more grounded but not less marvellous land.

To Emanuele Prati and all the friends of the "Il procione nella foto è" group; still crazy to think we've known each other for more than ten years now.

And to my family, whom I never properly thanked enough, but who made all of this possible: thanks for always being there for me.

A. Supplementary Graphs

Raw Signal Graphs – Standard Setup

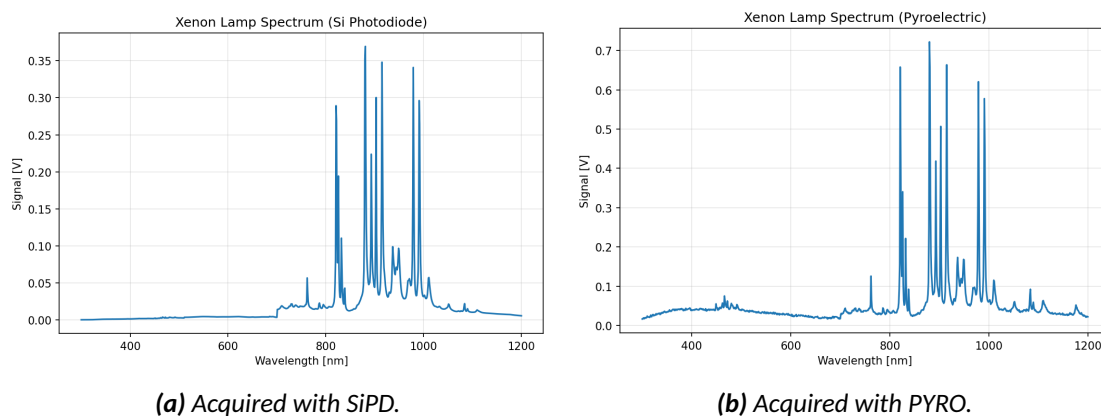


Figure A.1: Xenon lamp raw spectra in linear scale.

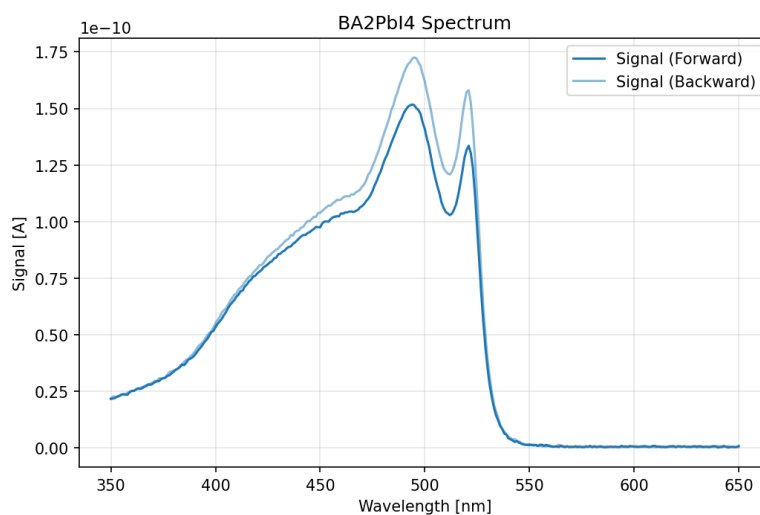


Figure A.2: BA_2PbI_4 raw photocurrent spectrum. Both forward and backward scan are shown.

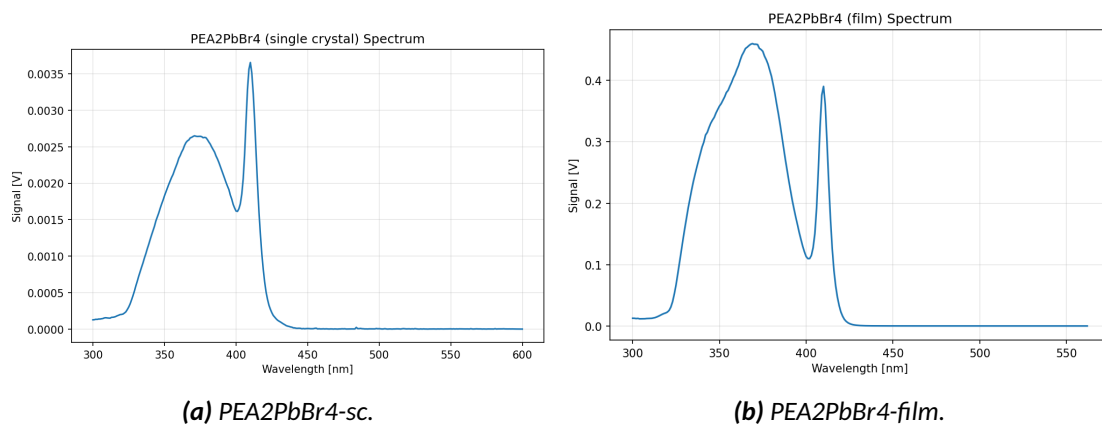


Figure A.3: PEA2PbBr4 samples raw photocurrent spectra.

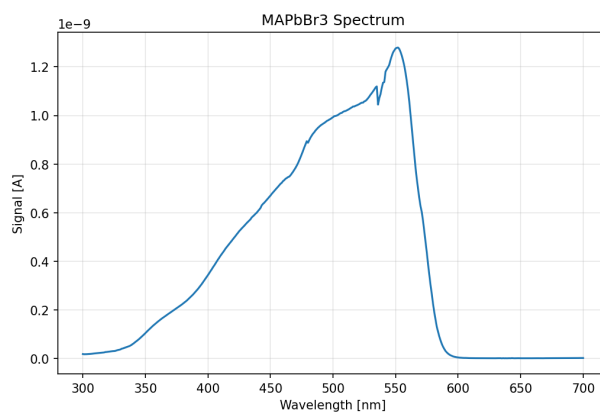


Figure A.4: MAPbBr3 raw photocurrent spectrum.

