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PHYSICS

Investigation of Semiconductor Quantum Dot Growth Dynamics by In Situ X-ray Absorption Spectroscopy

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Abstract

Copper indium sulphide (CuInS_2 , CIS) quantum dots are promising semiconductor nanomaterials for optoelectronic and photovoltaic applications owing to their low toxicity and tunable optical properties. Despite the extensive use of colloidal synthesis routes, the microscopic mechanisms governing their nucleation and growth are still not fully understood because of the transient nature of the intermediate species involved.

This thesis investigates physical and chemical processes occurring on different timescales using synchrotron-radiation-based techniques. It combines a feasibility study of pump & probe experiments at the LISA beamline (ESRF) with an in situ XAS investigation of CuInS_2 quantum-dot growth. While the available laser source proved insufficient for pump & probe measurements, the XAS campaign successfully yielded static and time-resolved Cu and In K-edge spectra throughout the synthesis.

The EXAFS analysis allowed the evolution of the local coordination environment around both metal centres to be followed throughout the reaction. XANES analysis showed that indium remained as In(III) throughout the synthesis, whereas glutathione reduced Cu(II) to Cu(I).

The most significant outcome of this work was provided by the time-resolved XAS measurements. The different kinetic responses observed at the Cu and In K-edges support a reaction pathway involving the formation of an indium-sulphide intermediate immediately after sulphide injection, followed by the slower incorporation of copper into the growing CuInS_2 nanocrystals. To the best of our knowledge, this represents the first in situ XAS evidence supporting such an intermediate in this synthesis route.

Overall, this work demonstrates the capability of synchrotron XAS to probe both the structural evolution and the reaction kinetics of colloidal nanocrystal synthesis, providing a general experimental strategy for investigating reaction mechanisms in colloidal nanocrystal synthesis under operando conditions.

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Chapter 1

Introduction

The first chapter introduces the scientific background relevant to the work presented in this thesis. First, the fundamental concepts underlying pump–probe methodologies are briefly reviewed. The discussion then focuses on the synthesis and growth of semiconductor quantum dots (QDs), with particular emphasis on CuInS_2 (CIS) nanocrystals, which constitute the principal system investigated in this work. Finally, a concise overview of X-ray Absorption Spectroscopy (XAS), the experimental technique employed throughout the synchrotron measurements and a focus on the state of the art in XAS measurements of liquid samples in particular are provided.

The second chapter provides a brief overview of the LISA beamline, where the experiments presented in this thesis were carried out, together with a description of the experimental setup and the operating conditions adopted during the measurements.

The third and final chapter presents the results of the XAS experimental campaign devoted to the investigation of the synthesis of CIS nanocrystals and discusses the analyses performed on the collected data. The chapter concludes with the results of the feasibility study on pump & probe experiments.

1.1 Pump & probe transient absorption spectroscopy

Transient absorption (TA) spectroscopy encompasses a family of time-resolved techniques designed to probe the evolution of a system following an external perturbation. Among these methods, pump & probe spectroscopy is one of the most widely employed approaches for investigating photo-induced processes on timescales ranging from femtoseconds to milliseconds. In a pump & probe experiment, the sample is first excited by a short laser pulse (pump), and its transient state is subsequently interrogated by a second pulse (probe) after a controlled delay time Δt . By measuring the changes induced in the probe signal as a function of the pump-probe delay, it is possible to reconstruct the temporal evolution of the excited-state population and to access the dynamics of the underlying physical or chemical processes [1].



Figure 1.1: Schematic representation of a pump & probe transient absorption experiment (adapted from [1]). In the left image there is a schematic representation of a pump signal exciting the sample and the probe signal monitoring the system’s evolution after delay time Δt . In the right one the difference absorbance spectrum (ΔA) induced by the pump is sketched for different delay times t

The ability of transient absorption spectroscopy to resolve ultrafast phenomena is closely linked to the development of increasingly short laser pulses. Early flash-photolysis experiments, based on light pulses with durations in the microsecond–millisecond range, enabled the study of relatively slow photochemical processes [2]. The subsequent development of amplified femtosecond laser systems extended the accessible temporal window to timescales comparable to atomic and molecular motions, leading to the widespread adoption of ultrafast spectroscopy in physics, chemistry, and materials science [1].

Given the capability of pump & probe techniques to investigate photo-induced dynamics, the possibility of performing time-resolved synchrotron experiments was initially considered within the scope of this thesis. In particular, the objective was to evaluate whether pump & probe X-ray absorption measurements could be employed at the LISA beamline to investigate ultrafast processes in solution. Before

attempting such experiments, however, it was necessary to assess their practical feasibility by modeling the physical system and estimating the fraction of photoexcited molecules and the magnitude of the corresponding X-ray absorption signal expected under the available experimental conditions. The results of this analysis are shown in Chapter 3 (see 3.2).

1.2 Quantum dots growth

Semiconductor quantum dots (QDs) are nanometer-sized crystalline particles whose electronic and optical properties are strongly influenced by quantum confinement effects. As a consequence, their absorption and emission characteristics can be tuned by controlling parameters such as size, composition, and morphology. Owing to these unique properties, QDs have attracted considerable interest for applications ranging from light-emitting devices and photovoltaics to photocatalysis, biological imaging, and quantum technologies [3, 4, 5].

The practical implementation of quantum dots in such applications requires precise control over their size distribution, crystal structure, and surface chemistry, all of which are established during the synthesis process. Consequently, a detailed understanding of the nucleation and growth mechanisms governing colloidal semiconductor nanocrystals is essential for achieving precise control over their structural, optical, and electronic properties. As discussed by Cossairt [6], the formation of colloidal quantum dots often cannot be adequately described by classical nucleation theories alone. Instead, the synthesis of semiconductor nanocrystals involves a complex interplay of precursor chemistry, reaction conditions, and intermediate species, leading to growth pathways that may differ substantially from those observed in conventional crystalline systems.

Particular attention has been devoted to the role of intermediate clusters formed during the early stages of synthesis. Among these, so-called *magic-sized clusters* (MSCs) have been identified as key species in the formation of a wide range of semiconductor nanomaterials, including II-VI, IV-VI, and III-V quantum dots. Experimental evidence suggests that these atomically precise clusters can act as precursors to larger nanocrystals through different growth mechanisms. In particular, the transition from MSCs to QDs may proceed either through monomer-mediated growth, in which molecular species are progressively incorporated into the growing nanocrystal, or through cluster-assembly processes involving the aggregation and reorganization of pre-existing clusters.

The existence of multiple competing growth pathways, together with the transient nature of the intermediate species involved, highlights the need for experimental techniques capable of probing the reaction environment under realistic synthesis conditions and with sufficient temporal resolution. In this context, *in situ* spec-

troscopic methods have emerged as powerful tools for investigating nanocrystal formation processes. By enabling the direct observation of structural and electronic changes during synthesis, these techniques provide access to information that is often inaccessible through conventional *ex situ* characterization.

Among the available approaches, X-ray absorption spectroscopy is particularly well suited for studying the formation and growth of semiconductor quantum dots. Owing to its element selectivity and sensitivity to the local atomic and electronic structure, XAS can probe the evolution of precursor species, reaction intermediates, and nanocrystal products throughout the synthesis process. As noted by Cossairt [6], the application of *in situ* spectroscopic techniques represents a promising route toward elucidating the mechanisms governing QD nucleation and growth. This consideration constitutes one of the main motivations for the present work, in which *in situ* XAS measurements were employed to study the synthesis of a specific type of nanocrystals.

1.2.1 CuInS₂ quantum dots

Among the various classes of semiconductor quantum dots, ternary metal chalcogenide nanocrystals have attracted considerable attention owing to their compositional versatility and the possibility of tuning their optoelectronic properties through both size and stoichiometry. These materials have been extensively investigated for applications in photovoltaics, photocatalysis, light-emitting devices, biological imaging, and thermoelectric energy conversion. Within this family, Copper Indium Sulfide Quantum Dots (CIS-QDs) represent one of the most widely studied systems due to their favorable optical properties, low toxicity compared to Cd- and Hg-based quantum dots, and the possibility of synthesizing them with relatively good size control and high yields [7]. Images of CIS QDs are shown in Figure 1.2.

CuInS₂ can crystallise in two main structures, particularly at the nanometre scale: Chalcopyrite structure (tetragonal) or Wurtzite structure (hexagonal). The former derives from the zincblende (cubic) structure, in which Cu⁺ and In³⁺ alternately occupy the cation sites. The latter derives from the wurtzite structure of binary semiconductors, with Cu⁺ and In³⁺ distributed either randomly or in an ordered manner. The chalcopyrite structure is the most common as it is thermodynamically stable, whilst the wurtzite structure is thermodynamically metastable.

The development of environmentally benign and biocompatible synthetic routes has further increased the interest in CIS nanocrystals. While many conventional syntheses rely on hot-injection procedures carried out in high-boiling organic solvents, aqueous-phase approaches have emerged as attractive alternatives because they are simpler, less expensive, and more environmentally sustainable. In addition, water-based syntheses avoid the use of toxic heavy metals such as Cd and

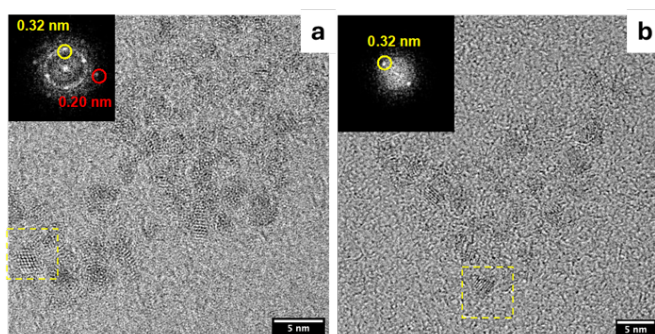


Figure 1.2: High resolution TEM micrographs of the CIS-QDs. Fourier transform in the inset (every FFT refers to a single particle, highlighted in the image by the square dotted in yellow), TEM micrographs were acquired by Alessandro Gradone, a collaborator in CNR Bologna (from [8]).

Hg, making the resulting nanomaterials more suitable for biological and biomedical applications [9]. As a consequence, significant efforts have been devoted to the development of highly luminescent, water-soluble CIS quantum dots.

CIS QDs, differ significantly from conventional II–VI semiconductor nanocrystals such as CdSe. While quantum confinement still influences their electronic structure, their optical response is largely governed by intra-band-gap states associated with copper-related defects. As a result, CIS-QDs typically exhibit broad absorption features without a well-defined excitonic peak, strongly red-shifted and broad photoluminescence bands, and unusually long emission lifetimes. These characteristics are generally attributed to defect-mediated radiative recombination involving localized electronic states, which reduce the overlap between electron and hole wavefunctions and consequently lower the radiative recombination rate [8].

Despite the considerable progress achieved in controlling the optical properties of CIS nanocrystals, the fundamental processes governing their formation remain only partially understood. In particular, the reaction pathways leading from molecular precursors to crystalline nanostructures, as well as the evolution of the nanocrystal surface during growth, are still the subject of active investigation

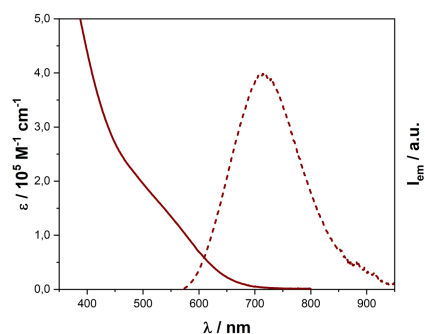


Figure 1.3: Absorption (solid line) and emission (dashed line, $\lambda_{exc} = 405\text{nm}$) spectra of CIS-QDs (4.1 nm) in CHCl_3 (from [8]).

[7]. A detailed understanding of these processes is essential for establishing reliable synthesis-structure-property relationships and for rationally optimizing the performance of CIS-based materials.

To address these questions, some studies have already employed synchrotron-based characterization techniques capable of probing the structural evolution of nanocrystals during synthesis. Beyond the case of CuInS_2 , synchrotron-based techniques have been successfully employed to investigate the formation mechanisms of a variety of nanocrystal systems, including CdSe quantum dots and nanoplatelets. In particular, *in situ* SAXS/WAXS measurements have provided direct information on nucleation and growth kinetics, while *in situ* XAS experiments have enabled the monitoring of precursor conversion and local structural evolution during nanocrystal formation. These studies demonstrate the unique capability of synchrotron radiation to probe reaction mechanisms under realistic synthesis conditions and highlight the potential of XAS as a complementary tool for elucidating the formation pathways of semiconductor nanocrystals. [10, 11, 12, 13]

As for the specific case of CuInS_2 , in 2017, the growth mechanism of CIS nanocrystals synthesized in dodecanethiol (DDT) was investigated at the ESRF synchrotron using a combination of small-angle and wide-angle X-ray scattering (SAXS/WAXS) measurements [7]. These experiments provided valuable information on the nucleation and growth stages of the reaction, highlighting the potential of synchrotron techniques for the study of nanocrystal formation mechanisms.

Following a similar rationale, the present work focuses on the investigation of a specific aqueous synthesis of CuInS_2 nanocrystals, described in detail in Chapter 2 (see Section 2.2). Rather than employing scattering techniques, the study exploits *in situ* X-ray absorption spectroscopy (XAS), introduced in Section 1.3, to monitor the evolution of the local atomic and electronic structure around the constituent elements during the synthesis process. Thanks to its element-selective character and sensitivity to short-range order, XAS provides complementary information to diffraction- and scattering-based methods, offering a powerful approach for elucidating the reaction pathways involved in the formation and growth of CIS QDs.

1.3 X-ray Absorption Spectroscopy (XAS)

1.3.1 General principles of XAS

As discussed in Section 1.2.1, the experimental work presented in this thesis relies on X-ray Absorption Spectroscopy (XAS), a synchrotron-based technique capable of providing element-specific information on the local electronic and structural environment of selected atomic species.

In a XAS experiment, a monochromatic X-ray beam is tuned across an absorption edge of the element of interest while the absorption of the sample is monitored as a function of photon energy. The quantity measured is the linear absorption coefficient $\mu(E)$, which describes the attenuation of the incident radiation according to the Beer–Lambert law:

$$I(E) = I_0(E)e^{-\mu(E)d}, \quad (1.1)$$

where $I_0(E)$ and $I(E)$ are the incident and transmitted intensities, respectively, and d is the thickness of the absorbing medium.

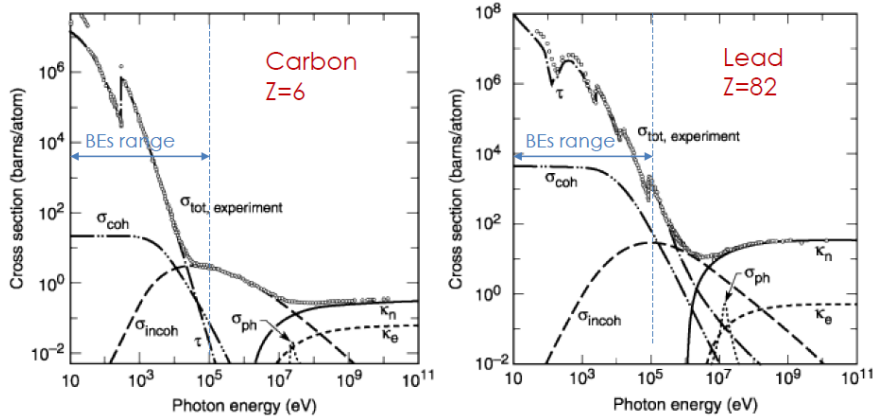


Figure 1.4: Cross section of matter-radiation interaction for a light (Carbon) and a heavy (Lead) atom (from [14])

When the photon energy matches the binding energy of a core-level electron, the probability of photoabsorption increases abruptly, producing the characteristic absorption edges observed in XAS spectra. Since each element possesses a unique set of core-electron binding energies, XAS is intrinsically element-selective and allows specific atomic species to be probed even in chemically complex materials.

1.3.2 Measurement modes

The spectrum can be obtained in different measurement modes:

1. Transmission measurement mode
2. Fluorescence yield mode
3. Auger electrons/ total electron yield mode

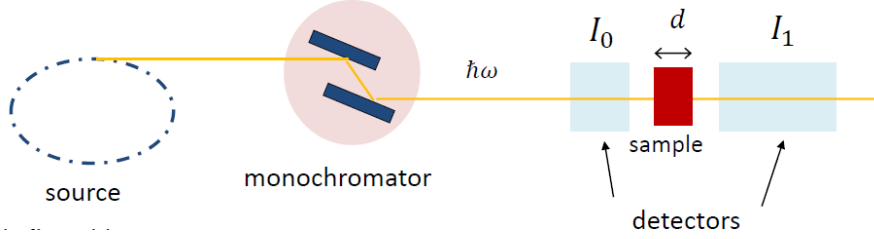


Figure 1.5: Scheme of a XAS experiment (from [14])

In the **Transmission** mode the $\mu(\hbar\omega)$ spectrum is measured as:

$$\mu(\hbar\omega) = -\ln\left(\frac{I_1}{I_0}\right) \quad (1.2)$$

where I_1 is the *transmitted beam*, measured in the second ionization chamber, after the beam has passed through the sample and I_0 is the *incident beam*, measured in the first ionization chamber, before the beam has probed the sample.

The fluorescence-yield and electron-yield modes exploit the relaxation processes that follow the creation of a core hole by photoabsorption. After the emission of a photoelectron, the excited atom returns to its ground state through either radiative or non-radiative decay channels.

In the radiative decay channel, commonly referred to as **fluorescence**, an electron from a higher electronic shell fills the core hole created by photoabsorption. The excess energy released in the transition is emitted as a characteristic X-ray photon, whose energy is equal to the difference between the binding energies of the two electronic levels involved in the transition. For an $L \rightarrow K$ transition:

$$\hbar\omega = E_L - E_K \quad (1.3)$$

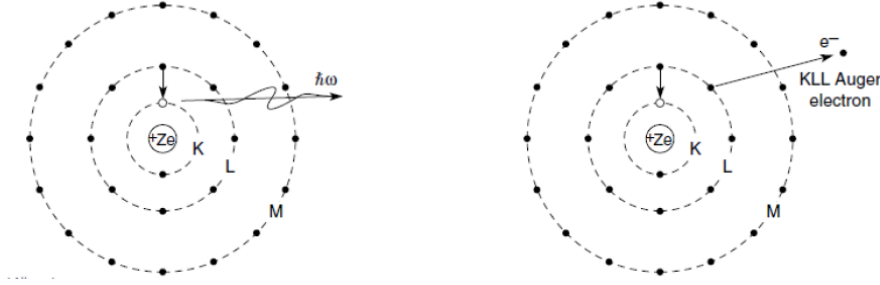


Figure 1.6: De-excitation atomic mechanisms after photoabsorption: *fluorescence* (left) or emission of *Auger electrons* (right) (from [14])

Alternatively, the atom may relax through a non-radiative process known as **Auger decay**. In this case, the energy released during the electronic transition is transferred to a second electron, which is ejected from the atom. For a KLL Auger process, the kinetic energy of the emitted electron is given by:

$$K_A = 2E_L - E_K \quad (1.4)$$

(which comes from the conservation of energy of the system composed by the two electrons involved in the de-excitation mechanism: $2E_L = K_A + E_K$).