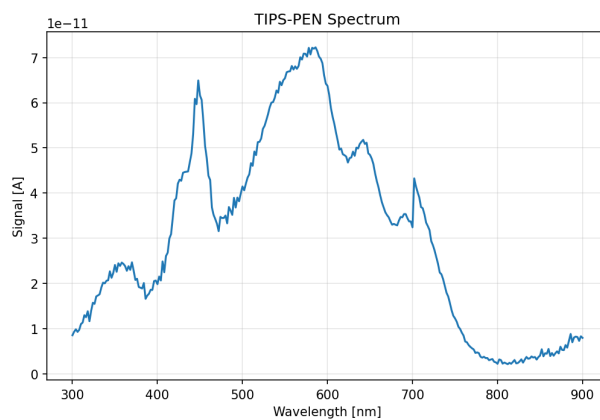
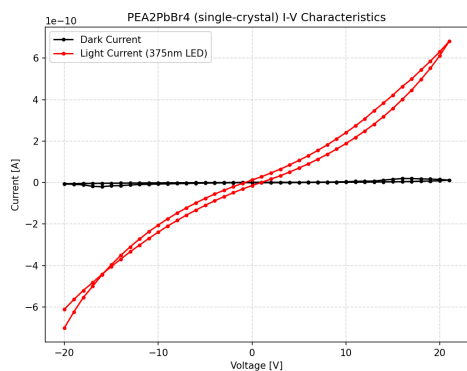
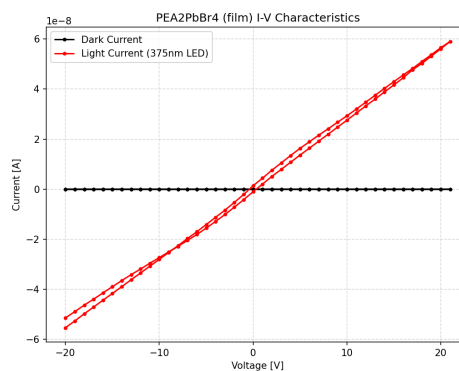


Figure A.5: TIPS-PEN raw photocurrent spectrum.

Linear-scale I-V Plots



(a) PEA2PbBr4 single-crystal (linear scale).



(b) PEA2PbBr4 thin film (linear scale).

Figure A.6: PEA2PbBr4 samples I-V characteristics (linear scale).

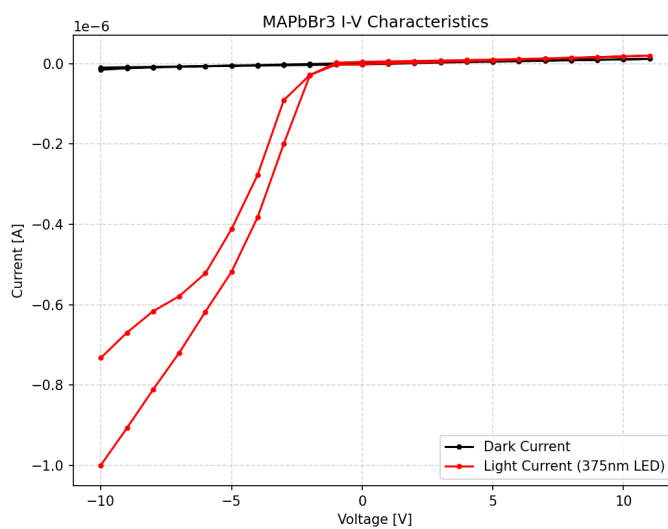


Figure A.7: MAPbBr3 I-V characteristics (linear scale).

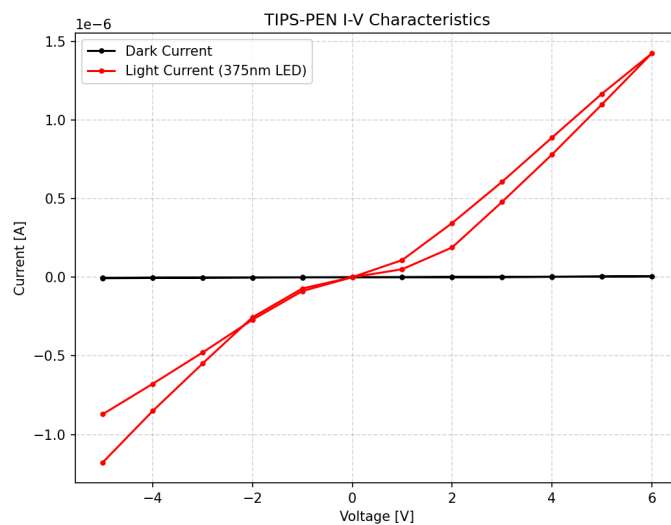


Figure A.8: TIPS-PEN I-V characteristics (linear scale).