The yields of the two de-excitation processes depends on the atomic number of the absorbed atoms. In particular, for core-excited low-Z elements, the Auger relaxation pathway dominates, as shown in Figure 1.7.

Therefore, the absorption coefficient can be reconstructed not only from the attenuation of the transmitted beam, but also from the intensity of the decay products generated following core-hole creation.

In particular, fluorescence detection is often preferred for dilute samples, for which the difference between the incident and transmitted intensities is too small to be measured accurately in transmission geometry.

Once the XAS spectrum has been acquired, it can be analysed by distinguishing two energy regions characterized by different physical processes and complementary structural information: the XANES region and the EXAFS region.

1.3.3 XANES region

The X-ray Absorption Near Edge Structure (XANES) region comprises the pre-edge and the first tens of electronvolts above the absorption edge. The spectral features observed in this energy range are strongly influenced by the local electronic structure and coordination geometry of the absorbing atom. Consequently, XANES analysis provides valuable information on oxidation states, local symmetry, and chemical bonding.

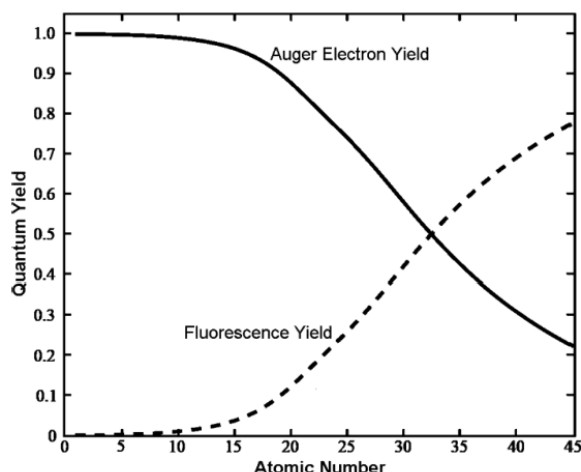


Figure 1.7: Quantum yields of Auger electrons and fluorescent x-rays per core-excited atom in function of atomic number (from [14])

One of the most commonly used descriptors in XANES analysis is the position of the absorption edge. Its determination allows the oxidation state of the photoabsorbing species to be estimated through the so-called *chemical shift*. Experimentally, an increase in oxidation state is generally accompanied by a shift of the absorption edge towards higher energies. By comparing the edge position of an unknown sample with those of suitable reference compounds characterized by known oxidation states, it is therefore possible to infer the average valence state of the absorbing element.

In addition to qualitative comparisons, quantitative interpretation of XANES spectra can be performed through theoretical simulations based on multiple-scattering calculations and *ab initio* methods. However, simpler semi-empirical approaches are often sufficient to extract chemically relevant information. Among these, Linear Combination Analysis (LCA) is particularly useful when the experimental spectrum is expected to originate from a mixture of different chemical species. In the LCA approach, the experimental spectrum is fitted as a weighted sum of reference spectra corresponding to compounds of known structure and composition. The coefficients obtained from the fit can then be interpreted as estimates of the relative abundance of the different species contributing to the measured signal. This method is especially valuable in operando and *in situ* studies, where several chemical states may coexist and evolve during the course of a reaction.

1.3.4 EXAFS region

The Extended X-ray Absorption Fine Structure (EXAFS) region extends from the end of the XANES region up to approximately 1000 eV above the absorption edge. In contrast to XANES, whose interpretation often requires detailed electronic-structure calculations, EXAFS analysis is based on a well-established theoretical framework and provides direct information on the local geometric structure surrounding the absorbing atom.

The physical origin of EXAFS lies in the interaction between the photoelectron emitted during the absorption process and the surrounding atomic environment. In a condensed material, the absorbing atom is not isolated: the outgoing photoelectron wave can be scattered by neighbouring atoms and partially redirected towards the absorber. The interference between the outgoing and backscattered waves modulates the photoabsorption probability, producing the oscillatory structure observed above the absorption edge.

The phase and amplitude of these oscillations depend on the distances between the absorber and the surrounding atoms, on their number, and on their scattering properties. Actually, the EXAFS signal contains quantitative information on the local atomic structure.

Experimentally, the EXAFS function is obtained from the normalized absorption coefficient according to

$$\chi(k) = \frac{\mu(k) - \mu_0(k)}{\mu_0(k)}, \quad (1.5)$$

where $\mu(k)$ is the measured absorption coefficient and $\mu_0(k)$ is the absorption coefficient of the isolated absorber atom. The spectrum is conventionally expressed as a function of the photoelectron wavevector

$$k = \sqrt{\frac{2m_e}{\hbar^2} (\hbar\omega - E_b)}, \quad (1.6)$$

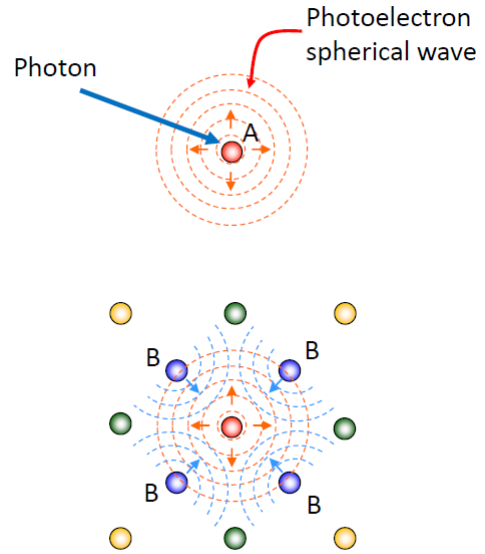


Figure 1.8: Schematic representation of the photoelectron emitted by the absorbing atom and backscattered by neighbouring atoms (from [14]).

which follows directly from the conservation of energy for the emitted photoelectron.

A rigorous derivation of the EXAFS equation can be obtained within multiple-scattering theory and the framework of quantum-mechanical transition probabilities. Only the final expression, obtained within the single-scattering approximation, relevant for data analysis is reported here:

$$\chi(k) = \frac{S_0^2}{k} \sum_{j=\text{shells}} \frac{N_j}{r_j^2} f_j(k, \pi) \sin(2kr_j + \phi_j(k)) e^{-2k^2\sigma_j^2} e^{-\frac{2r_j}{\lambda}} \quad (1.7)$$

This expression can be interpreted as the sum of the contributions arising from the different coordination shells surrounding the absorber. The oscillation frequency is primarily determined by the absorber-scatterer distance r_j , while the amplitude depends on the coordination number N_j , the scattering amplitude $f_j(k, \pi)$, and several damping factors.

The term S_0^2 , commonly referred to as the amplitude reduction factor, accounts for intrinsic many-body effects associated with the photoabsorption process and typically assumes values between 0.7 and 0.9. The factor $f_j(k, \pi)$ describes the scattering efficiency of the neighbouring atom and is characteristic of the chemical species involved, providing the element sensitivity of the EXAFS technique.

The exponential damping term

$$e^{-2r_j/\lambda} \quad (1.8)$$

accounts for extrinsic inelastic losses. Here λ represents the effective mean free path of the photoelectron and includes contributions from both the finite core-hole lifetime and inelastic scattering processes occurring during photoelectron propagation. The finite value of λ progressively attenuates contributions from more distant coordination shells, limiting the structural information accessible through EXAFS to the local atomic environment. For this reason, EXAFS is primarily sensitive to short- and medium-range order rather than to the long-range periodicity of the crystal lattice.

A second damping factor is represented by

$$e^{-2k^2\sigma_j^2}, \quad (1.9)$$

where σ_j^2 is the EXAFS Debye-Waller factor. This parameter describes the mean-square relative displacement between the absorbing atom and the atoms belonging to the j -th coordination shell and therefore accounts for both thermal vibrations and static structural disorder. Its effect is particularly pronounced at high k , where it reduces the amplitude of the EXAFS oscillations.

In practice, EXAFS analysis consists of fitting the experimental spectrum using a structural model describing the local environment of the absorbing atom. The fit

provides quantitative information on the average coordination number N_j , inter-atomic distances r_j , and structural disorder, commonly parameterized through the Debye–Waller factor σ_j^2 . Owing to the finite mean free path of the photoelectron, EXAFS is primarily sensitive to the first few coordination shells surrounding the absorber and therefore probes the local atomic structure rather than the long-range crystalline order. It represents a powerful tool for investigating the local structure of complex materials, including nanocrystalline and amorphous systems for which conventional diffraction techniques may provide only limited information.

1.4 XAS experiments of liquids and solutions with synchrotron source

The feasibility of performing *in situ* and *operando* X-ray absorption spectroscopy (XAS) experiments on liquid samples has been extensively demonstrated in the literature [15, 16, 17]. The development of dedicated sample-delivery systems over the past decades has enabled the successful acquisition of XAS spectra in liquid environments, providing the methodological foundation for the present work.

According to the review reported in Ref. [15], the first X-ray absorption spectrum of a liquid sample was obtained by Yang and Kirz in 1987 [18], who measured the EXAFS spectrum of water using a static liquid cell. Their setup consisted of a 1 μm thick water layer enclosed between two 150 nm thick silicon nitride windows, with the transmitted signal detected by a photomultiplier tube (PMT). Although this work demonstrated the feasibility of liquid-phase XAS measurements, the presence of the windows introduced significant absorption losses.

A major advancement was achieved in 2001, when Wilson *et al.* reported EXAFS and NEXAFS measurements of liquid water using a liquid microjet [19]. Originally developed by Faubel *et al.* in the late 1980s [20] for ultraviolet photoelectron spectroscopy (UPS), liquid microjets are generated by forcing a pressurized liquid through a micron-scale nozzle, producing a continuous stream with velocities typically ranging from 20 to 100 m s^{-1} . The continuously renewed sample and the absence of confining windows in the X-ray beam path significantly reduce absorption effects, leading to improved spectral quality.

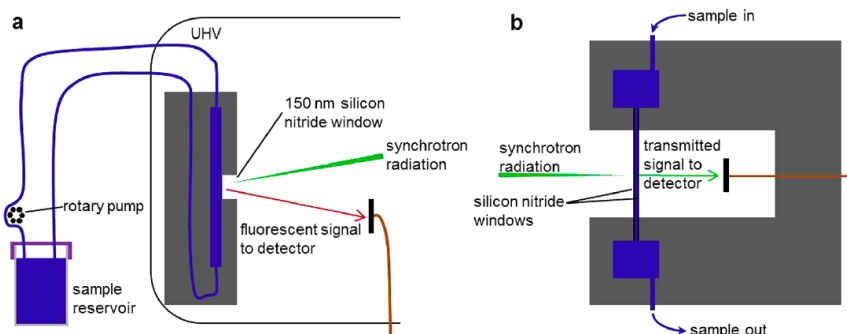


Figure 1.9: Schematic diagrams of several liquid flow cell apparatuses used for XAS experiments: (a) Single-window photon-in/photon-out flow cell for TFY experiments utilizing a recycled sample. (b) Dual-window flow cell for transmission mode experiments (from [15]).

As an alternative to liquid microjets, flow-cell-based approaches were introduced shortly thereafter. The first liquid XAS experiment employing a flow cell was reported by Freiwald *et al.* in 2004 [21]. Their apparatus, schematically illustrated in Figure 1.9a, consisted of a liquid chamber connected to inlet and outlet tubing, allowing continuous circulation of the sample. Incident X-rays entered the cell through a thin silicon nitride membrane, while the fluorescence signal emitted by the sample was collected by the detector.

Since then, several flow-cell designs have been developed, generally employing silicon nitride windows with thicknesses in the range of 100-150 nm. Similar to liquid microjets, flow cells allow continuous sample renewal without interrupting the experiment. However, the achievable flow rates are typically lower, as the pressure applied to the liquid must remain below the mechanical limits of the thin membranes. Moreover, the presence of the windows introduces a solid-liquid interface that is absent in microjet-based measurements.

Despite these limitations, flow cells offer several practical advantages. In particular, they are generally more robust and less susceptible to issues such as sample freezing, which may affect liquid microjet experiments.

Several flow-cell geometries have been proposed to address specific experimental requirements. For example, Nagasaka *et al.* developed a variable-thickness transmission cell, schematically shown in Figure 1.9b, in which the sample thickness can be adjusted *in situ* by controlling the helium pressure applied outside the silicon nitride windows. Conversely, Meibohm *et al.* employed rigid gold spacers to define a fixed sample thickness of 500 nm with high precision [22].

Overall, the successful implementation of both liquid microjets and flow cells has firmly established the feasibility of XAS measurements in liquid environments. In the present work, a flow-cell configuration was adopted owing to its robustness,

operational flexibility, and suitability for the experimental conditions investigated. The design and characteristics of the employed apparatus are discussed in detail in the next chapter (see 2.2).

Chapter 2

Experimental setup and experimental techniques

2.1 LISA beamline

As introduced in Chapter 1.3, the experimental work presented in this thesis was carried out at the LISA beamline of the European Synchrotron Radiation Facility (ESRF), located in Grenoble, France.

The ESRF is one of the world’s leading synchrotron radiation facilities. Established in 1988 through a collaboration among European countries, it was the first third-generation synchrotron source and remains among the brightest X-ray facilities currently in operation. Today, ESRF involves 19 partner nations and routinely delivers X-ray beams with a brilliance exceeding 10^{21} photons s^{-1} mm^{-2} mrad^{-2} (0.1% bandwidth) $^{-1}$. Every year, approximately 10 000 researchers perform more than 2 000 experiments at the facility, resulting in around 1 800 scientific publications.



Figure 2.1: Aerial view of ESRF’s synchrotron ring

The LISA beamline (*“Linea Italiana per la Spettroscopia d’Assorbimento X”*) is the Italian Collaborating Research Group (CRG) beamline at ESRF and is dedicated to X-ray Absorption Spectroscopy (XAS) and related techniques. Operational since 2018 as the successor of the GILDA beamline, LISA is funded by the *Consiglio Nazionale delle Ricerche* (CNR). The beamline is designed to provide a highly stable, high-flux X-ray beam over a wide energy range, approximately

spanning from 4 to 70 keV, enabling XAS measurements under a variety of experimental conditions, including highly dilute samples, low-noise transmission measurements, grazing-incidence geometries, differential-mode acquisition, and time-resolved pump-probe experiments [23].

LISA exploits the radiation emitted by a bending magnet of the ESRF storage ring, which operates with electron bunches accelerated to an energy of ~ 6.03 GeV and a typical current of ~ 200 mA in uniform filling mode.

The beamline is organized into three lead hutches (see Figure 2.2):

- the *optics hutch (OH)*: where the X-ray beam is conditioned;
- the *first experimental hutch (EH1)* with the instrumentation for experiments with a non-focused beam and low-energy harmonic rejection mirrors;
- the *second experimental hutch (EH2)*: containing all the instrumentation for experiments with a focused beam

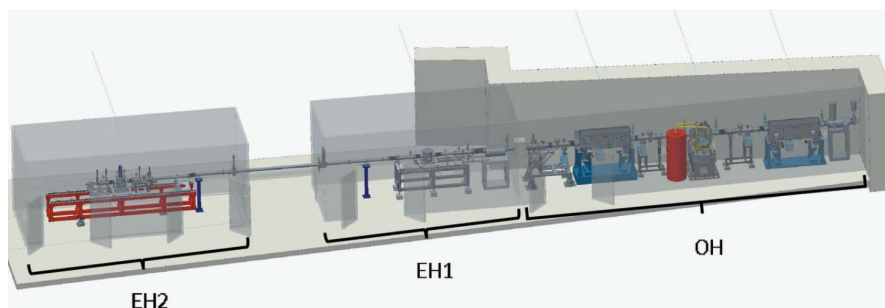


Figure 2.2: General layout of the LISA beamline (from [23]).

2.1.1 Optical hutch

The optical layout consists of a collimating mirror (M1), a fixed-exit double-crystal monochromator, and a focusing mirror (M2). M1 has a cylindrical shape and consists of a single-crystal Si substrate with two optical regions each 35 mm wide and 900 mm long; one exposing the silicon, the other coated with Pt. The Si region is used for harmonic rejection below 15 keV, while the Pt region works between 15 keV and 40 keV. The monochromator is equipped with two interchangeable pairs of silicon crystals cut along the (111) and (311) planes, allowing the optimization of either photon flux or energy resolution depending on the experimental requirements. They are indirectly cooled by liquid nitrogen fed by an external cryocirculator connected with the general liquid-nitrogen distribution network.

The final focusing stage is provided by the double toroidal mirror M2, which consists of a single substrate of crystalline silicon with two parallel cylindrical

channels and focuses the beam onto the second experimental hutch. At photon energies below ~ 6 keV, harmonic suppression is guaranteed by a pair of Pt-coated flat mirrors installed in EH1.

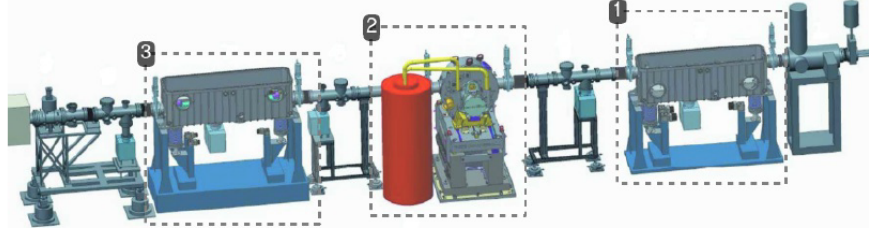


Figure 2.3: Side view of the optics hutch. Numbers label the various elements: 1, first mirror M1; 2, monochromator with cryocooler; 3, second mirror M2 (from [23]).

2.1.2 Experimental hutches

Data acquisition can be performed in two different experimental stations, denoted EH1 and EH2.

EH1 (Figures 2.4, 2.5) is located upstream of the focal point of the beamline optics and is therefore used when a relatively large, unfocused beam is required. Typical beam dimensions in this configuration are approximately 1×2 mm². The hutch is equipped with ionization chambers for transmission measurements and with a sample manipulation system housed inside a vacuum chamber.

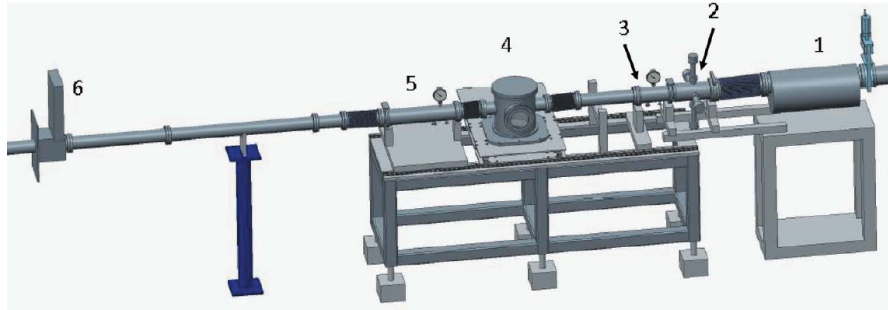


Figure 2.4: Side view of the EH1 cabin. Numbers label the various elements: 1, chamber with low-energy mirrors; 2, slits; 3, ion chamber I_0 ; 4, sample chamber; 5, ion chamber I_1 ; 6, shutter (from [23]).