Raw Signal Graphs – Compact Setup

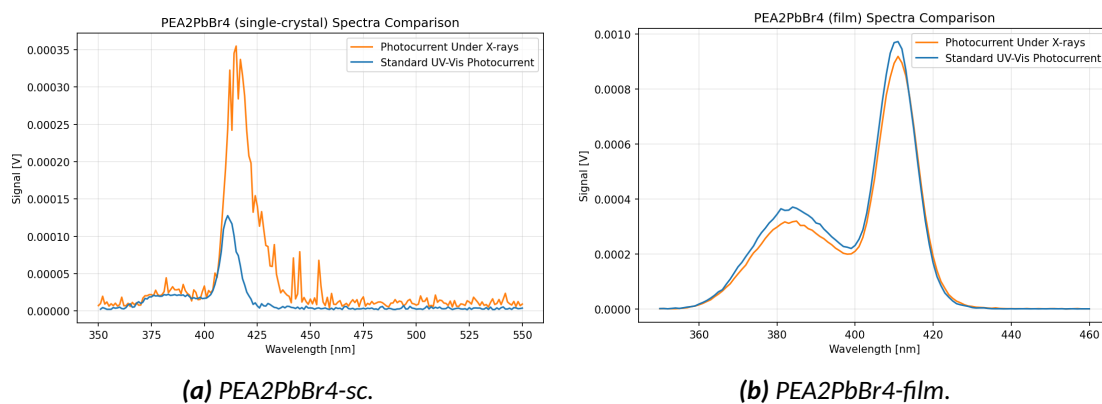


Figure A.9: Effects of X-rays on PEA2PbBr4 samples photocurrent spectra (raw signal).

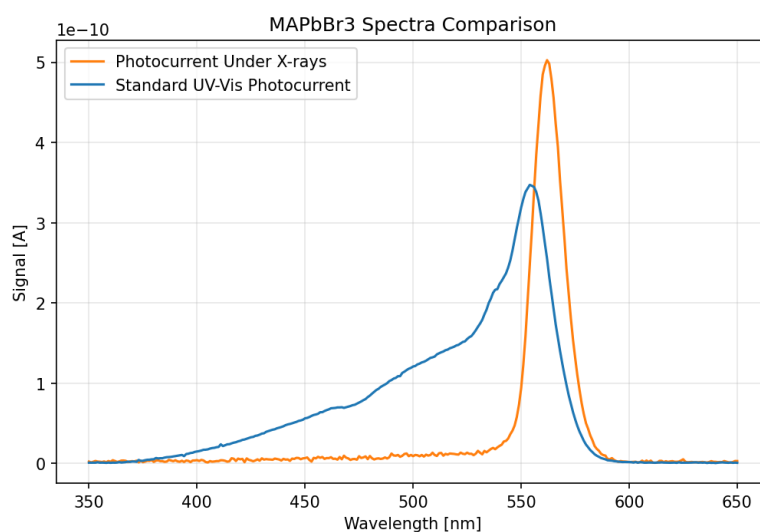


Figure A.10: Effects of X-rays on MAPbBr₃ photocurrent spectrum (raw signal).

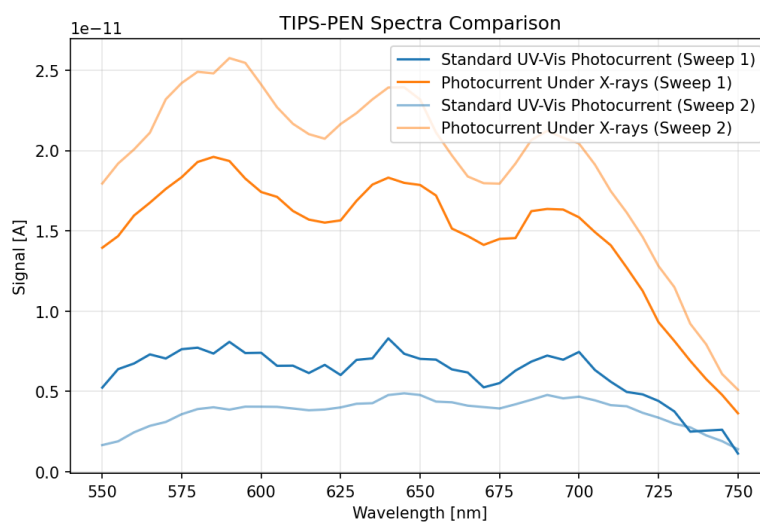


Figure A.11: Effects of X-rays on TIPS-PEN photocurrent spectra (raw signal).

B. Interpolation of SiPD Responsivity Curve

As detailed in Chapter 2, the spectral range of the Si photodiode detector covers wavelengths from 190 to 1110 nm. In this window, the responsivity has a crescent trend up to the peak at ~760 nm, then decreases slowly till ~900 nm and from here drops rapidly to near-zero values at 1110 nm (the upper wavelength limit of silicon absorption edge). Due to this behaviour, when dividing the lamp signal for the rapidly falling values of the detector responsivity, at the critical wavelength $\lambda_{\text{CRIT}} = 900$ nm, the numbers spike up, dwarfing the signal in the flatter-response area of the spectrum.

To solve this issue, two different strategies have been attempted:

1. Data truncation;
2. Flat tail extension.

Data truncation

This method consists simply in dropping the data after the critical wavelength λ_{CRIT} . Both the raw lamp signal and the SiPD responsivity data are discarded after λ_{CRIT} and the resulting plot is a faithful flux but on a narrower wavelength region. This approach can be therefore followed only if the subsequent operations involving the flux are performed at wavelengths $< \lambda_{\text{CRIT}}$.

Flat tail extension

This method involves substituting the detector's responsivity data after λ_{CRIT} with the constant value $\mathcal{R}(\lambda_{\text{CRIT}})$.

This removes the divergence of the data and the mathematical artifacts at 1110 nm, yielding a plot which preserves the overall shape of the flux.

Of course, the issue of this approach is that the values of the flux after λ_{CRIT} are uncalibrated, and therefore cannot be used to return reliable results. At the same time, it remains a valid strategy to visualize the full shape of the flux at wavelengths $> \lambda_{\text{CRIT}}$.