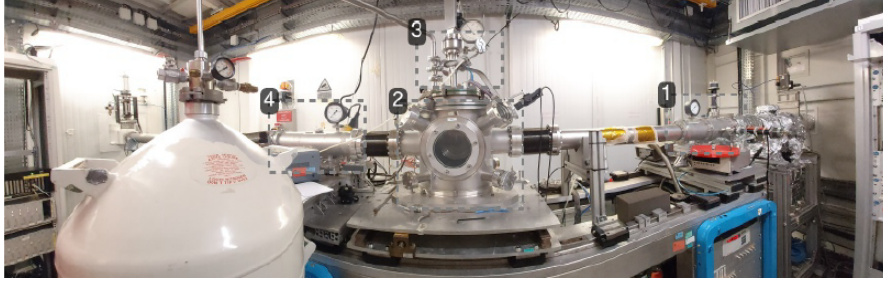


Figure 2.5: Photo of EH1. Numbers label the various elements: 1, ionization chamber ($I_{0,eh1}$); 2, sample chamber; 3, cold finger manipulator ; 4, ionization chamber $I_{1,eh1}$ (from [24]).

EH2 (Figures 2.6, 2.7) is positioned at the focal point of the toroidal mirror and receives the fully focused beam. This station hosts the instrumentation used for the experiments discussed in the present work. The setup includes three ionization chambers for transmission measurements and several fluorescence detectors. For photon energies above approximately 15~keV, two high-purity germanium detector arrays (12 and 13 elements, respectively) are available, whereas lower-energy measurements can be performed using a four-channel silicon drift detector (SDD). In both cases, signal acquisition is based on digital pulse processing.

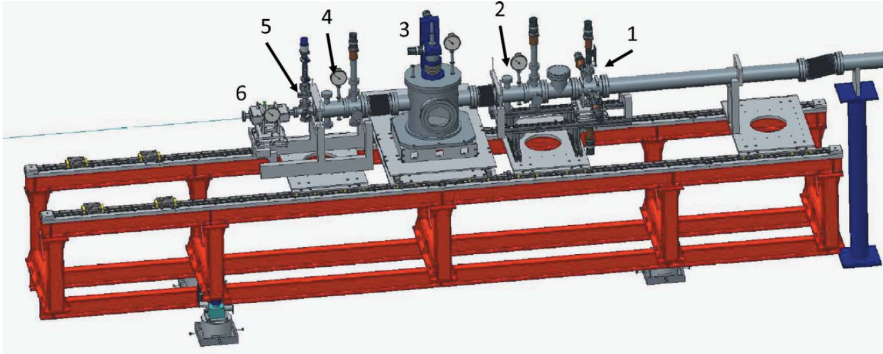


Figure 2.6: Side view of the EH2 cabin. Numbers label the various elements: 1, slits; 2, ion chamber I_0 ; 3, sample chamber; 4, ion chamber I_1 ; 5, reference foils holder; 6, ion chamber I_{ref} (from [23]).

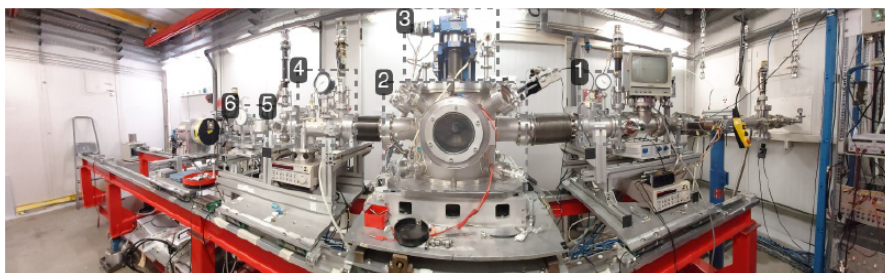


Figure 2.7: Photo of EH2. Numbers label the various elements: 1, ionization chamber ($I_{0,eh2}$); 2, sample chamber; 3, cold finger cryostat ; 4, ionization chamber $I_{1,eh2}$; 5, chamber for reference standard; 6, ionization chamber ($I_{x,eh2}$) (from [24]).

The experimental stations can accommodate a variety of sample environments, including cryogenic systems operating down to ~ 20 K and high-temperature reaction cells capable of reaching temperatures up to 1300 K. The modular design of the beamline allows these sample environments to be exchanged rapidly between the two hutches according to the experimental requirements.

2.2 Experimental working conditions

Now let's delve into the specific working conditions in which the experiments have been performed.

Experimental cell and synthesis procedure

The experimental campaign described in this thesis was prepared within a collaboration between the *N-REX* group of the Department of Physics and the “Giacomo Ciamician” Department of Chemistry of the University of Bologna. In particular, the work was carried out in close connection with the research activities of Dr. Caterina Bellatreccia from the Chemistry Department, whose doctoral project, supervised by prof. Paola Ceroni, focused on the synthesis and characterization of CuInS_2 -based quantum dots for light-driven applications [8]. The synthesis investigated at the ESRF corresponds to the aqueous-phase CuInS_2 quantum-dot synthesis studied within that research activity and originally derived from the procedure reported by Huang *et al.* [9]. This thesis project represented an occasion for directly probing the evolution of the Cu and In local environments through X-ray absorption spectroscopy. The synthetic protocol involved the sequential addition of the reagents into water. First, the metal precursors CuCl_2 and InCl_3 were introduced, followed by the stabilizing ligands sodium citrate (CIT) and glutathione (GSH). Finally, Na_2S was added to initiate nucleation and nanocrystal growth. To ensure accurate reagent dosing, all compounds were prepared as stock solutions

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prior to the measurements, with the exception of glutathione, which was added as a solid. Water was used as solvent for all stock solutions except InCl_3 , which was dissolved in ethanol. A detailed description of the preparation procedure is reported in Appendix 3.2.3.

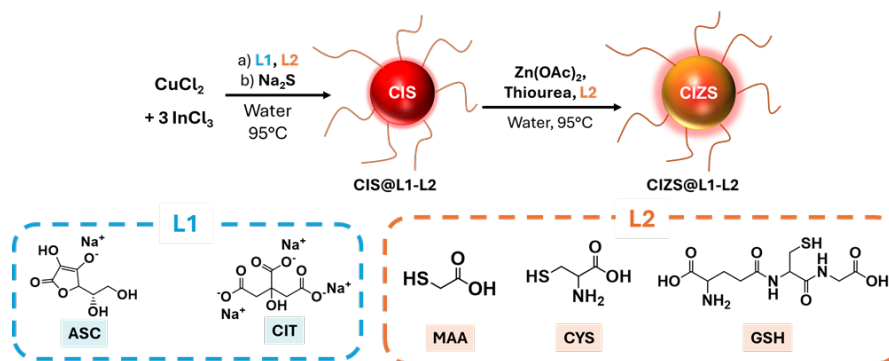


Figure 2.8: Schematic representation of the complete CIZS@L1-L2 synthesis and chemical structures of the ligands employed in the work of Bellatreccia [8]. The present study focuses exclusively on the formation of the CIS core.

The synthesis performed during the synchrotron experiments was limited to the formation of the CuInS_2 cores. The final shell-growth step reported in Ref. [9], involving the addition of Zn(II) acetate, thiourea, and the ligand L2 to form Zn-coated nanocrystals, was intentionally omitted in order to focus exclusively on the formation mechanism of the CIS cores.

All reagents were supplied by the Department of Chemistry of the University of Bologna and transported to the ESRF, prior to the experimental campaign. Particular care was devoted to the storage of moisture-sensitive compounds. InCl_3 , being strongly hygroscopic, was stored in a desiccator, while glutathione was kept refrigerated to minimize degradation.

To enable *in situ* monitoring of the synthesis, a dedicated flow-cell setup was developed prior to the experimental campaign at the N-Rex laboratories and installed in the EH2 experimental hutch. The reaction was carried out inside a vial connected to a closed circulation loop composed of Teflon tubing and a Kapton capillary positioned in the X-ray beam path. The reagents were injected into the reaction vessel through a custom-designed cap equipped with dedicated access ports. The reaction mixture was continuously circulated by means of a computer-controlled peristaltic pump based on an Arduino platform. The solution flowed from the reaction vial through the tubing network, reached the Kapton capillary exposed to the X-ray beam, and subsequently returned to the reaction vessel, thus ensuring continuous recirculation throughout the experiment. To realize the setup, the vial cap and the C-shaped support used to mount the Kapton capillary

inside the sample chamber were designed using the CAD software *Fusion 360* and fabricated by 3D printing.

A photograph of the mounted capillary is shown in Figure 2.9, while a complete view of the experimental setup and the 3D printed components is reported in the pictures inside 2.11.

Across three different experimental sessions carried out between May and July 2025, complete CIS synthesis and “static measurements” after each synthesis step, have been performed, acquiring XAS spectra around the Cu and In K-edges. Additional control syntheses were carried out to isolate key chemical contributions: at the Cu K-edge, a synthesis without InCl_3 and one with excess glutathione; at the In K-edge, a synthesis without CuCl_2 .

During this kind of measurements, the following procedure was followed: the stock solutions were prepared in advance, close enough to the beam-times, to ensure that the most sensitive compounds did not degrade in the meantime; once the chamber had been set up for the measurements, the cell was installed in EH2 and the solutions were added one at a time; after each addition, the flow was started via the Arduino programme installed on the PC; the flow was checked to ensure it was uniform and bubble-free, adjusting the rotation speed of the peristaltic pump if necessary, waited a few minutes to make sure that the reagents had taken effect; the hutch was closed, the beam was switched on, and we proceeded to monitor the measurements in the control room. With the help of a remotely controlled pump syringe (see Figure 2.10) provided by the PSCM (Partnership for Soft Condensed Matter) of ESRF, it has been possible to investigate even the dynamic of the reaction at the last synthesis step both at Cu and In K-edges, by injecting the appropriate amount of Na_2S directly into the vial without having to access to the hutch and collecting time-resolved data at pre-selected energies.

Finally, complementary scans were collected in EH1 on a purified CIS nanocrystal sample (obtained via acetone precipitation by Dr. Bellatreccia at the laboratories of the Department of Chemistry, University of Bologna) at both room temperature and 80 K. All EH2 measurements were carried out in air and at room temperature.

All the measurements of the synthesis carried out in EH2 were performed using fluorescence, with the SDD detector “*Ardesia*” for Cu-K edge and the Ge- detector “*Ruby*” for In-K edge. The measurements of the CIS pellet carried out in EH1,

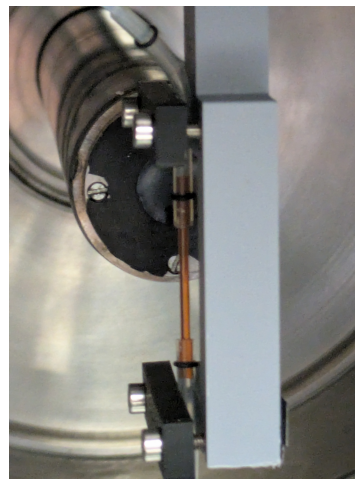


Figure 2.9: Kapton capillary mounted on the custom C-shaped support inside EH2.



Figure 2.10: Photo of the remotely controlled pump syringe

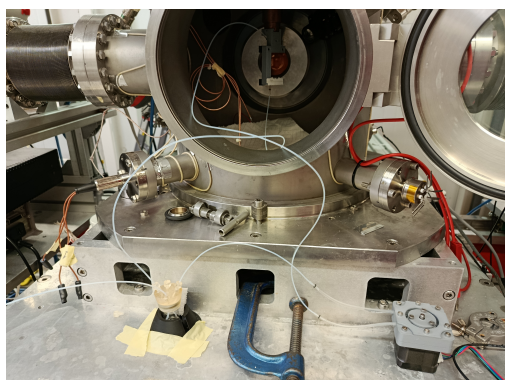
on the other hand, were performed in transmission mode. For the measurements performed in fluorescence mode, for each scan it has been acquired also a reference scan of a metal foil corresponding to the selected K-edge. This reference was then used to calibrate the acquired spectra.

It is worth noting that, during the measurement campaign, technical problems with the experimental apparatus arose only during the first measurement session. Specifically, the original setup involved the use of an extremely thin-walled Teflon capillary in the section exposed to X-rays (wall's thickness=0,025 mm), a feature originally designed for the pump-and-probe experiments that had initially been planned. However, during the initial measurements, the Teflon capillary developed a leak after some time under X-ray irradiation, despite having held up during flow tests without the beam and having lasted several hours when a small amount of solution was placed in a static capillary without flow. It is likely that the combined effect of fluid pressure and the beam caused the capillary's extremely thin walls to fail. On the evening of the first day of measurements, the Teflon capillary was replaced with a Kapton one with slightly thicker walls, available in the LISA laboratory. With this configuration, the experimental setup proved robust and it was possible to carry out all the other measurements of the campaign without encountering any further problems of this kind.

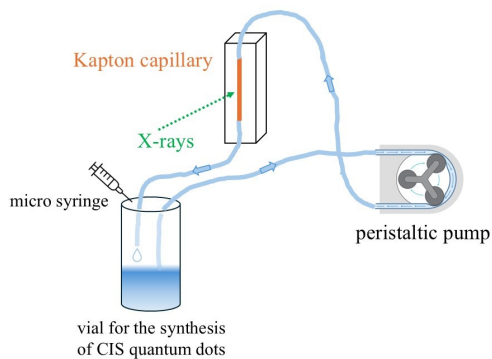
It was only during the last measurement session in July that another technical problem arose: at the start of the measurements, it was noticed that, upon the addition of indium(III) chloride, the spectrum being recorded did not match the expected one, which had already been recorded during the first measurement session in May. It was realised that this was due to the degradation of the indium(III) chloride brought by the laboratories in Bologna, which, despite the care taken in its storage, had degraded in the meantime. Fortunately, it was possible to obtain

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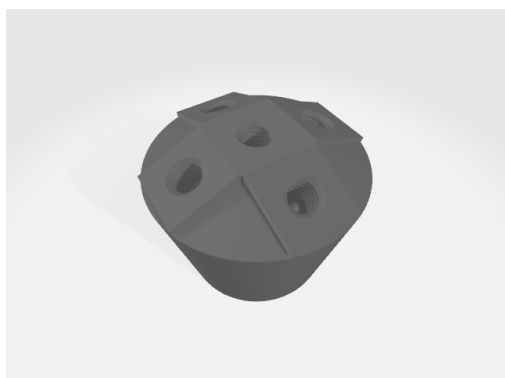
the same compound from the ESRF Chemistry laboratory and in this way it was possible to continue the measurements without further problems.



(a) Photo of the experimental setup mounted inside EH2



(b) Schematic representation of the experimental setup



(c) 3D printed vial cap



(d) 3D printed C-shaped support

Figure 2.11: The experimental setup

Workflow of the EXAFS analysis via the software *Athena* and *Artemis*

The preliminary processing of the XAS data and the extraction of the EXAFS signal were performed using the software *Athena*, while EXAFS analysis and fitting were carried out with *Artemis*. Both programs are part of the Demeter package (version 0.9.26 [25]) developed by Bruce Ravel (NIST) and are widely used within the XAS community for data reduction and analysis.

The procedure used for the first phase of data extraction, carried out using *Athena*, aims to convert the acquired raw absorption spectrum expressed as $\mu(E)$ into the corresponding oscillating EXAFS function $\chi(k)$.

To this end, given that multiple scans of the same measurement have almost always been performed, data were first merged. The first step consisted of energy calibration and merging of repeated scans. The reference spectrum associated with the first acquired scan was calibrated by assigning the maximum of the first derivative in the edge region to the nominal edge energy (Cu K-edge = 8979 eV, In K-edge = 27940 eV). The reference spectra of all subsequent scans were then aligned to the calibrated reference before averaging the corresponding spectra.

The next step was to define the pre-edge and post-edge zones. To this end, *Athena* allows the user to select the range of the pre-edge and post-edge zones respectively, and then approximates them using a linear and quadratic function respectively.

The atomic background was subsequently removed using a spline function. The spline parameters were optimized by minimizing the low- R contribution of the Fourier-transformed signal below a user-defined value R_{bkg} , typically chosen to be approximately 1 Å.

The image at the top right in Figure 2.12 represents an example of a normalized spectrum with the background function also displayed, in particular it is the spectrum acquired at the Cu K-edge energy after the first step of the synthesis, i.e. the addition to water of the precursors CuCl_2 .

The EXAFS function $\chi(k)$, shown in the bottom-left panel of Figure 2.12, was obtained after normalization and background subtraction of the experimental spectrum. For visualization purposes, the signal was multiplied by k^2 in order to enhance the high- k oscillations. At this point, *Athena* allows the user to view the result of the Fourier transform of the normalized signal, obtained from the user's selection of the k -range within which to perform the transform. By Fourier transforming $\chi(k)$ over the selected k -range ($3 \leq k \leq 12 \text{ Å}^{-1}$), a pseudo-radial distribution function $\chi(R)$ is obtained. An example is shown in the bottom-right panel of Figure 2.12, where the contribution of the first coordination shell is clearly visible.