C. Alternatives to Tauc plots for TIPS-PEN

An alternative to Tauc plots for the organic films is provided by Franck-Condon Vibronic Progression Model[56, 57]:

$$\alpha(E) = \alpha_0 \cdot E \sum_{v'=0}^{\infty} \frac{S^{v'}}{v'!} e^{-S} \cdot \mathcal{G}(E - (E_{00} + v'\hbar\omega), \Gamma) \quad (\text{C.1})$$

in which E_{00} is the energy of the 0-0 vibrational transition and S is Huang-Rhys factor, related to the strength of the exciton-phonon coupling.

The following graphs are obtained via implementations of the above formula in accordance to experimental practices found in literature [56–58].

In general, it has been observed that the UV-Vis absorption spectra of OSCs, apart from some minor energy shifts, has little differences with that of the isolated organic molecules. This is due to the fact that the electron-hole relative motion is mainly confined inside the respective molecules[12].

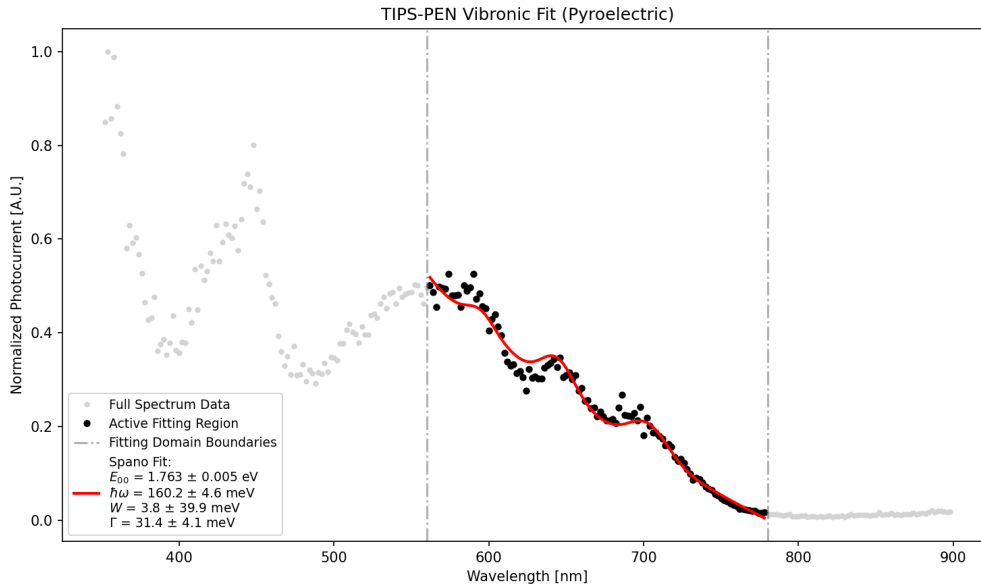


Figure C.1: TIPS-PEN Spano fit. The fitting window covers the wavelengths between 560 and 780 nm.

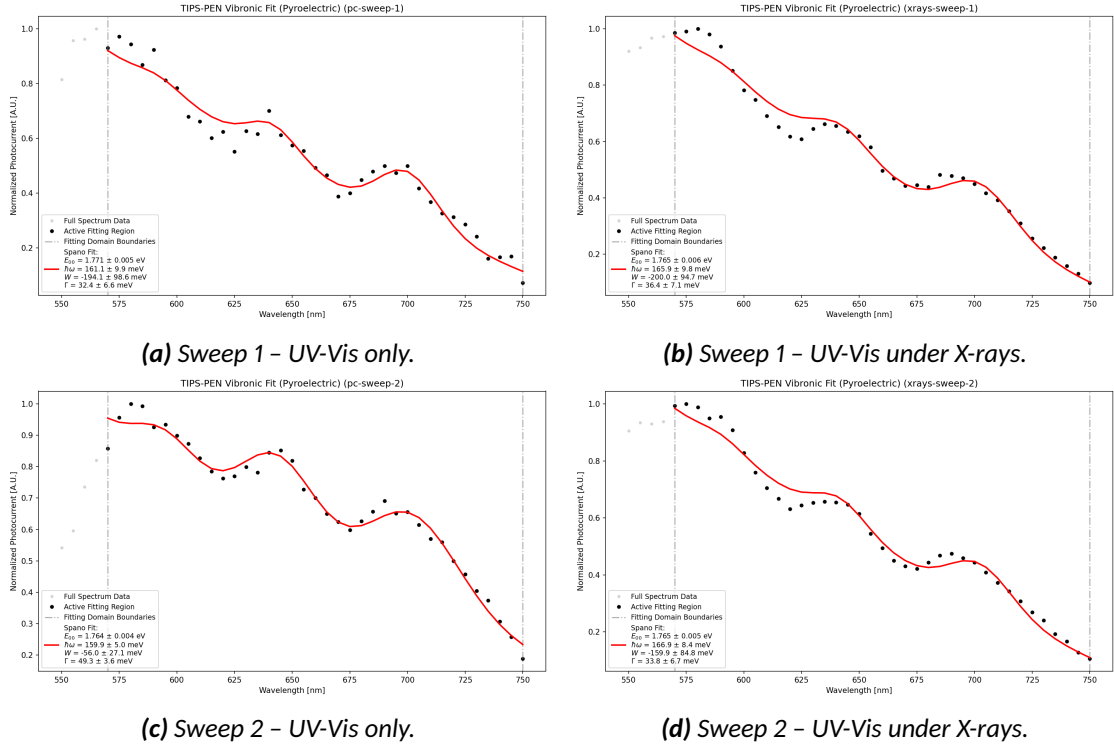


Figure C.2: Spano fit on TIPS-PEN spectra acquired with the compact setup. The fitting window is the same for every image, spanning from 570 to 750 nm. Between the spectra displayed in (b) and in (c), 17 hours have passed.

Even if this fitting approach based on the theory described by Spano et al. is able to capture the shape of the vibronic peaks, the function

- has a higher number of fitting parameters than Tauc plots;
- is based on a model which is still in development;
- is less used in literature, making comparisons more uncertain.