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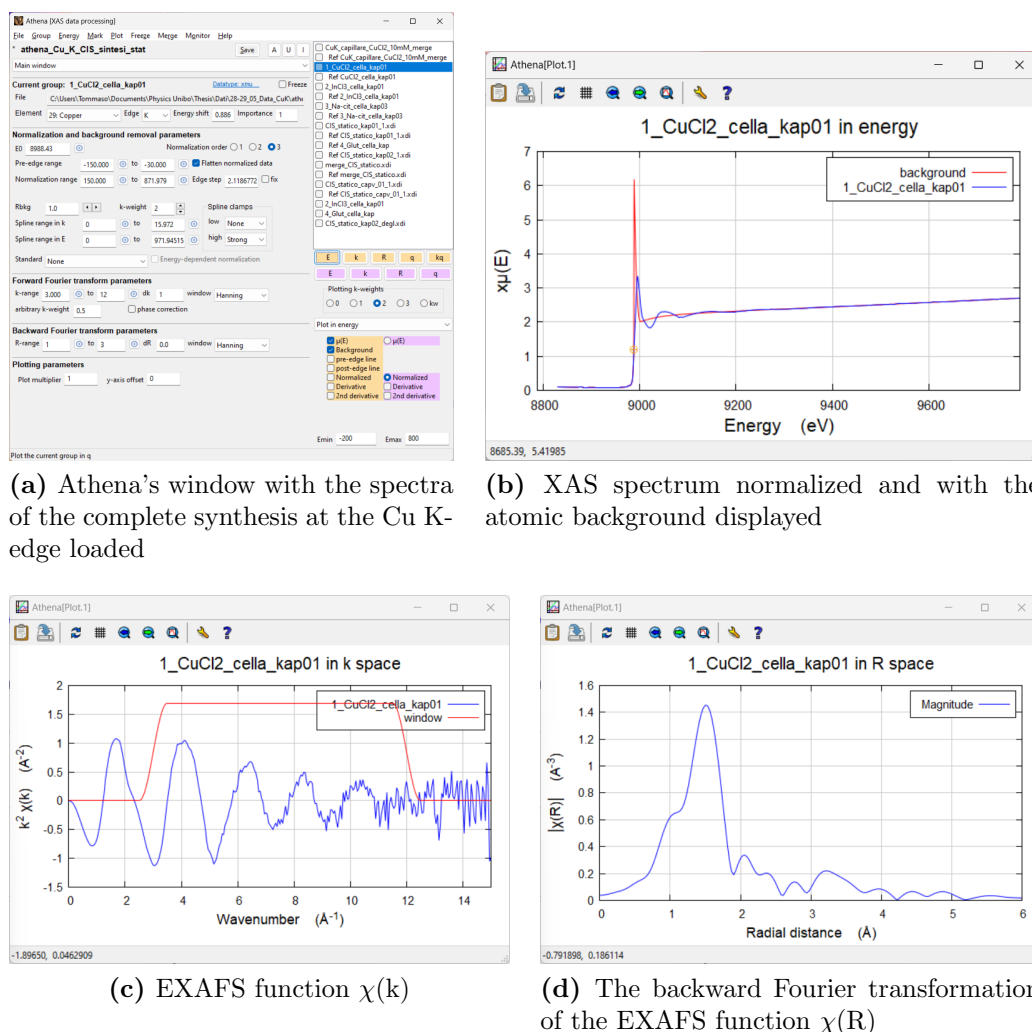


Figure 2.12: Athena workflow analysis – example of the first synthesis step (post addition of CuCl₂) at the Cu K-edge

Once the EXAFS signal had been extracted, quantitative analysis was performed using Artemis. As discussed in Section 1.3.4, EXAFS fitting relies on the comparison between the experimental spectrum and theoretical signals calculated from an appropriate structural model representative of the local environment of the absorbing atom. The choice of the appropriate reference models, made during the analysis of each spectrum, will be discussed in the next chapter (see 3). Here, we will simply present the procedure followed in performing the fit, which was carried out using the resources offered by Artemis. The first step is carried out using the Atoms programme, which is part of Artemis. Atoms (see the bottom right image in Figure 2.13 to visualize an Atoms window) allows the creation of

a feff.inp input file, associated with the crystal structure provided as input to the programme (as a .cif file) and by specifying the atom considered as the centre (in the case of the measurements carried out, the atomic centres have been Copper and Indium ones). The .cif files for the selected reference compounds were downloaded from databases on websites such as: <https://ixdb.jxafs.org/> (“International XAFS DB portal”) or <https://www.ruff.net/> (from the “RRUFF project”, see [26]).

The theoretical EXAFS signals were generated using the FEFF code, which is integrated within Artemis. Starting from the structural model (feff.inp) provided by Atoms, FEFF calculates the atomic potentials, scattering phase shifts, and the relevant single- and multiple-scattering paths contributing to the EXAFS signal. All these operations are sequentially done by a series of modules and as a result Feff gives back the list of the scattering paths with the specification of the associated *degeneracy* (that, in case of single scattering path is the number of neighbours), the effective path length R_{eff} (half the loop length, for single scattering coincides with the bond length), the amplitude ratio *Rank* respect to the first path and the scattering order L (which can be defined as the number of lines (legs) you draw between scatterers to describe the process under analysis).

When considering a given atomic arrangement, a limited number of different paths have to be considered to correctly account for its contribution or the total χ signal.

The sum over paths in the EXAFS equation includes also *multiple-scattering paths*, which are included too inside the list obtained from Feff calculations. For first shell analysis, to which the analyses carried out have almost always been limited, multiple scattering is hardly ever needed.

Once the Feff calculations have been executed, it has been possible to perform the fit of the experimental $\chi(k)_{exp}$ function build-up using the theoretical EXAFS paths previously calculated with Feff. The fitting procedure consists of minimizing the difference between the experimental EXAFS function $\chi_{exp}(k)$ and the theoretical signal $\chi_{th}(k)$ obtained from the selected scattering paths by varying a set of structural parameters (already introduced in the first Chapter while discussing EXAFS analysis method, Sect. 1.3.4): N , R , σ . To complete the fit, Artemis therefore requires the following inputs:

- an experimental $\chi(k)$ spectrum (extracted with Athena);
- the theoretical paths generated by FEFF

Successively, the details for FT transformation and fit have to be added, like: k-range (the range in k space for FT), k-weight n in the k^n weight for exp. data, dk, dr (the “width” of the window), k window (the window type), R range (the fit range in R space (if used)), fitting space (can be k, R or q).

Once the experimental data are provided to Artemis, we need to add to Artemis’

path list, from the paths generated previously the ones that we want to include in our fit (see the bottom left image in Figure 2.13). For each scattering path, Artemis requires the definition of the fitting parameters: the amplitude reduction factor S_0^2 , the edge-energy shift ΔE_0 , the deviation from the nominal path length ΔR , and the Debye–Waller factor σ^2 . Parameters can either be fixed (*set*) or refined during the fit (*guess*). The initial value to which the parameter is fixed or from which the fit is performed can be chosen by the user.

Generally, the parameters ΔE_0 and ΔR , whose values have been considered the same for each path included in the fit, have been always left free, while their initial values always fixed to 0. Also σ^2 has always been considered free and his initial value has always been set to a standard value of 0.003, but generally a different value has been considered for different paths. Then, generally, the fits were carried out as follows.

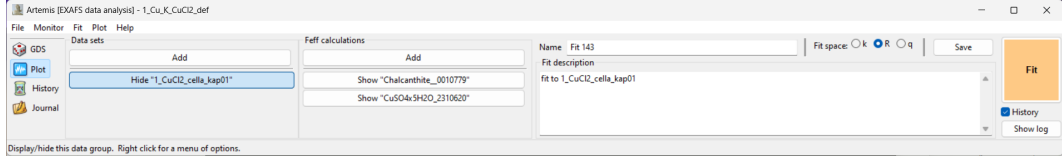
For each CIS synthesis carried out, once the reference compound had been selected, the fit for the first step of the synthesis was performed by setting the value of N to the nominal value of the corresponding path, whilst the value of S_0^2 was set to *guess* so that, by performing an initial fit with these settings, the value of S_0^2 could be obtained (generally set to a value between 0.7 and 0.9). If this procedure did not yield a realistic estimate of S_0^2 , the value was set to a value within the expected range. Once the amplitude reduction factor S_0^2 had been determined, it was fixed in all subsequent fits. In the EXAFS equation, N and S_0^2 appear multiplied ($N \cdot S_0^2$), that term governs the overall amplitude of the contribution associated with a given scattering path, therefore it has been chosen to set the parameter N to 1 and include in the definition of S_0^2 the product itself $N \cdot S_0^2$, where the starting value of N was chosen to be equal to the nominal coordination number expected from the structural model.

XANES analysis

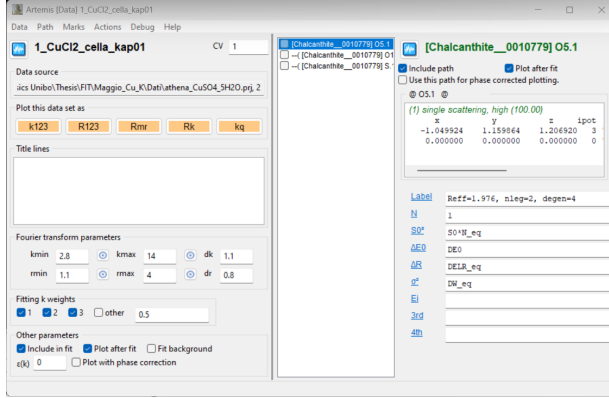
A key aspect of the XANES analysis is the determination of the absorption-edge energy E_0 , which is commonly used as an indicator of the oxidation state of the absorbing atom. Rather than defining E_0 as the energy corresponding to the maximum of the first derivative of the spectrum, an integral method proposed in Refs. [27, 28] was adopted. This approach is generally less sensitive to local distortions and noise in the vicinity of the absorption edge. It consists in defining an (integral) average edge energy as:

$$E^{edge} = \frac{1}{\mu_2 - \mu_1} \int_{\mu_1}^{\mu_2} E(\mu) d\mu \quad (2.1)$$

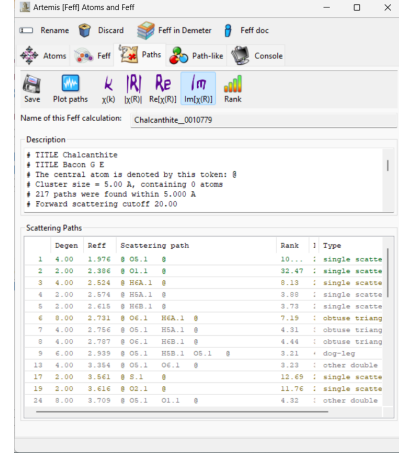
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(a) Artemis main window



(b) Artemis window with the Athena data uploaded



(c) Atoms window with the scattering paths generated starting from a chalcantite structure

Figure 2.13: Artemis windows – example with the analysis of the first synthesis step (post addition of CuCl_2) at the Cu K-edge

By taking the integral of the inverse function of the spectrum ($E(\mu)$), the same value for E^{edge} can be obtained by:

$$E^{edge} = E(\mu_1) + \frac{1}{\mu_2 - \mu_1} \int_{E(\mu_1)}^{E(\mu_2)} \mu_2 - \mu(E) dE \quad (2.2)$$

Once $\mu(E)$ has been properly defined in such a way as to account for the fact that it is discrete and may not be monotonic due to perturbations caused by measurement noise, the numerical integration is well defined and the last formula 2.2 provides an estimate of E^{edge} that is independent of the interval borders. However, the E^{edge} -value depends on the parameters μ_1 and μ_2 . We have chosen $\mu_1=0.15$ and $\mu_2=1.00$, as suggested in [28]. The first value was chosen to ensure that the magnitude of the pre-edge feature does not affect E^{edge} significantly; the second value was chosen to ensure that the determined edge position is not too strongly affected by the magnitude of the “edge-peak”, the more or less broad maximum in $\mu(E)$ following the rising part of the edge. The resulting value of E^{edge} was subsequently used to evaluate the oxidation state of the absorbing species through comparison with

CHAPTER 2. EXPERIMENTAL SETUP AND EXPERIMENTAL TECHNIQUES

suitable reference compounds, as discussed in the next section.

In the XANES analysis carried out, we also made use of the LCA method introduced in the previous chapter (see 1.3.3). To this end, it has been possible to use Athena directly, as it incorporates this computational capability.

Chapter 3

Results

3.1 Analysis of in-situ XAS of CuInS₂ quantum dot's growth

In this section, the results of the XAS investigation of the CIS nanocrystal synthesis are presented and discussed. The analysis is organised according to the selected absorption edge. The Cu K-edge results are discussed first, followed by those obtained at the In K-edge. For each absorption edge, the static measurements are presented before the dynamic measurements. The static analysis includes both the complete synthesis and the control syntheses performed in the absence of one of the two metal precursors, whereas the dynamic measurements are used to investigate the reaction kinetics during the final stage of the synthesis.

All EXAFS analyses reported in this work were performed in **R-space**. For completeness, the values of the χ^2 and reduced χ^2 statistics are reported for each EXAFS fit. However, these quantities should be interpreted with caution. As noted by Bruce Ravel in the Demeter documentation, EXAFS fitting using FEFF does not constitute a well-posed problem in the strict statistical sense required by Gaussian error analysis. The experimental signal is not composed of ideal sinusoidal components, the uncertainties associated with the fitted parameters are not necessarily normally distributed, and several sources of systematic error—including sample inhomogeneity, detector non-linearity, and limitations of the theoretical model used to describe the EXAFS signal—cannot be fully quantified [25]. Consequently, the absolute values of χ^2 and reduced χ^2 are often less informative than in conventional regression analyses.

Decades of practical experience in EXAFS analysis have shown that the reliability of a fit is more effectively assessed through a combination of indicators. Among these, the R-factor provides a particularly useful measure of the agreement between experimental and calculated spectra, with lower values generally

indicating a better fit. Equally important is the physical plausibility of the fitted parameters. For example, excessively large parameter correlations may indicate an over-parameterised model, while values of E_0 far outside the range ± 10 eV, negative Debye–Waller factors, or negative values of S_0^2 are generally regarded as unphysical and therefore indicative of an unreliable fit [25].

It should also be noted that the R-factor may occasionally overestimate the apparent discrepancy between experiment and theory. In several fits presented in this work, the fitting range was intentionally extended somewhat distant from the peak of interest in order to retain a sufficient number of independent data points and avoid overfitting. As a consequence, small mismatches between theory and experiment in regions of relatively low structural significance may contribute to the overall R-factor, despite having little impact on the structural parameters of interest. This effect can be recognised in some of the fit plots, where minor residual oscillations are visible at distances of approximately 2.5–4 Å from the main first-shell peak (see Figure 3.3).

3.1.1 Analysis @Cu K-edge

Static measurements

EXAFS analysis The discussion begins with the EXAFS analysis of the static measurements collected during the complete synthesis at the Cu K-edge. The reference compounds employed in the fitting procedure, together with the corresponding FEFF scattering paths, are listed in Table 3.1, while schematic representations of the adopted structural models are shown in Figure 3.1. The fitted structural parameters are reported in Table 3.2, and the corresponding goodness-of-fit indicators are summarised in Table 3.3. The resulting fits, superimposed on the experimental spectra in both k- and R-space, are presented in Figure 3.3.

Reference compound	Path	N	R_{eff} ($\text{\AA}$)
$\text{CuSO}_4 \times 5(\text{H}_2\text{O})$ (Chalcanthite)	Cu-O (O $\in$ 1 st shell)	6	1.976
$\text{CuSO}_4 \times 5(\text{H}_2\text{O})$ (Chalcanthite)	Cu-O (O equatorials)	4	1.976
$\text{CuSO}_4 \times 5(\text{H}_2\text{O})$ (Chalcanthite)	Cu-O (O axials)	2	2.386
$\text{Cu}(\text{C}_5\text{H}_7\text{O}_2)_2$ (Cu(II) acetylacetonate)	Cu-C	4	2.860
Cu_2S (Chalcocite)	Cu-S	3	2.298
Cu_2S (Chalcocite, <i>with a C site in place of S</i>)	Cu-C	3	2.651
CuInS_2 (Chalcopyrite)	Cu-S	4	2.309
CuInS_2 (Chalcopyrite)	Cu-In	8	3.911

Table 3.1: Reference compounds and related paths employed in the fit @ Cu K-edge

The spectra collected during the first two stages of the synthesis were found to be essentially identical, as expected. Indeed, the addition of the indium precursor (InCl_3) is not expected to affect the local environment of copper, which remains in a hydrated state. In hydrated copper, the first coordination shell consists of six oxygen atoms: four equatorial oxygen atoms located at a nominal distance of 1.976 $\text{\AA}$ and two axial oxygen atoms at a larger distance of 2.386 $\text{\AA}$ (Table 3.1). A close-up view of the local coordination environment of hydrated copper is shown in Figure 3.2.

For this reason, chalcanthite pentahydrate was selected as the reference compound for modelling the first-shell contribution in the first two spectra, since its local Cu–O coordination environment closely resembles that expected for hydrated copper ions in solution. The amplitude reduction factor S_0^2 was determined following the procedure described in Section 2.2, yielding a value of $S_0^2=0.704$.

For both spectra, satisfactory fits were obtained by considering only the first coordination shell, as the second-shell contribution was too weak to be reliably resolved. Although the FEFF calculation distinguishes between equatorial and axial oxygen atoms, improved fit stability was achieved by describing the first shell using a single Cu–O scattering path with a nominal distance corresponding to the equatorial oxygen atoms. Within this simplified model, the fitted coordination parameters were fully consistent with a hydrated copper environment. It can

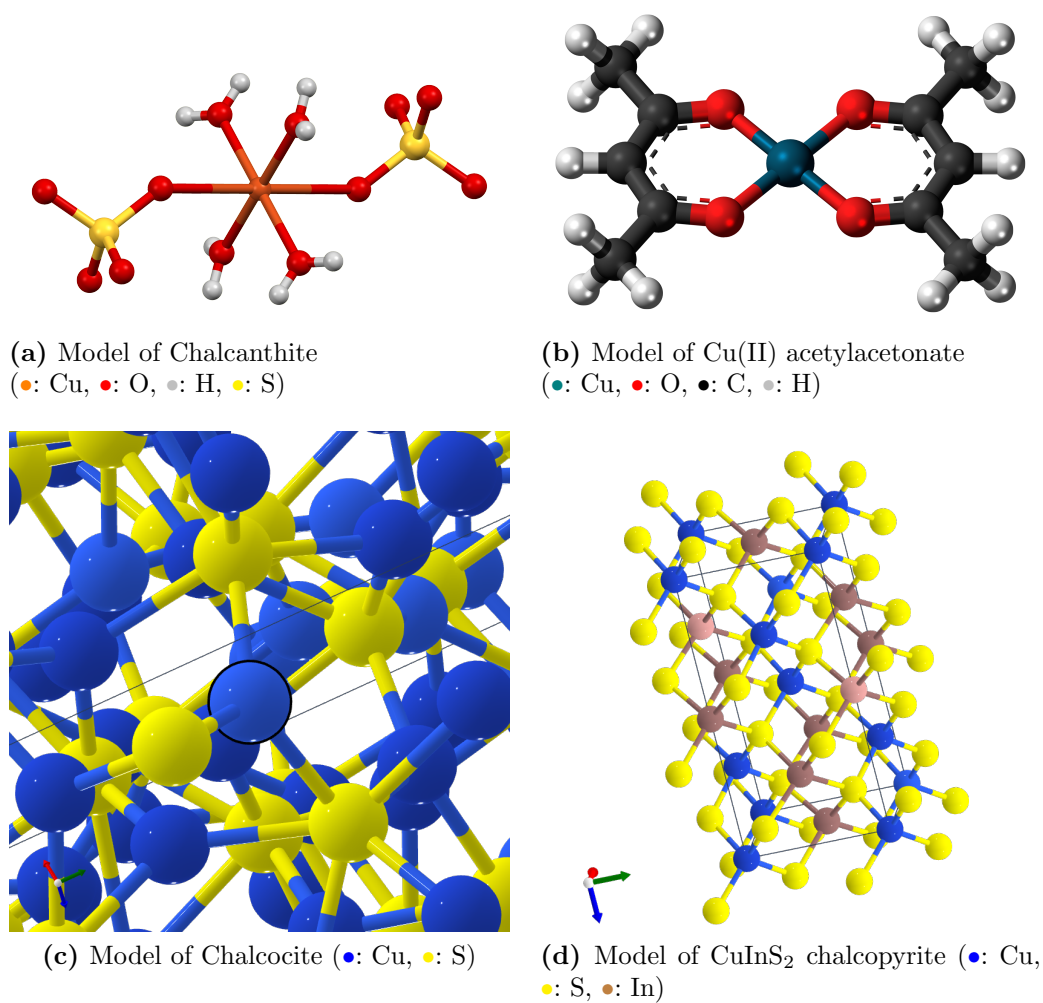


Figure 3.1: Models of the compounds used as references in the EXAFS fits @Cu K-edge