The fits in the above images are only partially stable, since some of the parameters are hitting their limit boundaries.

Bibliography

- [1] Sumona Sinha, Susmita Jana, and Debnarayan Jana. Overview of modern inorganic, organic, and hybrid semiconductors. In Shadia Ikhmayies, editor, *Advanced Semiconductors*, pages 1–53. Springer Nature Switzerland, Cham, 2025. ISBN 978-3-031-88283-8. doi: 10.1007/978-3-031-88283-8_1.
- [2] Basudev Pradhan. *Perovskite Optoelectronic Devices*. Engineering Materials. Springer International Publishing AG, Cham, 1 edition, 2024. ISBN 978-3-031-57662-1.
- [3] Arthur Marronnier. *Anharmonicity and Instabilities in Halide Perovskites for Last Generation Solar Cells*. PhD thesis, June 2018.
- [4] Yuting Gao, Yufeng Pan, Feng Zhou, Guangda Niu, and Chunjie Yan. Lead-free halide perovskites: A review of the structure–property relationship and applications in light emitting devices and radiation detectors. *Journal of Materials Chemistry A*, 9(20):11931–11943, May 2021. ISSN 2050-7496. doi: 10.1039/D1TA01737C.
- [5] Wan-Jian Yin, Ji-Hui Yang, Joongoo Kang, Yanfa Yan, and Su-Huai Wei. Halide perovskite materials for solar cells: A theoretical review. *Journal of Materials Chemistry A*, 3(17):8926–8942, April 2015. ISSN 2050-7496. doi: 10.1039/C4TA05033A.
- [6] Sarah Brittmann, Gede Widia Pratama Adhyaksa, and Erik Christian Garnett. The expanding world of hybrid perovskites: Materials properties and emerging applications. *MRS Communications*, 5(1):7–26, March 2015. ISSN 2159-6867. doi: 10.1557/mrc.2015.6.
- [7] Mohammad Rahil, Rashid Malik Ansari, Chandra Prakash, S. S. Islam, Ambesh Dixit, and Shahab Ahmad. Ruddlesden–Popper 2D perovskites of type $(\text{C}_6\text{H}_9\text{C}_2\text{H}_4\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_n\text{Pb}_{n-1}\text{I}_{3n+1}$ ($n = 1\text{--}4$) for optoelectronic applications. *Scientific Reports*, 12(1):2176, February 2022. ISSN 2045-2322. doi: 10.1038/s41598-022-06108-8.
- [8] Michael B. Johnston and Laura M. Herz. Hybrid Perovskites for Photovoltaics: Charge-Carrier Recombination, Diffusion, and Radiative Efficiencies. *Accounts of Chemical Research*, 49(1):146–154, January 2016. ISSN 0001-4842. doi: 10.1021/acs.accounts.5b00411.

- [9] Xupeng Gao, Xiangtong Zhang, Wenxu Yin, Hua Wang, Yue Hu, Qingbo Zhang, Zhifeng Shi, Vicki L. Colvin, William W. Yu, and Yu Zhang. Ruddlesden–Popper Perovskites: Synthesis and Optical Properties for Optoelectronic Applications. *Advanced Science*, 6(22):1900941, 2019. ISSN 2198-3844. doi: 10.1002/advs.201900941.
- [10] Dumitru Sirbu, Folusho Helen Balogun, Rebecca L. Milot, and Pablo Docampo. Layered Perovskites in Solar Cells: Structure, Optoelectronic Properties, and Device Design. *Advanced Energy Materials*, 11(24):2003877, 2021. ISSN 1614-6840. doi: 10.1002/aenm.202003877.
- [11] Parsa Darman, Amin Yaghoobi, and Sara Darbari. Pinhole-free 2D Ruddlesden–Popper perovskite layer with close packed large crystalline grains, suitable for optoelectronic applications. *Scientific Reports*, 13(1):8374, May 2023. ISSN 2045-2322. doi: 10.1038/s41598-023-35546-1.
- [12] Shuichiro Ogawa, editor. *Organic Electronics Materials and Devices*. Springer Japan, Tokyo, 2024. ISBN 978-4-431-56935-0. doi: 10.1007/978-4-431-56936-7.
- [13] Debashis Maji, Arun Dev Dhar Dwivedi, and Parthsarathi Chakrabarti. *Organic Electronics - From Fundamentals to Applications*. IntechOpen, October 2025. ISBN 978-1-83634-082-9 978-1-83634-083-6 978-1-83634-084-3. doi: 10.5772/intechopen.111086.
- [14] L. Basirico, A. Ciavatti, and B. Fraboni. Solution-Grown Organic and Perovskite X-Ray Detectors: A New Paradigm for the Direct Detection of Ionizing Radiation. 2021. doi: 10.1002/admt.202000475.
- [15] ChemistryLibreTexts. 13.1: The Electromagnetic Spectrum, 2023. URL https://chem.libretexts.org/Courses/Pacific_Union_College/Quantum_Chemistry/13%3A_Molecular_Spectroscopy/13.01%3A_The_Electromagnetic_Spectrum.
- [16] P. E. J. Flewitt and R. K. Wild. *Physical Methods for Materials Characterisation*. Series in Materials Science and Engineering. Institute of Physics Pub, Bristol ; Philadelphia, 2nd ed edition, 2003. ISBN 978-0-7503-0808-3.
- [17] StackExchange. optical absorption processes in semiconductors spectrum, 2014. URL https://www.bing.com/images/search?view=detailV2&ccid=8%2b2SJb%2fV&id=9793CA6E14993641558E5393578AD5E5B38AEA54&thid=0IP.8-2SJb_V6wpb5AJ_efBpzAHaGa&mediaurl=https%3a%2f%2fi.stack.imgur.com%2fDqoEW.png&cdnurl=https%3a%2f%2fth.bing.com%2fth%2fid%2fR.f3ed9225bfd5eb0a5be4027f79f069cc%3frfk%3dV0qKs%2f

252bXVileTUw%26pid%3dImgRaw%26r%3d0&exph=2096&expw=2422&q=optical+absorption+processes+in+semiconductors+spectrum&FORM=IRPRST&ck=86E4BA9AF988CC7D3A6035C8DC394FAF&selectedIndex=37&itb=1&ajaxhist=0&ajaxserp=0.