		First shell					Second shell				
Last compound added	ΔE_0 (eV)	Reference compound	Path	N_1	R_1 ($\text{\AA}$)	σ_1^2 ($\times 10^{-3} \text{\AA}^2$)	Reference compound	Path	N_2	R_2 ($\text{\AA}$)	σ_2^2 ($\times 10^{-3} \text{\AA}^2$)
CuCl ₂	1.6 ± 1.1	CuSO ₄ $\times 5(\text{H}_2\text{O})$	Cu-O	6.0 ± 0.5	1.945 ± 0.009	5.3 ± 1.2	\	\	\	\	\
InCl ₃	1.3 ± 1.1	CuSO ₄ $\times 5(\text{H}_2\text{O})$	Cu-O	6.0 ± 0.5	1.942 ± 0.009	5.4 ± 1.1	\	\	\	\	\
CIT	2 ± 2	CuSO ₄ $\times 5(\text{H}_2\text{O})$	Cu-O	$N_{\text{eq}}: 5.1 \pm 1.0$ $N_{\text{ax}}: 0.9 \pm 1.2$	$R_{\text{eq}}: 1.94 \pm 0.02$ $R_{\text{ax}}: 2.37 \pm 0.09$	3 ± 2	Cu(C ₅ O ₇ H ₂) ₂	Cu-C	5 ± 5	2.85 ± 0.06	7 ± 13
GSH	3.7 ± 1.5	Cu ₂ S	Cu-S	2.7 ± 0.5	2.245 ± 0.013	4 ± 2	Cu ₂ S (with a C site in place of Cu)	Cu-C	3 ± 2	2.66 ± 0.02	2 ± 5
Na ₂ S (CIS in solution)	1.6 ± 0.8	CuInS ₂	Cu-S	4.2 ± 0.3	2.303 ± 0.007	8.4 ± 0.9	CuInS ₂	Cu-In	10 ± 12	3.94 ± 0.04	41 ± 27
CIS pellet	4.5 ± 0.6	CuInS ₂	Cu-S	4.5 ± 0.2	2.314 ± 0.005	7.0 ± 0.7	CuInS ₂	Cu-In	8 ± 3	3.93 ± 0.02	25 ± 9

Table 3.2: Cu K-edge EXAFS fitted parameters - complete synthesis ($S_0^2 = 0.704$)

therefore be concluded that, following the dissolution of CuCl_2 in water—and also after the subsequent addition of InCl_3 —the copper centres dissociate from chloride ligands and become coordinated by approximately six oxygen atoms, as expected for hydrated Cu(II) species in aqueous solution.

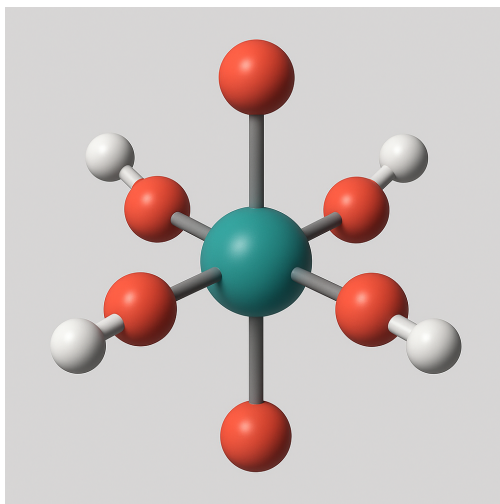


Figure 3.2: Molecular model of the hydrated Copper
(●: Cu, ●: O, ●: H)

Following the addition of citrate, both the first- and second-shell contributions could be included in the EXAFS analysis. The first-shell environment was modelled using the same Cu–O scattering path employed for the previous stages of the synthesis, again taking chalcanthite as the reference compound. In contrast to the earlier spectra, a better fit was obtained by treating the equatorial and axial oxygen atoms as distinct contributions.

The resulting fit suggests a coordination environment comprising approximately five equatorial and one axial oxygen atom. At first sight, this may indicate a slight distortion of the hydrated copper geometry. However, the uncertainties associated with the fitted coordination numbers are sufficiently large that the estimated values remain compatible with coordination numbers in the ranges [4:6] and [0:2] for the equatorial and axial oxygen atoms, respectively. Consequently, a conventional hydrated-copper environment consisting of four equatorial and two axial oxygen atoms cannot be excluded. The available data therefore do not provide conclusive evidence for a genuine distortion of the first coordination shell following citrate addition.

A second-shell contribution also becomes detectable at this stage. The fit indicates the presence of carbon atoms at approximately the expected distance for the carboxylate groups of citrate coordinated to the oxygen ligands surrounding copper. The fitted coordination number is close to five, suggesting that most of

the oxygen atoms in the first shell may participate in the coordination of citrate-derived carbon-containing groups. Nevertheless, the uncertainty associated with the second-shell parameters remains large, with the error on N_2 approaching 100%. These results therefore provide qualitative evidence for citrate coordination, while preventing a reliable quantitative description of the second-shell environment.

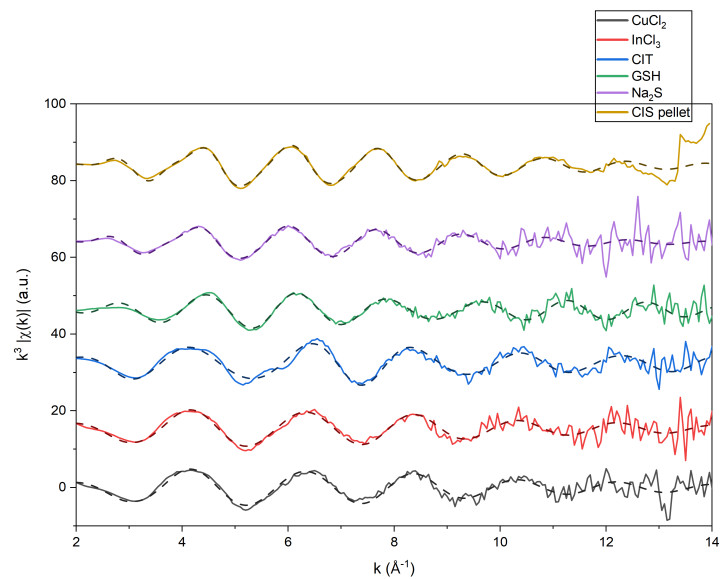
The subsequent addition of glutathione leads to a substantial modification of the local copper environment. In particular, the oxygen ligands present in the first shell are replaced by sulphur atoms originating from the thiol group of glutathione. At the same time, a carbon-containing second-shell contribution remains detectable. The fit yields coordination numbers of approximately three for both the first-shell sulphur atoms and the second-shell carbon atoms. This environment was successfully modelled using a Cu–S scattering path derived from the structure of chalcocite (Cu_2S), together with a modified second-shell path obtained from the same structure by replacing the neighbouring sulphur atoms with carbon atoms. Compared with the citrate-containing stage, the second-shell parameters are determined with significantly improved precision, indicating a more clearly defined local environment around the copper centres.

The final stage of the synthesis corresponds to the addition of sodium sulphide, which is expected to trigger the formation of CuInS_2 nanocrystals. In this case, sulphur atoms are expected in the first coordination shell, while indium atoms should replace carbon atoms in the second shell if the chalcopyrite-like structure is formed. Using CuInS_2 quantum dots crystallised in the chalcopyrite structure as the reference model, both coordination shells could be included in the fit. The first shell was found to contain approximately four sulphur atoms located at a distance of about 2.3 Å, in excellent agreement with the expected chalcopyrite geometry. The fitted second-shell indium contribution was likewise compatible with the structural model, although the associated uncertainties remained relatively large, particularly for the Debye–Waller factor.

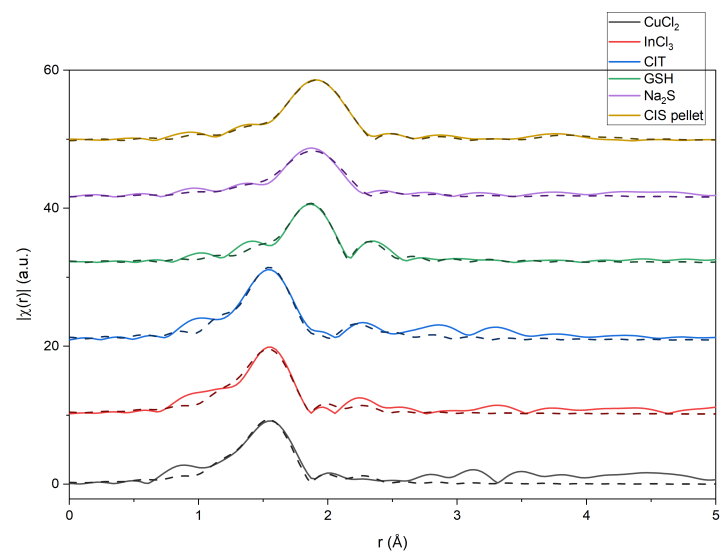
The same fitting procedure was subsequently applied to the spectrum of a purified CIS pellet. To maximise data quality, the spectrum selected for analysis was that of the 76 mg pellet measured at low temperature (80 K) during the July beamtime. A comparison between the two fits shows that the first-shell parameters are essentially identical within experimental uncertainty, particularly with regard to the coordination number and bond distance. The Debye–Waller factor is slightly smaller for the purified pellet, indicating a modest reduction in local disorder. More significant differences are observed in the second shell, where the coordination number can be determined with substantially greater precision and the structural disorder is considerably reduced compared with the colloidal sample. This is attributable to the fact that the measurements were performed out of solution and at low temperatures.

Although the second-shell indium contribution remains relatively weak, especially in the case of the nanocrystals dispersed in solution, its detection represents an important indication of successful CuInS_2 formation. In particular, the EXAFS analysis of the purified sample is consistent with a Cu–In coordination number characteristic of the chalcopyrite structure ($N_{\text{Cu–In}} \approx 8$). By contrast, the colloidal nanocrystals exhibit a substantially larger second-shell Debye–Waller factor ($\sigma_2 = 0.041 \text{ \AA}^2$), indicative of significant structural and thermal disorder. This degree of disorder prevents a reliable determination of the coordination number and does not allow an unambiguous distinction between a highly disordered chalcopyrite phase and a wurtzite-like or otherwise disordered structure.

Figures 3.4 and 3.5 show the trends in the estimated parameters for the first and second shells respectively, as the synthesis step under consideration increases.



(a) k-space fits



(b) R-space fits

Figure 3.3: Stacked plot of the EXAFS fits at the Cu K-edge for the complete synthesis (solid lines: spectra, dot lines: fits)

Last compound added	k-range ($\text{\AA}^{-1}$)	R-range ($\text{\AA}$)	χ^2	χ^2_{red}	R-factor
CuCl ₂	[2.8–14]	[1.1–4]	560	34	0.04
InCl ₃	[2.8–14]	[1.1–4]	231	14	0.03
CIT	[2.8–14]	[1.1–4]	1406	122	0.06
GSH	[3.4–14]	[1–4]	284	22	0.03
Na ₂ S (CIS in solution)	[3.4–12]	[1–5]	159	11	0.03
CIS pellet	[3.4–12]	[1–5]	3500	241	0.01

Table 3.3: Goodness-of-fit parameters - Cu K-edge complete synthesis

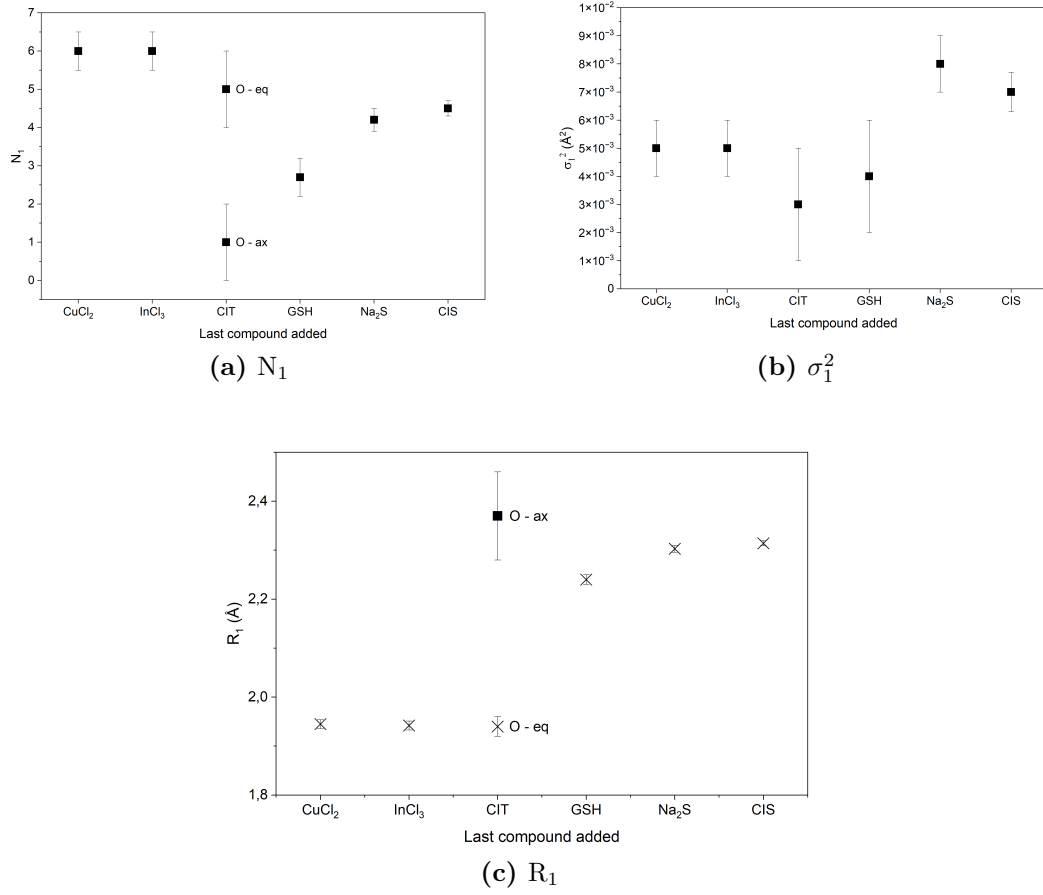


Figure 3.4: Trend of the 1st shell fitted variables as the synthesis step varies for the spectra at Cu K-edge of the complete synthesis

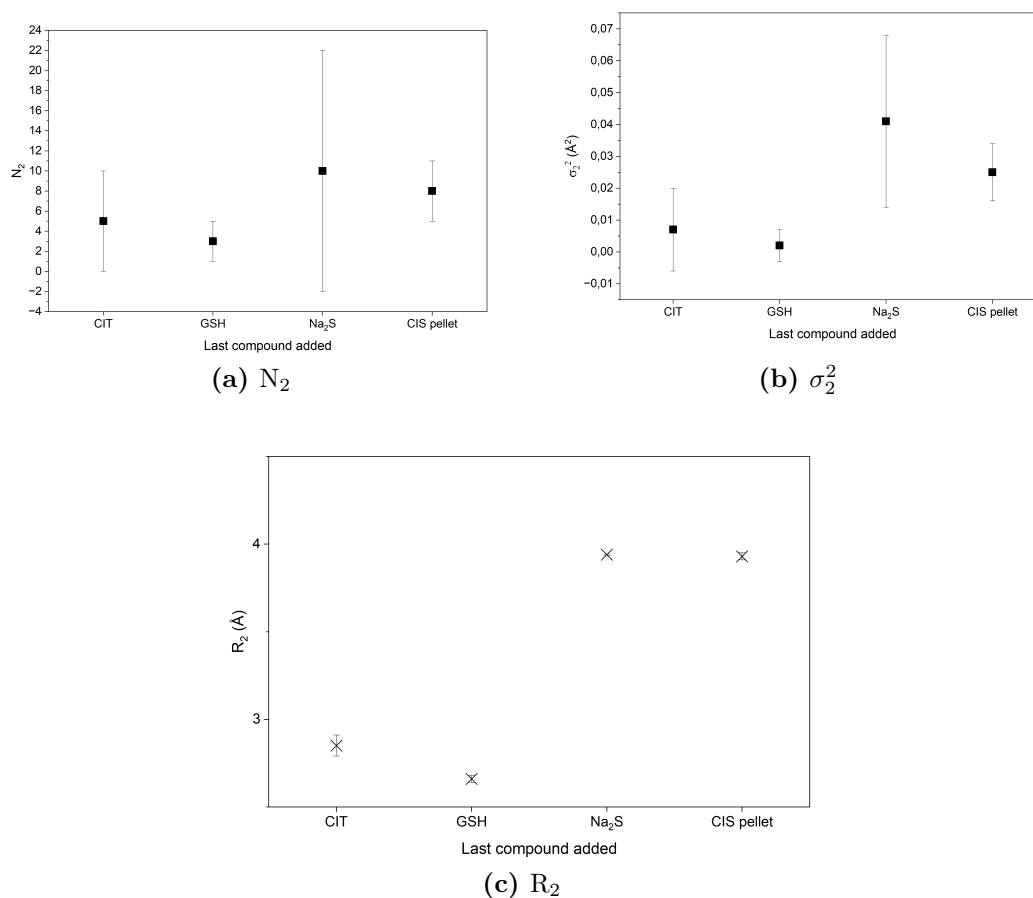


Figure 3.5: Trend of the 2nd shell fitted variables as the synthesis step varies for the spectra at Cu K-edge of the complete synthesis

XANES analysis The XANES analysis of the spectra collected during the complete synthesis at the Cu K-edge began with the determination of the absorption edge energy, E_0 , using the integral method described in Chapter 2 (Section 2.2).

The evolution of the estimated E_0 values throughout the synthesis is shown in Figure 3.6. The most pronounced edge shift occurs during the fourth stage of the synthesis, following the addition of glutathione. This behaviour is also evident from the enlarged XANES spectra reported in Figure 3.7. The uncertainty associated with the edge determination was evaluated through error propagation and found to be approximately 0.1 eV. This value coincides with the intrinsic energy uncertainty of a single measurement, all other contributions being negligible by comparison (see Appendix 3.2.3 for details).