- [18] Michael P. Marder. *Condensed Matter Physics*. John Wiley & Sons, November 2010. ISBN 978-0-470-94994-8.
- [19] Charles Kittel. *Introduction to Solid State Physics*. Wiley, 1996. ISBN 978-0-471-11181-8.
- [20] Subhabrata Dhar. *Excitons in Semiconductors*, volume 204 of *Springer Series in Solid-State Sciences*. Springer Nature Switzerland, Cham, 2025. ISBN 978-3-031-87277-8 978-3-031-87278-5. doi: 10.1007/978-3-031-87278-5.
- [21] Patrycja Makuła, Michał Pacia, and Wojciech Macyk. How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra. *The Journal of Physical Chemistry Letters*, 9(23):6814–6817, December 2018. doi: 10.1021/acs.jpcllett.8b02892.
- [22] R. J. Elliott. Intensity of Optical Absorption by Excitons. *Physical Review*, 108(6): 1384–1389, December 1957. doi: 10.1103/PhysRev.108.1384.
- [23] S. (Shaul) Mukamel. *Principles of Nonlinear Optical Spectroscopy*. New York : Oxford University Press, 1995. ISBN 978-0-19-509278-3. URL <http://archive.org/details/principlesofnonl0000muka>.
- [24] Hartmut Haug and Stephan W. Koch. *Quantum Theory of the Optical and Electronic Properties of Semiconductors*. World Scientific, 2009. ISBN 978-981-283-883-4.
- [25] Christopher Charles Busby. The Secondary Photoelectron Effect: Gamma Ray Ionisation Enhancement in Tissues from High Atomic Number Elements. In *The Secondary Photoelectron Effect: Gamma Ray Ionisation Enhancement in Tissues from High Atomic Number Elements*. July 2019. ISBN 978-1-83962-259-5. doi: 10.5772/intechopen.86779.
- [26] Claude Leroy and Pier-Giorgio Rancoita. *Principles of Radiation Interaction in Matter and Detection*. World Scientific, 2009. ISBN 978-981-281-827-0.
- [27] James R. Connolly. Introduction to X-Ray Powder Diffraction, 2007. URL https://www.cigs.unimo.it/CigsDownloads/labs/xrdp/manuali_lettura/02-Rad-Safety.pdf.
- [28] John H Moore, Christopher C Davis, and Michael A Coplan. *BUILDING SCIENTIFIC APPARATUS, Fourth Edition*. 2009.

- [29] R.A. Yotter and D.M. Wilson. A review of photodetectors for sensing light-emitting reporters in biological systems. *IEEE Sensors Journal*, 3(3):288–303, June 2003. ISSN 1558-1748. doi: 10.1109/JSEN.2003.814651.
- [30] Beatrice Fraboni, Andrea Ciavatti, Laura Basiricò, and Alessandro Fraleoni-Morgera. Organic semiconducting single crystals as solid-state sensors for ionizing radiation. *Faraday Discussions*, 174(0):219–234, December 2014. ISSN 1364-5498. doi: 10.1039/C4FD00102H.
- [31] A. L. van der Feltz. VIS/NIR photocurrent spectroscopy on organic semiconductors by lock-in amplification. Master’s thesis, 2016. URL <https://studenttheses.uu.nl/handle/20.500.12932/24459>.
- [32] Newport. QTH Lamps | QTH Light Sources, 2026. URL <https://www.newport.com/f/qth-lamps>.
- [33] Thorlabs. Hg-Xe Short-Arc Lamp Manual, 2017. URL <https://media.thorlabs.com/globalassets/items/s/sl/sls/sls402/doc-103216.pdf?v=0116025446>.
- [34] ChemistryLibreTexts. 7.2: Sources of Radiation, June 2020. URL https://chem.libretexts.org/Courses/Providence_College/CHM_331_Advanced_Analytical_Chemistry_1/07%3A_Components_of_Optical_Instruments_for_Molecular_Spectroscopy_in_the_UV_and_Visible/7.02%3A_Sources_of_Radiation.
- [35] Christopher Palmer. *DIFFRACTION GRATING HANDBOOK, Eighth Edition*. March 2020.
- [36] Kirsty McGhee. Spectrometer Configurations: Littrow, Czerny-Turner and More, 2026. URL <https://www.ossila.com/pages/spectrometer-optics>.
- [37] StanfordResearchSystems. SR830-UserManual, 2004. URL <https://www.thinksrs.com/downloads/pdfs/manuals/SR830m.pdf>.
- [38] ZurichInstruments. Principles of Lock-in Detection, December 2019. URL <https://www.zhinst.com/europe/it/resources/principles-of-lock-in-detection/>.
- [39] Ashim Kumar Bain. *Pyroelectric Materials: Physics and Applications*. Wiley-VCH, Weinheim, Germany, 2023. ISBN 978-3-527-83974-2.
- [40] FEMTO. FEMTO-DLPVA-100-Datasheet, 2018. URL <https://www.eoc-inc.com/wp-content/uploads/FEMTO-DLPVA-100-BS-BD-R7.pdf>.

- [41] FEMTO. FEMTO-DHPCA-100-Datasheet, 2019. URL <https://www.femto.de/images/pdf-dokumente/de-dhpca-100.pdf>.
- [42] FEMTO. FEMTO-DLPCA-200-Datasheet, 2019. URL <https://www.femto.de/images/pdf-dokumente/de-dlpca-200.pdf>.
- [43] OxfordInstrumentsXraysTechnologies. Typical X-ray Spectra by Anode Material - X-Ray Technology, 2026. URL <https://xray.oxinst.cn/application-notes/typical-x-ray-spectra-by-anode-material>.
- [44] Giovanni <1995> Armaroli. *Optoelectronic Investigation of Defects in Hybrid Metal Halide Perovskites*. Doctoral Thesis, Alma Mater Studiorum - Università di Bologna, June 2023.
- [45] Giovanni Armaroli, Laura Ferlauto, Ferdinand Lédée, Matilde Lini, Andrea Ciavatti, Alessandro Kovtun, Francesco Borgatti, Gabriele Calabrese, Silvia Milita, Beatrice Fraboni, and Daniela Cavalcoli. X-ray-induced modification of the photophysical properties of MAPbBr₃ single crystals. *ACS applied materials & interfaces*, 13(49): 58301–58308, December 2021. ISSN 1944-8252. doi: 10.1021/acsami.1c16072.
- [46] Nicola Sestu, Michele Cadelano, Valerio Sarritzu, Feipeng Chen, Daniela Marongiu, Roberto Piras, Marina Mainas, Francesco Quochi, Michele Saba, Andrea Mura, and Giovanni Bongiovanni. Absorption F-Sum Rule for the Exciton Binding Energy in Methylammonium Lead Halide Perovskites. *The Journal of Physical Chemistry Letters*, 6(22):4566–4572, November 2015. doi: 10.1021/acs.jpcllett.5b02099.
- [47] J.-C. Blancon, H. Tsai, W. Nie, C. C. Stoumpos, L. Pedesseau, C. Katan, M. Kepenekian, C. M. M. Soe, K. Appavoo, M. Y. Sfeir, S. Tretiak, P. M. Ajayan, M. G. Kanatzidis, J. Even, J. J. Crochet, and A. D. Mohite. Extremely efficient internal exciton dissociation through edge states in layered 2D perovskites. *Science*, 355(6331):1288–1292, March 2017. doi: 10.1126/science.aal4211.
- [48] Aochen Du, Debing Shen, Wenxiao Zhao, Yongzhen Liu, Xinzhi Qin, Zexi Lin, Yun Ye, Enguo Chen, Sheng Xu, and Tailiang Guo. Structural, vibrational, photoelectrochemical, and optical properties of two-dimensional Ruddlesden–Popper perovskite BA₂PbI₄ crystals. *Nanoscale*, 15(19):8675–8684, May 2023. ISSN 2040-3372. doi: 10.1039/D2NR06860E.
- [49] Vito Fodera. *Characterization of In-Gap Electronic States in Two-Dimensional Single Crystal PEA₂PbBr₄ Perovskite for x-Ray Detection*. Tesi di laurea, November 2022. URL <https://amslaurea.unibo.it/id/eprint/27130/>.
- [50] Camilla Bordoni, Lorenzo Calcaterra, Andrea Ciavatti, Silvia Milita, Valentina Bonino, Lorenzo Margotti, Sara Cepić, Marisa Di Sabatino, Federico Boscherini,

- Daniela Cavalcoli, and Beatrice Fraboni. Linking Device Performance to Nanoscale Photoactivation of Grain Boundaries in 2D Hybrid Halide Perovskites. *Advanced Materials Technologies*, n/a(n/a):e00004, 2026. ISSN 2365-709X. doi: 10.1002/admt.202600004.
- [51] Ferdinand Lédée, Andrea Ciavatti, Matteo Verdi, Laura Basiricò, and Beatrice Fraboni. Ultra-stable and robust response to x-rays in 2D layered perovskite micro-crystalline films directly deposited on flexible substrate. *Advanced Optical Materials*, 10(1):2101145, 2022. ISSN 2195-1071. doi: 10.1002/adom.202101145.
- [52] Andrea Ciavatti, Vito Foderà, Giovanni Armaroli, Lorenzo Maserati, Elisabetta Colantoni, Beatrice Fraboni, and Daniela Cavalcoli. Radiation hardness and defects activity in PEA2PbBr4 single crystals. 2024. doi: 10.1002/adfm.202405291.
- [53] Shan Wei, Hyung Choi, Ghassan Jabbour, Arokia Nathan, and Jun Yu. Fully Inkjet-Printed, Flexible TIPS-Pentacene Photodetector for Photoplethysmogram. *Advanced Optical Materials*, 13, September 2025. doi: 10.1002/adom.202501942.
- [54] Francesco Maccaferri. *Organic Thin-Film Transistors Fabricated via Pneumatic Nozzle Printing as Direct Detectors for Ionizing Radiations*. Tesi di laurea, April 2021. URL <https://amslaurea.unibo.it/id/eprint/23204/>.
- [55] Ilaria Fratelli, Laura Basiricò, Andrea Ciavatti, Zachary A. Lamport, John E. Anthony, Ioannis Kyminis, and Beatrice Fraboni. Trap states ruling photoconductive gain in tissue-equivalent, printed organic x-ray detectors. *Advanced Materials Technologies*, 8(3):2200769, 2023. ISSN 2365-709X. doi: 10.1002/admt.202200769.
- [56] Stefanie Neutzner, Félix Thouin, Daniele Cortecchia, Annamaria Petrozza, Carlos Silva, and Ajay Ram Srimath Kandada. Exciton-polaron spectral structures in two-dimensional hybrid lead-halide perovskites. *Physical Review Materials*, 2(6):064605, June 2018. doi: 10.1103/PhysRevMaterials.2.064605.
- [57] Nicholas J. Hestand and Frank C. Spano. Expanded Theory of H- and J-Molecular Aggregates: The Effects of Vibronic Coupling and Intermolecular Charge Transfer. *Chemical Reviews*, 118(15):7069–7163, August 2018. ISSN 0009-2665. doi: 10.1021/acs.chemrev.7b00581.
- [58] Duc Viet Le, Jessica M. de la Perrelle, Thanh Nhut Do, Xuan Leng, Patrick C. Tapping, Gregory D. Scholes, Tak W. Kee, and Howe-Siang Tan. Characterization of the ultrafast spectral diffusion and vibronic coherence of TIPS-pentacene using 2D electronic spectroscopy. *The Journal of Chemical Physics*, 155(1):014302, July 2021. ISSN 0021-9606. doi: 10.1063/5.0055528.