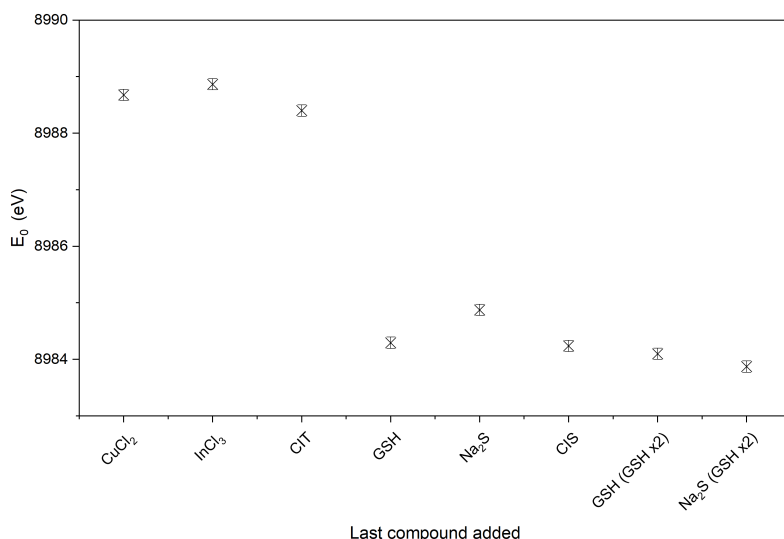


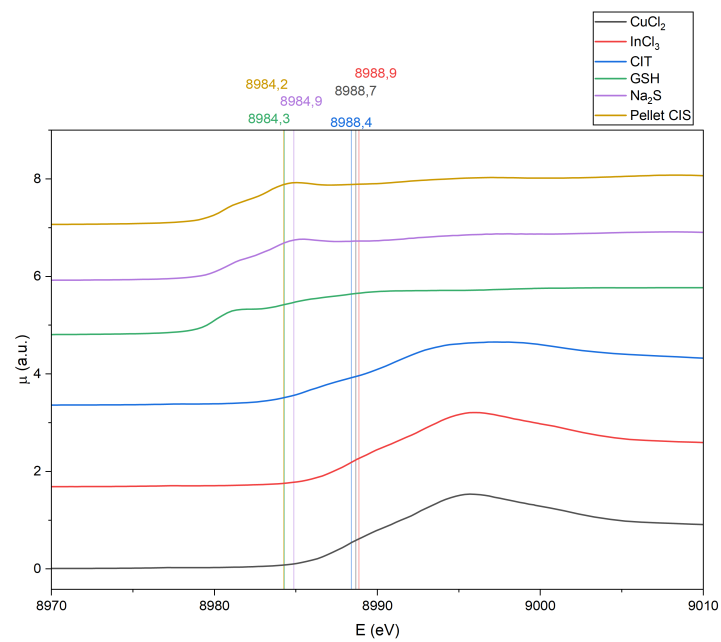
Figure 3.6: Trend of the estimated values of E_0 as the synthesis step varies for the spectra at Cu K-edge of the complete synthesis

The observed shift towards lower energy is consistent with the reduction of copper by glutathione, suggesting the conversion of Cu(II) into Cu(I). In order to quantify this process, a calibration procedure was carried out using reference compounds containing copper in known oxidation states. The reference samples employed are listed in Table 3.4. A linear relationship between oxidation state and edge energy was obtained, as shown in Figure 3.8; the corresponding fit parameters are reported in panel (b) of the same figure.

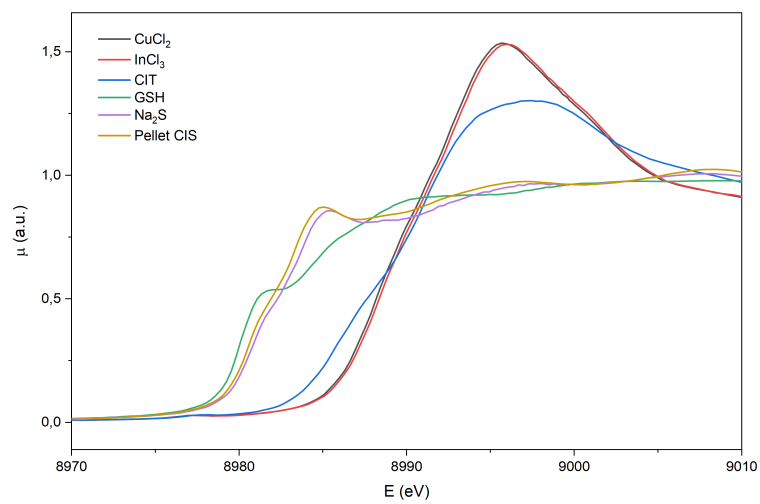
The resulting calibration equation was

$$y = 8979.4 + 4.4x \quad (3.1)$$

where y represents the edge energy E_0 and x the oxidation state of copper. The oxidation state corresponding to each synthesis stage was then obtained by substituting the measured E_0 values into Eq. 3.1. The resulting estimates are reported in Table 3.5, with uncertainties determined by error propagation (see Appendix 3.2.3). These clearly show that copper remains fully consistent with the +2 oxidation state throughout the first three stages of the synthesis. Following the addition of glutathione, however, the estimated oxidation state decreases and becomes fully compatible with Cu(I), thereby confirming the hypothesis that glutathione acts as the reducing agent responsible for the $\text{Cu(II)} \rightarrow \text{Cu(I)}$ conversion.



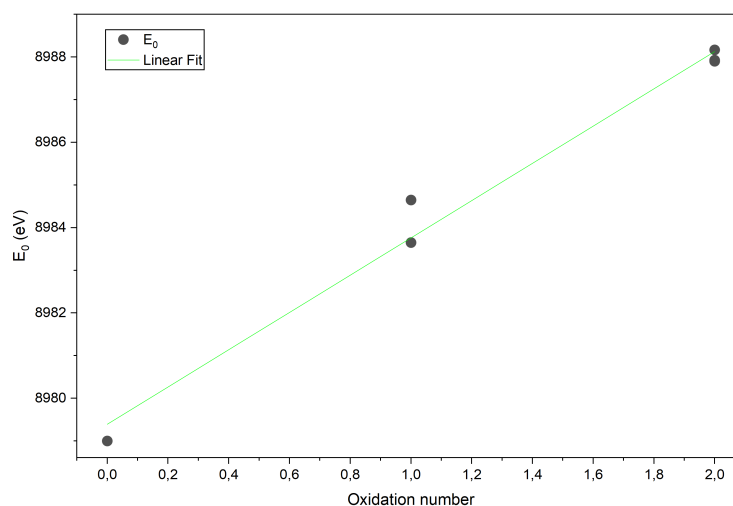
(a) Stacked XANES spectra with the found values of E_0 displayed



(b) Overlaid XANES spectra

Figure 3.7: XANES spectra at Cu K-edge for the complete synthesis

Reference compound	Oxidation number	E_0 - integral method (eV)
Cu metal foil	0	8979.0 ± 0.1
Cu_2O	1	8984.6 ± 0.1
Cu_2S	1	8983.7 ± 0.1
CuO	2	8988.2 ± 0.1
CuS	2	8988.0 ± 0.1
Malachite	2	8988.0 ± 0.1

Table 3.4: The compounds used as references in the calibration fit**(a)** Plot of the fit

$y=A+Bx$		Fit statistics	
A (eV)	B (eV)	Pearson's r	R-square
8979.4 ± 0.4	4.4 ± 0.3	0,992	0,984

(b) Estimated and goodness-of-fit parameters**Figure 3.8:** Calibration fit for the determination of Cu oxidation state

Last compound added	E_0 - integral method (eV)	Oxidation number
CuCl_2	8988.7 ± 0.1	2.1 ± 0.6
InCl_3	8988.9 ± 0.1	2.2 ± 0.6
CIT	8987.6 ± 0.1	1.9 ± 0.5
GSH	8984.3 ± 0.1	1.1 ± 0.3
Na_2S (CIS in solution)	8984.9 ± 0.1	1.3 ± 0.4
CIS pellet	8984.2 ± 0.1	1.1 ± 0.3
GSH (GSH x2)	8984.1 ± 0.1	1.1 ± 0.3
Na_2S (GSH x2) (CIS in solution)	8984.9 ± 0.1	1.0 ± 0.3

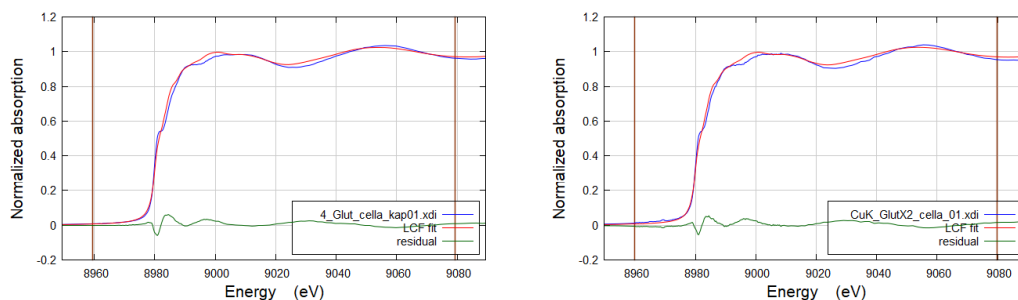
Table 3.5: E_0 and estimated oxidation number of Cu

Figure 3.6 also includes the edge energies measured during the July beamtime for a synthesis performed with twice the amount of glutathione specified in the standard protocol. This additional experiment was designed to verify whether the standard glutathione concentration was sufficient to achieve complete reduction of the copper present in solution. A visual inspection of the graph already suggests that no significant difference exists between the standard and high-glutathione syntheses. This conclusion is further supported by the oxidation-state estimates reported in Tab. 3.5, which are statistically indistinguishable within the experimental uncertainty.

To further investigate this point, a Linear Combination Analysis (LCA), introduced in Section 1.3.3, was performed. The spectrum acquired after the addition of glutathione was modelled as a linear combination of CuS , taken as a Cu(II) reference, and Cu_2S , taken as a Cu(I) reference. The analysis was carried out for both the standard synthesis and the synthesis performed with double the glutathione concentration.

The fraction of the Cu(I) reference component obtained from the fit was not larger in the high-glutathione synthesis. On the contrary, a slightly smaller contribution was obtained, although the difference lies well within the likely uncertainties associated with the fitting procedure. The LCA analysis therefore provides no evidence that increasing the glutathione concentration enhances the reduction of copper beyond that already achieved under standard synthesis conditions.

It can therefore be concluded that the amount of glutathione specified in the synthesis protocol (27 mg for 3 mL of solution) is sufficient to fully exert its reducing action on the copper species present in solution and that the $\text{Cu(II)} \rightarrow \text{Cu(I)}$ conversion is already effectively saturated under the standard reaction conditions.



(a) Synthesis with standard quantity of GSH (27 mg in 3 ml of solution)
 CuS (Cu(II)): **0.119**, Cu₂S (Cu(I)): **0.881**

(b) Synthesis with double quantity of GSH (54 mg in 3 ml of solution)
 CuS (Cu(II)): **0.168**, Cu₂S (Cu(I)): **0.832**

Figure 3.9: Results of the LCA applied to the spectra obtained after the addition of glutathione

Dynamic measurements

During the July beamtime, before performing the time-resolved measurements at the final stage of the synthesis, Cu K-edge spectra were collected both before and after the addition of sodium sulphide. The aim was to identify the energies at which the largest spectral differences occurred. Two energies were selected on this basis: 8984.5 eV and 9007.6 eV (see Figure 3.10).

By fixing the beam energy at each of these values, it was possible to perform time-resolved measurements while sodium sulphide was injected into the reaction mixture using a syringe pump, thereby monitoring the subsequent formation of the nanocrystals.

As shown in Graph (c) of Figure 3.11, the signal recorded at 9007.6 eV exhibited only minor variations over time. Moreover, a slight decrease in intensity was observed, whereas the static spectra suggested that an increase would be expected. For this reason, the subsequent analysis focused exclusively on the measurements collected at 8984.5 eV.

Since the syringe pump flow rate could be accurately controlled, it was also possible to estimate the time required for the complete injection of Na₂S into the reaction vial. With the flow rate set to 300 $\mu\text{l min}^{-1}$ and a total injected volume

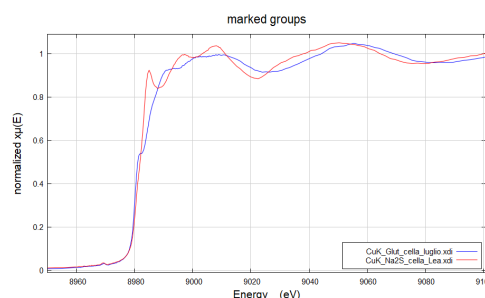


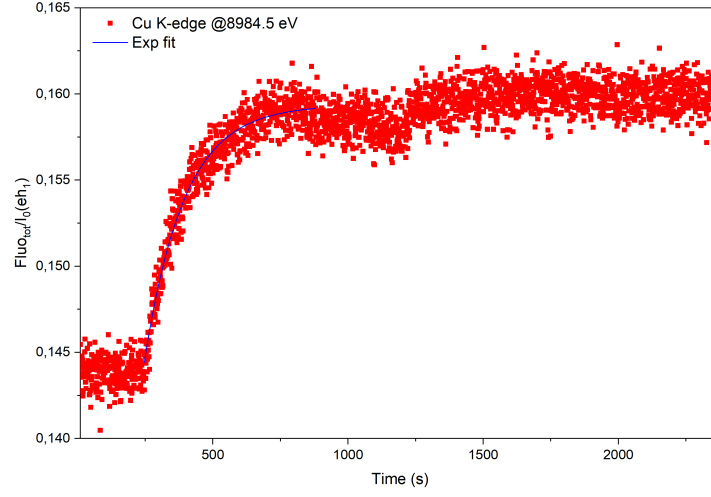
Figure 3.10: Comparison between the spectra post addition of glutathione and Na₂S at Cu K-edge acquired pre dynamic measurements

of 144 μl , the injection time was estimated to be approximately $\Delta t \approx 30$ s.

During the experiment, the onset of the injection was determined from the trigger signal sent remotely from the control room to the syringe pump. For the dataset considered here, the injection started at 210 s. To estimate when the chemical changes should become observable in the XAS signal, one must also account for the injection time (approximately 30 s) and for the residence time required for the solution to travel from the reaction vial to the Kapton capillary, estimated to be about 15–20 s. The increase in the signal is therefore expected to begin at approximately 255–260 s, in good agreement with the experimental observations.

The resulting time-dependent profile was fitted using a single-exponential function of the form $y = A_1 \exp\left(-\frac{t}{t_1}\right) + y_0$, in order to estimate the characteristic kinetics of the process at the copper centres. The fit is shown in Graph (a) of Figure 3.11, while the fitted parameters are reported in Tab. (b) of the same figure. The most relevant parameter is the characteristic time constant t_1 , which was determined to be:

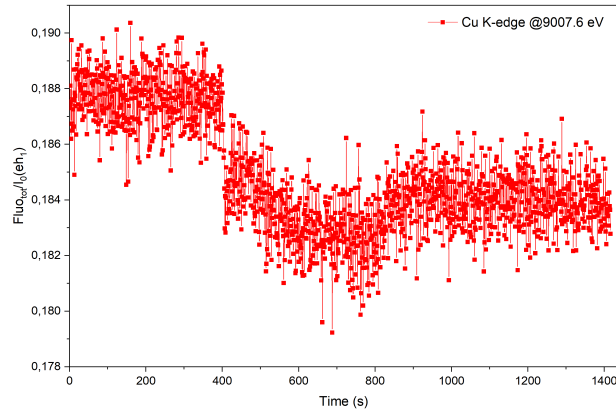
$$\mathbf{t_1 = (147 \pm 3) s.}$$



(a) Time resolved Cu K-edge spectrum of the last step of the synthesis at 8984.5 eV

$y=A_1\exp(-(t-t_0)/t_1)+y_0$ (with $t_0=247$ s)			Fit statistics	
A_1	t_1	y_0	χ^2_{red}	R-factor
-0.080 ± 0.003	(147 ± 3) s	0.15936 ± 0.00008	8×10^{-7}	0.95

(b) Estimated and goodness-of-fit parameters (spectrum at 8984.5 eV)



(c) Time resolved Cu K-edge spectrum of the last step of the synthesis at 9007.6 eV

Figure 3.11: Dynamic analysis at Cu K-edge

3.1.2 Analysis @In K-edge

Static measurements

EXAFS analysis The static measurements collected at the In K-edge were analysed following the same procedure adopted for the Cu K-edge data. In this case, spectrum acquisition began only after the addition of the indium precursor (InCl_3), since indium was naturally absent from the solution following the initial addition of CuCl_2 . Tab. 3.6 reports the reference compounds used in the EXAFS analysis together with the corresponding scattering paths employed in the fits. Only schematic representations of $\text{In}(\text{OH})_3$ and In_2S_3 are shown in Figure 3.12, as the In–C scattering path was generated from a manually constructed .cif structure, while the crystal structure of the CIS nanocrystals has already been presented in the Cu K-edge analysis. The fitted structural parameters and the corresponding fit-quality indicators are reported in Tables 3.7 and 3.8, respectively. The resulting fits, superimposed on the experimental spectra in both k- and R-space, are shown in Figure 3.13.

Reference compound	Path	N	R_{eff} ($\text{\AA}$)
$\text{In}(\text{OH})_3$	In-O	6	2.161
<i>Self-built</i>	In-C	3	2.999
CuInS_2 (Chalcopyrite)	In-S	4	2.492
In_2S_3	In-S	2	2.537

Table 3.6: Reference compounds and related paths employed in the fit @ Cu K-edge

For the indium analysis, the procedure described in Chapter 2 (Section 2.2) for determining the amplitude reduction factor S_0^2 did not provide a reliable estimate. Consequently, S_0^2 was fixed at a value of 0.9 throughout the fitting procedure.

As in the case of copper, the addition of the precursor to the aqueous solution is expected to result in the dissociation of the metal–chlorine bonds and the formation of hydrated indium species. The local structure of hydrated indium is characterized by an approximately octahedral coordination environment, with six oxygen atoms surrounding the absorber in the first shell. Consequently, the first spectrum collected after the addition of InCl_3 was fitted using the In–O scattering path generated from the structure of $\text{In}(\text{OH})_3$, whose local coordination environment provides a reasonable approximation to that of hydrated indium. The resulting fit was found to be fully consistent with this model.

The addition of citrate does not produce significant changes in the first-shell

		First shell					Second shell				
Last compound added	ΔE_0 (eV)	Reference compound	Path	N ₁	R ₁ (Å)	σ_1^2 ($\times 10^{-3} \text{\AA}^2$)	Reference compound	Path	N ₂	R ₂ (Å ²)	σ_2^2 ($\times 10^{-3} \text{\AA}^2$)
InCl ₃	7.0 ± 1.1	In(OH) ₃	In-O	6.6 ± 0.7	2.196 ± 0.011	4 ± 2	\	\	\	\	\
CIT	2.7 ± 0.7	In(OH) ₃	In-O	6.7 ± 0.5	2.156 ± 0.007	5.6 ± 1.1	Self-built	In-C	3 ± 2	2.99 ± 0.03	5 ± 7
GSH	2.3 ± 0.7	In(OH) ₃	In-O	6.8 ± 0.5	2.151 ± 0.007	5.7 ± 1.1	Self-built	In-C	2.1 ± 1.5	2.98 ± 0.03	2 ± 7
Na ₂ S (CIS in solution)	3.8 ± 0.5	CuInS ₂	In-S	4.8 ± 0.2	2.458 ± 0.004	4.3 ± 0.5	\	\	\	\	\
CIS pellet	2.6 ± 1.0	CuInS ₂	In-S	4.8 ± 0.5	2.453 ± 0.008	4.5 ± 1.2	\	\	\	\	\

Table 3.7: In K-edge EXAFS fitted parameters - complete synthesis ($S_0^2 = 0.9$)

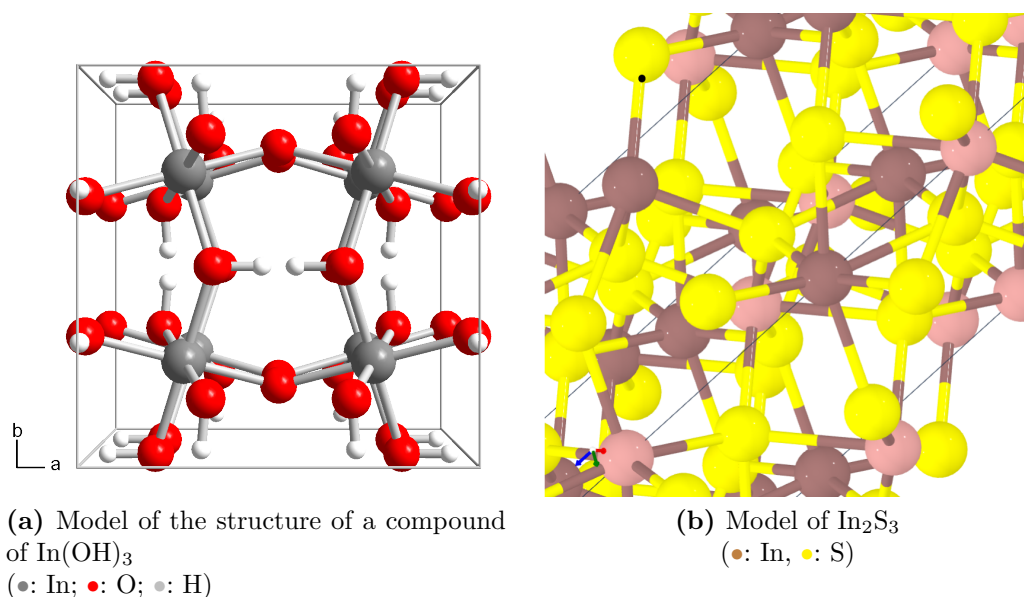


Figure 3.12: Schematic representation of the model compound used for the In k-edge fits

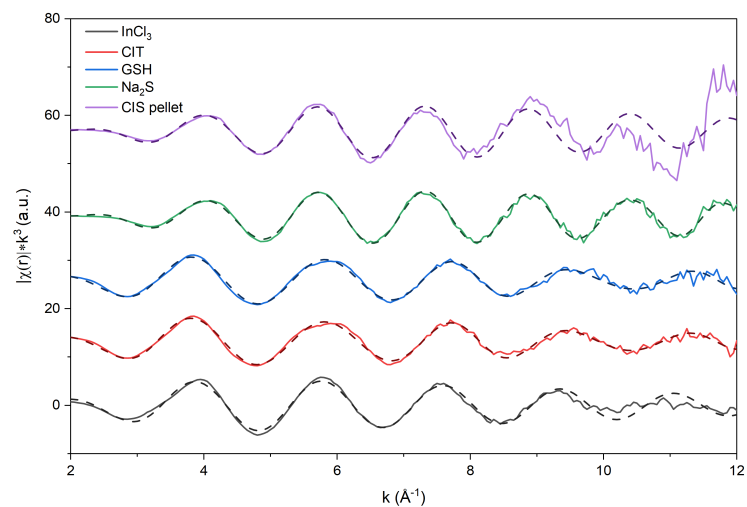
environment of indium. However, a second-shell contribution becomes clearly detectable and can be attributed to carbon atoms belonging to the citrate ligand. These atoms are located at a distance of approximately 3 Å from the absorber, with an estimated coordination number of about 3. Owing to the associated uncertainty, the latter should be considered compatible with values in the range 1–5.

Similarly, the subsequent addition of glutathione does not lead to any observable modification of the indium spectrum. The fitted structural parameters remain essentially unchanged with respect to the previous step, indicating that glutathione does not significantly affect the local coordination environment of indium. This observation suggests that the role of glutathione in the synthesis is primarily associated with copper, to which the thiol group binds, inducing the reduction of $\text{Cu}(\text{II})$ to $\text{Cu}(\text{I})$, as discussed in the Cu K-edge analysis.

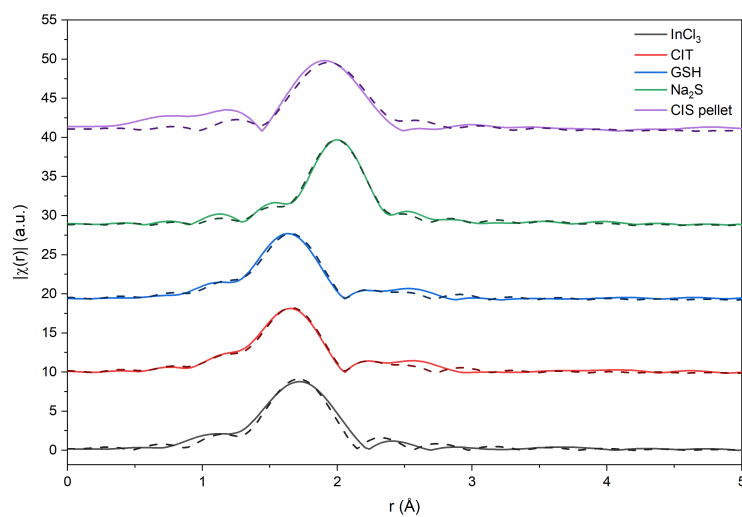
Overall, the first-shell environment remains remarkably stable throughout the first three stages of the synthesis. The coordination number is consistently found to lie between six and seven oxygen atoms, while the average In–O distance decreases only slightly, from approximately 2.19 to 2.15 Å following citrate addition. Once detected, the second shell also remains essentially unchanged up to the final synthesis step. Although its coordination number cannot be determined accurately, the results suggest the presence of approximately two to three carbon atoms at a distance close to 3 Å from the indium centres.

The most significant structural modification occurs only after the addition

of sodium sulphide. At this stage, the chemical nature of the first-shell ligands changes, with oxygen atoms being replaced by sulphur atoms originating from the sulphide precursor. The fit indicates the presence of approximately five sulphur neighbours at a distance of about 2.46 Å from the indium atoms. The Cu-containing second-shell contribution expected for fully formed CuInS₂ nanocrystals could not be reliably detected, even in the purified CIS pellet analysed as a reference sample. Nevertheless, the first-shell fit parameters are in good agreement with the expected local structure of Chalcopyrite CuInS₂, despite the presence of minor deviations from the ideal model.



(a) k-space fits



(b) R-space fits

Figure 3.13: Stacked plot of the EXAFS fits at the In K-edge for the complete synthesis (solid lines: spectra, dot lines: fits)

Last compound added	k-range ($\text{\AA}^{-1}$)	R-range ($\text{\AA}$)	χ^2	χ_{red}^2	R-factor
InCl ₃	[2.8–10.5]	[1–4]	10558	1006	0.03
CIT	[2.8–11.5]	[1.1–5]	2102	147	0.014
GSH	[2.8–11.5]	[1.1–5]	1974	138	0.012
Na ₂ S (CIS in solution)	[3–12.5]	[1–4]	885	64	0.009
CIS pellet	[3–10]	[1.1–5]	1697	129	0.04

Table 3.8: Goodness-of-fit parameters - In K-edge complete synthesis

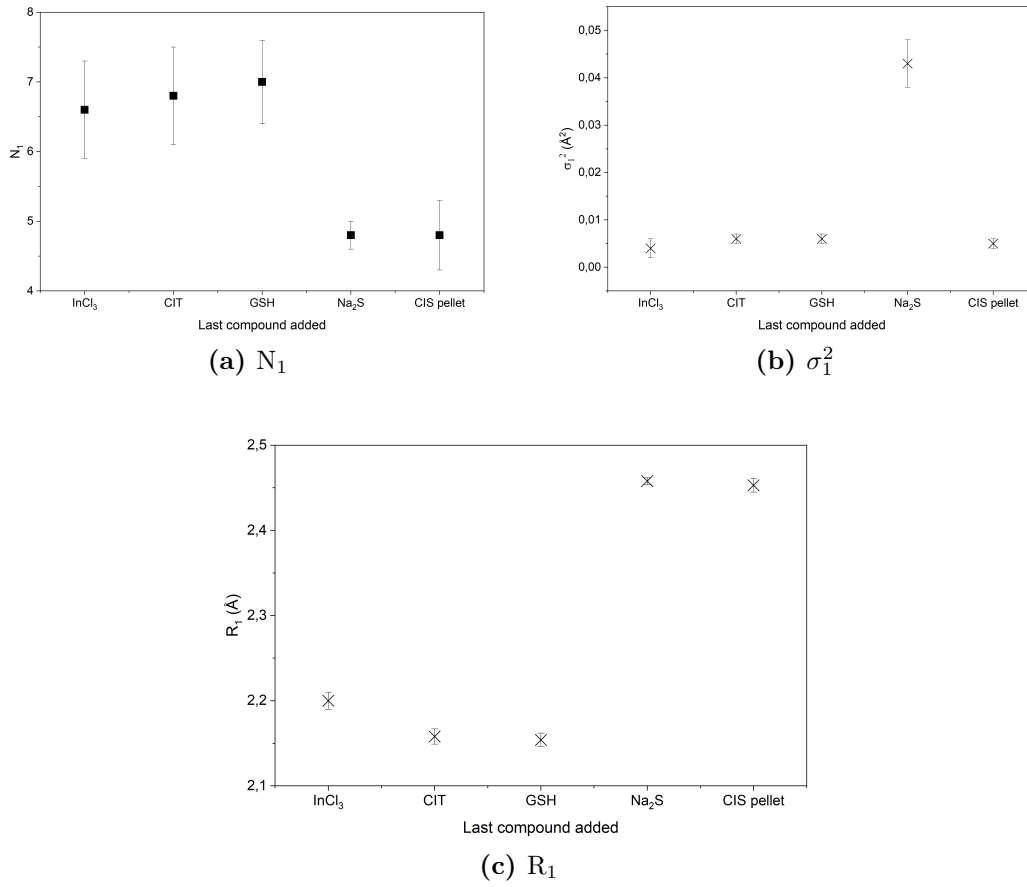


Figure 3.14: Trend of the 1st shell fitted variables as the synthesis step varies for the spectra at In K-edge of the complete synthesis

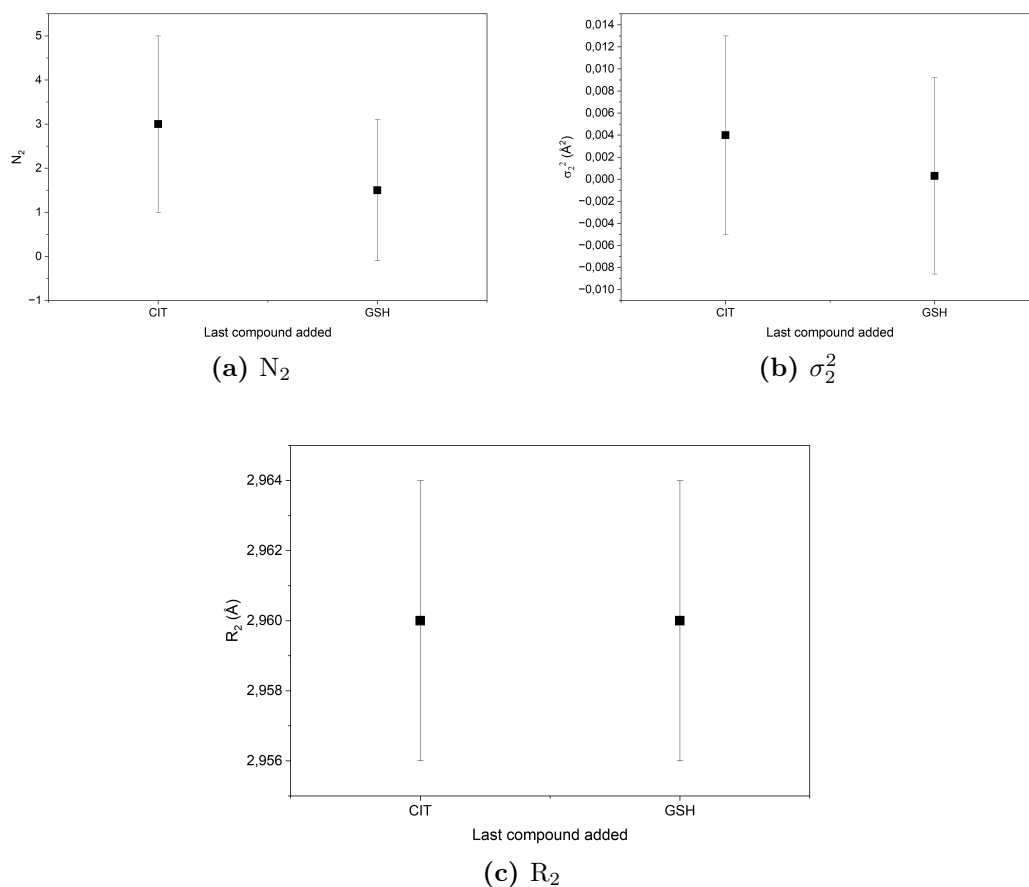
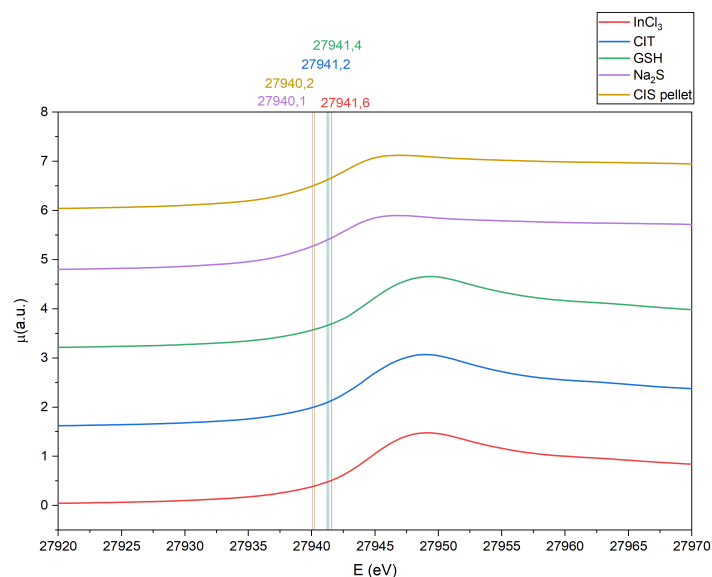


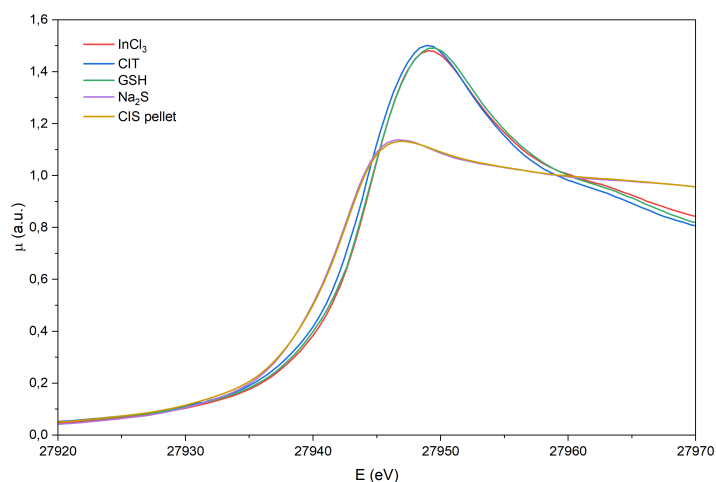
Figure 3.15: Trend of the 2nd shell fitted variables as the synthesis step varies for the spectra at In K-edge of the complete synthesis

XANES analysis XANES analysis was also performed on the spectra collected at the In K-edge during the complete synthesis. As in the case of copper, the integral method described in Section 2.2 was used to determine the edge energy E_0 for each acquired spectrum.

The XANES regions of the spectra, together with the corresponding E_0 values obtained from the analysis, are shown in Figure 3.17. A visual inspection of the spectra already suggests the absence of any significant edge shift throughout most of the synthesis. The only appreciable variation is observed after the addition of sodium sulphide, where the absorption edge shifts towards lower energy by approximately 1 eV relative to the previous spectra, whose E_0 values are mutually consistent within the experimental uncertainty.



(a) Stacked XANES spectra with the found values of E_0 displayed



(b) Overlaid XANES spectra

Figure 3.16: XANES spectra at In K-edge for the complete synthesis

In order to investigate the oxidation state of indium in a more quantitative manner, an approach analogous to that adopted for the Cu K-edge analysis was considered. In contrast to copper, however, the selection of suitable reference compounds proved considerably more challenging. With the exception of a few rare and unstable species, indium is almost exclusively found in the +3 oxidation

state. As a result, it was not possible to collect spectra from reference compounds spanning different oxidation states and therefore no calibration curve relating E_0 to the oxidation number could be established.

Reference compound	Oxidation number	E_0 - integral method (eV)
InP (80 K)	3	27940.4 ± 0.1
InAs	3	27939.1 ± 0.1

Table 3.9: Indium’s oxidation number reference compounds

The analysis was therefore limited to the determination of the average edge energy of the available In(III) reference compounds (Table 3.9). The resulting mean value was found to be: $E_0 = (27939.7 \pm 0.9) \text{ eV}$, where the reported uncertainty corresponds to the standard deviation of the reference dataset.

The compatibility between the E_0 values determined for the experimental spectra and this reference value was then evaluated. The results are reported in Table 3.10. All measured edge energies were found to be compatible with the expected In(III) oxidation state throughout the synthesis. A slight decrease in the edge energy was nevertheless observed in the final synthesis step, after the addition of sodium sulphide, and was present in both the colloidal solution and the purified CIS pellet. Although this shift remains fully compatible with the In(III) oxidation state, it is consistent with the change in the first coordination shell revealed by the EXAFS analysis, namely the replacement of oxygen ligands by sulphur atoms around the indium centres.

These results indicate that, unlike copper, indium does not undergo any measurable change in oxidation state during the synthesis. Instead, the observed shift in the absorption edge is most likely associated with the modification of the local chemical environment accompanying the formation of In–S bonds. Since the expected Cu second-shell contribution could not be directly detected by EXAFS, this spectroscopic change cannot by itself be regarded as direct evidence for the formation of CuInS_2 nanocrystals, but should rather be interpreted as being consistent with the ligand exchange occurring in the final stage of the synthesis.