Index

A

Absorbed Dose, 12
Active Area, 25
Amplifier
 Lock-in, 23
 Transimpedance, 27
 Voltage, 26
Anion, 3
Arc Discharge, 18

B

Blaze
 Angle, 19
 Condition, 21
Bremsstrahlung Radiation, 29

C

Cable
 Coaxial, 27
 GPIB, 37
 RS-232, 37
Cation
 Divalent Metallic, 3
 Monovalent, 3
 Organic, 4
Chopper, 24
Coefficient
 Absorption, 9
 Linear Attenuation, 11
 Mass Attenuation, 11
Collimator, 31
Compton Scattering, 11
Confinement
 Dielectric, 6
 Quantum, 6
Continuum, 10

Coolidge X-ray Tube, 29

Cooling
 Fan, 18
 Water, 31

Current
 Dark, 14
 Electronic, 30
 Filament, 31

D

Defects, 3
 Electrically Active, 17
Detector
 EMR, 12
 Optical, 13
 Pyroelectric, 25
 Silicon Photodiode, 25
 X-rays, 14
Diffraction Grating, 19
Dispersion
 Angular, 21
 Reciprocal Linear, 21
Dose Rate, 30
Dwell Time, 24
Dynamic Reserve, 24

E

Effective Active Area, 39
Electrodes
 Interdigitated, 44
Electromagnetic Radiation, 12
Electron
 Auger, 11
 Compton, 12
 Core Shell, 11
Elemental Charge, 14

Elliott Formula, 10
 Truncated 3D, 48
 Enabling Shutter, 31
 Exciton
 Bound, 9
 Free, 9
 Frenkel, 11
 Wannier-Mott, 11
 Exciton Binding Energy, 10
 External Quantum Efficiency, 13

F

Factor
 Coulomb Enhancement, 11
 Huang-Rhys, 77
 Figures of Merit, 13
 Filter
 Low Pass, 24
 Roll-off, 24
 Flux, 39
 Function
 Dirac Delta, 11
 Gaussian Broadening, 48
 Heaviside Step, 11
 Fundamental Absorption Edge, 9

G

Gap
 Electronic, 10
 Optical, 10
 Goldschmidt's Tolerance Factor, 3
 Graphical User Interface, 37
 Grating Equation, 20
 Graybody, 18
 Grooves, 19

H

Halogen Cycle, 18
 Higher-order Diffractions, 20

I

I-V Curve, 50

Ion Migration, 3

L

Lamp
 Quartz-Tungsten-Halogen, 18
 Xenon Arc, 18
 Laser, 35
 Lead-Glass Enclosure, 31
 Light Speed, 8
 Limit
 of Detection, 14
 of Resolution, 21
 Littrow Configuration, 21

M

Micromanipulators, 27
 Mirror
 Parabolic, 34
 Molecular Orbitals
 Highest Occupied, 7
 Lowest Unoccupied, 7
 Monochromator, 19
 Multi-Quantum Well, 6

N

Noise, 43
 Normalization, 47

O

Optical Fibre, 31
 Optical Power, 13
 Organic Semiconductor, 7
 Output Focal Length, 21

P

Pair Production Processes, 11
 Peak
 Excitonic, 9
 Vibronic, 62
 Penetration Depth, 8
 Perovskites, 3
 inorganic-organic hybrid, 4

Phase-Sensitive Detection, 23

Photoconductor, 13

 Lateral, 13

 Vertical, 13

Photocurrent, 16

 Actual, 40

 Spectroscopy, 16

Photodetector, 13

 Performance, 13

 Photonic, 13

 Thermal, 13

Photoelectric Absorption, 11

Photoelectron, 11

Photolithography, 44

Photons, 8

Planck Constant, 8

Power Supply, 17

 High Voltage, 31

Powermeter, 35

Python, 37

Q

Quartz Glass Envelope, 18

Quasiparticles, 9

Quenching, 61

R

Radiation

 Hardness, 57

 Transparency, 57

Radiocurrent, 1

Reference Frequency, 23

Resolution, 21

Resolving Power, 21

Responsivity, 13

Ruddlesden-Popper, 5

S

Safety Systems, 31

Sensitivity, 14

Slit, 21

Source

 Line, 18

 Calibration, 39

 Incoherent Continuum, 18

Spectral Response, 13

Spectrometer, 36

Stopping Power, 14

Study

 Ex-situ, 1

 In-situ, 1

Substrate, 44

T

Tab

 Manual/Aux, 38

 Scan, 38

Target, 29

Tauc

 plot, 10

Tauc Plot

 Modified, 49

Threads, 38

Time

 Fall, 14

 Response, 14

 Rise, 14

Time Constant, 24

V

Van der Waals, 5

Voltage

 Cathodic, 30

W

Wavelets, 20