Last compound added	E_0 - integral method (eV)	Compatibility with reference value
InCl_3	27941.6 ± 0.1	2.3
CIT	27941.2 ± 0.1	1.9
GSH	27941.4 ± 0.1	2.0
Na_2S (CIS in solution)	27940.1 ± 0.1	0.4
CIS pellet	27940.2 ± 0.1	0.6

Table 3.10: E_0 of In in the complete synthesis and compatibility with reference value for In(III)

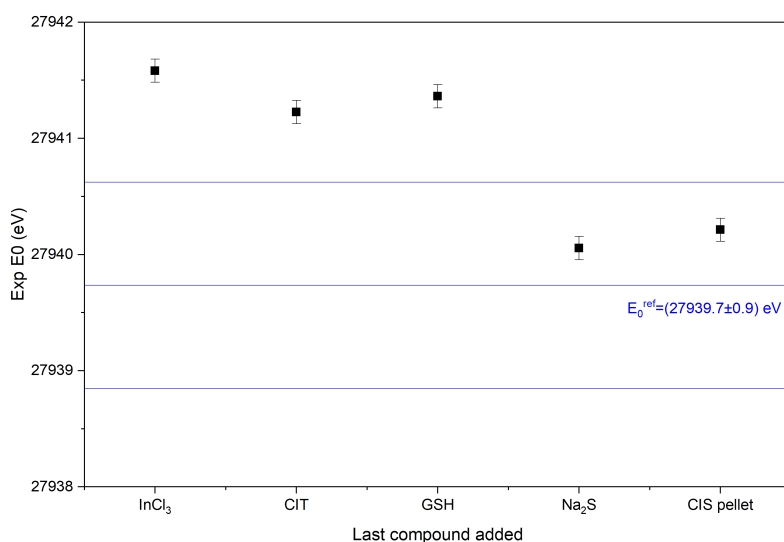


Figure 3.17: Trend of the estimated value of E_0 as the synthesis step varies for the complete synthesis at In K-edge with the reference value with his error displayed as a band

Dynamic measurements

As for the Cu K-edge measurements, static spectra were first collected at the In K-edge for the final two stages of the synthesis, namely after the addition of glutathione and after the addition of Na_2S . The purpose was to identify the energies at which the largest spectral changes occurred and, consequently, the most suitable energies for time-resolved measurements. The largest differences between the two spectra were observed at 27948 eV and 27971 eV (see Figure 3.18).

The beam energy was therefore fixed at each of these values, and time-resolved measurements were performed during the final stage of the synthesis. As in the Cu K-edge analysis, only one of the two datasets was subsequently considered for quantitative analysis. In particular, the spectrum collected at 27971 eV exhibited only a limited variation in intensity and showed several points deviating from the overall trend during the transition region. For this reason, the kinetic analysis was restricted to the dataset acquired at 27948 eV.

For this measurement, the Na₂S injection began at 987 s. Given the syringe flow rate, the injection was completed approximately 30 s later, at about 1017 s. Taking into account the additional time required for the solution to travel through the capillary and reach the Kapton section intersected by the X-ray beam, the onset of the spectral variation would be expected at approximately 1035 s. Experimentally, however, the first detectable changes occur slightly earlier, at around 1025 s. This small discrepancy can reasonably be attributed to the large amplitude of the spectral variation, which allows the initial changes to be detected as soon as the first fraction of sulphide-containing solution reaches the probed region.

The resulting time-dependent profile was fitted using a single-exponential function. The fit is shown in Figure 3.19(a), while the corresponding fitting parameters are reported in Figure 3.19(b). The characteristic time constant obtained from the fit was:

$$t_1 = (33.0 \pm 0.3) \text{ s}.$$

The most significant result emerging from the dynamic measurements is the marked difference between the characteristic times observed at the In and Cu K-edges. The structural transformation occurring around indium is substantially faster than that observed around copper:

$$\Delta t_{In} = (33.0 \pm 0.3) \text{ s} \text{ and } \Delta t_{Cu} = (147 \pm 3) \text{ s}.$$

Assuming an exponential behaviour, approximately 95% of the total variation is completed after a time interval corresponding to roughly three characteristic times. The overall kinetic times can therefore be estimated as:

$$\Delta t_{In}^{tot} = (99.0 \pm 0.9) \text{ s} \text{ and } \Delta t_{Cu}^{tot} = (441 \pm 9) \text{ s}.$$

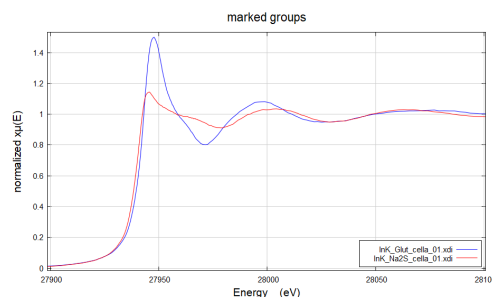
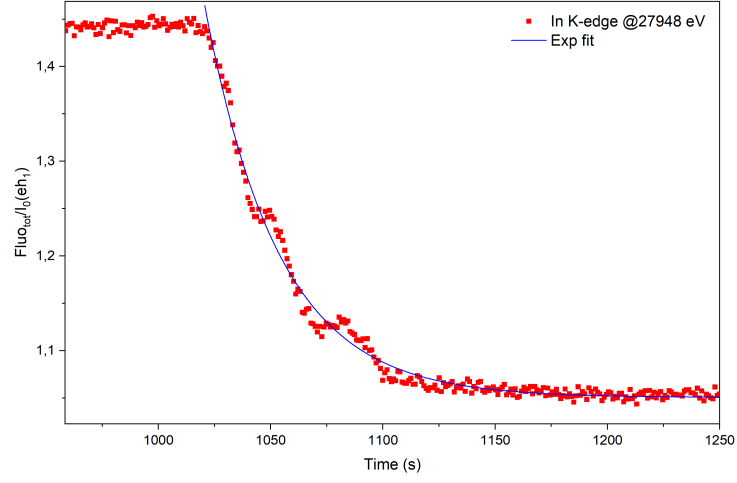


Figure 3.18: Comparison between the spectra post addition of glutathione and Na₂S at In K-edge acquired pre dynamic measurements

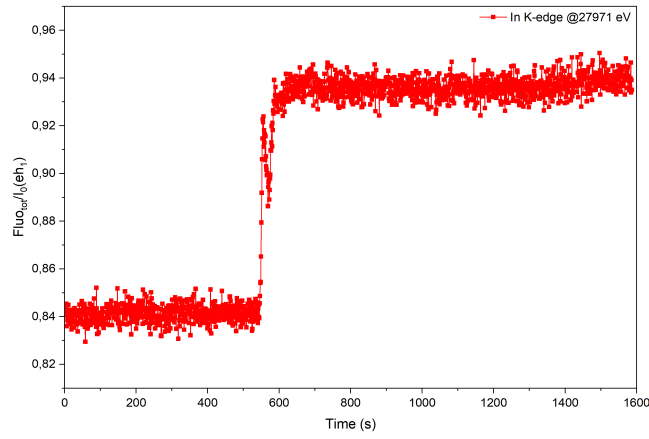
The different characteristic times observed at the In and Cu K-edges are consistent with the transient formation of an intermediate phase during nanocrystal synthesis. The rapid spectral evolution at the In K-edge suggests the prompt formation of an indium–sulphide intermediate immediately after sulphide injection, whereas the slower response at the Cu K-edge indicates that copper incorporation occurs on a longer timescale. This intermediate would therefore act as a precursor to the final CuInS_2 nanocrystalline structure.



(a) Time resolved In K-edge spectrum of the last step of the synthesis at 27948 eV

$y=A_1\exp(-(t-t_0)/t_1)+y_0$ (with $t_0=1021$ s)			Fit statistics	
A_1	t_1	y_0	χ^2_{red}	R-factor
$(1.1 \pm 0.3) \times 10^{13}$	(33.0 ± 0.3) s	$1.1 \pm 2.5 \times 10^{-4}$	4×10^{-5}	0.989

(b) Estimated and goodness-of-fit parameters (spectrum at 27948 eV)



(c) Time resolved In K-edge spectrum of the last step of the synthesis at 27971 eV

Figure 3.19: Dynamic analysis at In K-edge

3.1.3 Synthesis tests without metal precursors

Synthesis without InCl_3 @Cu K-edge

EXAFS analysis As previously mentioned, Cu K-edge spectra were collected during the July beamtime from a synthesis conducted without the addition of InCl_3 , allowing the role of the indium precursor to be assessed independently.

We first discuss the macroscopic changes observed during the synthesis, as several differences with respect to the complete synthesis were evident even upon visual inspection. Upon citrate addition, the solution remained relatively clear and exhibited a less intense blue colour than that observed during the complete synthesis. Following the addition of glutathione, the solution became transparent, similarly to what was observed in the complete synthesis. Finally, after the addition of sodium sulphide, the solution developed a brownish coloration, although it remained noticeably lighter than that observed in the complete synthesis.

Moving on to the XAS measurements, spectra were acquired only from the citrate-addition step onwards, to see whether any differences would be detected compared with the spectra acquired during the complete synthesis. For all three spectra, the second-shell contribution could not be reliably fitted because its signal was too weak to be resolved. In the fit corresponding to the third step of the synthesis, following the addition of citrate, the fit suggests a first-shell coordination number of approximately 4 oxygen atoms around the copper centres, compared with about 5 in the complete synthesis. In this case, therefore, the copper environment would appear to be more in line with the standard case of hydrated copper, and the distortion observed in the complete synthesis does not seem to be present. However, it should be noted that the N_1 estimations considered here carry a significant error, of approximately 20 % and 17 % for the complete and incomplete synthesis respectively; indeed, if one calculates the compatibility of the two estimations as reported in the Appendix (see 3.2.3), the two estimates are found to be statistically compatible ($\lambda_{N_1^{compl}-N_1^{incompl}} \approx 0.8$). Consequently, given the measurement errors, it is not possible to support the presence of an actual difference in the local coordination environment of the copper centres between the two cases.

The fit results obtained after glutathione addition are essentially identical to those obtained for the first-shell contribution in the complete synthesis. In the final synthesis step, direct evidence for the absence of nanocrystal formation could not be obtained, since the second-shell contribution around copper could not be resolved in the indium-free synthesis. Nevertheless, indirect evidence supporting this interpretation was obtained. In fact, by carrying out two fit analyses using chalcocite and CIS nanocrystals respectively as the reference compounds for the FEFF calculations, very similar results were obtained (as can be seen from Tab.

3.12 and Tab. 3.11), except that the number of sulphur atoms in the first shell was found to be approximately 3, thus providing greater agreement with the chalcocite model. This observation supports the hypothesis that, in the absence of indium, copper remains coordinated to sulphur atoms originating from glutathione-derived thiolate species rather than participating in the formation of CuInS_2 nanocrystals.

Last compound added	ΔE_0 (eV)	First shell				
		Reference compound	Path	N_1	R_1 ($\text{\AA}$)	σ_1^2 ($\times 10^{-3} \text{\AA}^2$)
CIT	-0.1 ± 2.4	$\text{CuSO}_4 \times 5(\text{H}_2\text{O})$	Cu-O	$N_{\text{O,eq}}: 4.1 \pm 0.7$	$R_{\text{O,eq}}: 1.927 \pm 0.015$	2 ± 2
GSH	5.6 ± 1.4	Cu_2S	Cu-S	3.3 ± 0.4	2.266 ± 0.012	6.5 ± 1.6
Na_2S (CIS in solution)	5.4 ± 1.2	Cu_2S	Cu-S	3.0 ± 0.3	2.284 ± 0.011	7.3 ± 1.5
Na_2S (CIS in solution)	5.1 ± 1.2	CuInS_2	Cu-S	3.0 ± 0.3	2.284 ± 0.011	7.4 ± 1.5

Table 3.11: Cu K-edge EXAFS fitted parameters - synthesis without InCl_3 ($S_0^2 = 0.9$)

Last compound added	k-range ($\text{\AA}^{-1}$)	R-range ($\text{\AA}$)	χ^2	χ_{red}^2	R-factor
CIT	[3–11.5]	[1.1–5]	5767	343	0.14
GSH	[3.5–11.2]	[1–5]	1061	69	0.06
Na_2S (CIS in solution) ref. compound: Cu_2S	[3.4–11.5]	[1–4]	701	62	0.03
Na_2S (CIS in solution) ref compound: CuInS_2	[3.4–11.5]	[1–4]	698	62	0.03

Table 3.12: Goodness-of-fit parameters - Cu K-edge synthesis without InCl_3

Synthesis without CuCl_2 @In K-edge

EXAFS analysis As observed for the synthesis performed without InCl_3 and analysed at the Cu K-edge, noticeable macroscopic differences were also evident in the synthesis carried out without the copper precursor. Following the addition of citrate, the solution remained transparent and did not develop the characteristic bluish colour observed in the complete synthesis. The solution remained clear after the addition of glutathione and, even after the introduction of sodium sulphide, it did not acquire the dark brown colour typically associated with nanocrystal formation. Instead, it remained nearly transparent, exhibiting at most a slight pinkish tint.

For the synthesis performed without CuCl_2 and analysed at the In K-edge, spectra were collected starting from the citrate-addition step, following the same procedure adopted for the analogous experiment conducted at the Cu K-edge. In order to maintain the same indium concentration as in the complete synthesis, 2.5 mL of water was initially added instead of 1.5 mL to compensate for the absence of the copper precursor.

The results of the EXAFS analysis are reported in Tables 3.13 and 3.14. For the first two investigated stages, the fitted structural parameters are essentially identical to those obtained for the complete synthesis. The only notable difference is that, after the addition of glutathione, the carbon-containing second-shell contribution could no longer be reliably detected.

Similarly, no second-shell contribution could be resolved in the spectrum collected after the final addition of sodium sulphide. To model the first-shell environment, two alternative In–S scattering paths were considered, one derived from chalcopyrite CuInS_2 and the other from In_2S_3 . The resulting fits were essentially indistinguishable, yielding comparable structural parameters. As in the analysis of the complete synthesis, the absence of a detectable second-shell signal prevented the direct observation of structural features associated with nanocrystal formation. Consequently, neither the successful formation of CIS nanocrystals in the complete synthesis nor their presumed absence in the Cu-free synthesis could be demonstrated directly from the local environment of indium.

Nevertheless, the fitted first-shell parameters indicate that the local coordination environment around indium is largely unaffected by the presence or absence of copper in solution. In both cases, the first shell is characterised by approximately five sulphur neighbours located at a distance of about 2.45 Å from the absorber.

Last compound added	ΔE_0 (eV)	First shell					Second shell				
		Reference compound	Path	N ₁	R ₁ (Å)	σ_1^2 ($\times 10^{-3} \text{\AA}^2$)	Reference compound	Path	N ₂	R ₂ (Å ²)	σ_2^2 ($\times 10^{-3} \text{\AA}$)
CIT	-0.7 ± 0.7	In(OH) ₃	In-O	5.9 ± 0.5	2.143 ± 0.007	3.5 ± 0.9	<i>Self-built</i>	In-C	4 ± 3	2.96 ± 0.04	7 ± 9
GSH	0.3 ± 0.7	In(OH) ₃	In-O	7.2 ± 0.5	2.151 ± 0.007	6.5 ± 1.0	\	\	\	\	\
Na ₂ S (<i>CIS in solution</i>)	3.2 ± 0.5	CuInS₂	In-S	4.7 ± 0.2	2.454 ± 0.004	4.2 ± 0.5	\	\	\	\	\
Na ₂ S (<i>CIS in solution</i>)	2.7 ± 0.5	In₂S₃	In-S	4.6 ± 0.2	2.453 ± 0.004	4.1 ± 0.5	\	\	\	\	\

Table 3.13: In K-edge EXAFS fitted parameters - synthesis without CuCl₂ ($S_0^2 = 0.9$)

Last compound added	k-range ($\text{\AA}^{-1}$)	R-range ($\text{\AA}$)	χ^2	χ^2_{red}	R-factor
CIT	[2.5–11.6]	[1.1–5]	1860	121	0.014
GSH	[2.7–11.5]	[1.1–5]	1635	93	0.02
Na ₂ S (CIS in solution) ref: CuInS ₂	[3–12]	[1–5]	164	9	0.015
Na ₂ S (CIS in solution) ref: In ₂ S ₃	[3–12]	[1–5]	168	9	0.016

Table 3.14: Goodness-of-fit parameters - In K-edge synthesis without CuCl₂

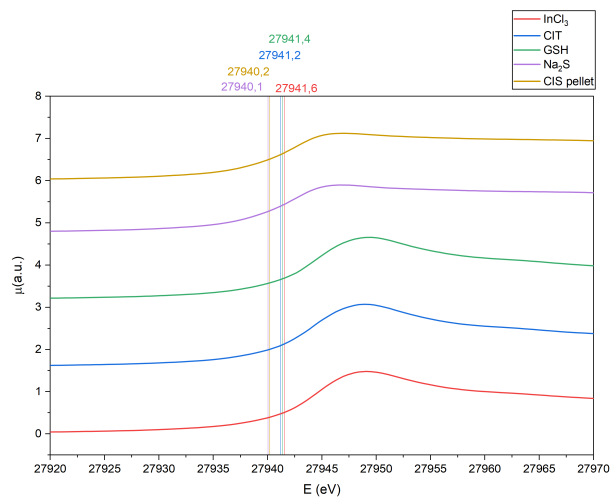
XANES analysis The XANES spectra acquired during the synthesis performed without CuCl₂ are shown in Figure 3.20. The edge energies were determined using the same integral method employed throughout this work in order to verify the oxidation state of indium at each stage of the synthesis.

Although the estimated E_0 values are systematically slightly lower than those obtained for the complete synthesis, all values remain compatible, within experimental uncertainty, with the reference energy associated with the In(III) oxidation state, $E_0 = (27939.7 \pm 0.9) \text{ eV}$, as reported in Tab. 3.15.

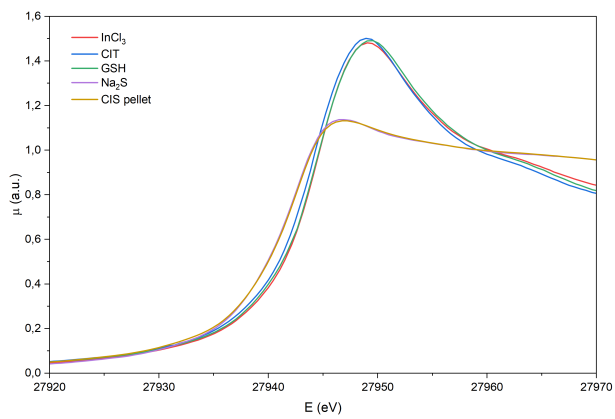
These results indicate that the omission of the copper precursor does not produce any measurable change in the oxidation state of indium. As observed in the complete synthesis, indium remains in the +3 oxidation state throughout the reaction, confirming that the structural modifications detected by EXAFS arise from changes in the local coordination environment rather than from redox processes involving the indium centres.

Last compound added	E_0 - integral method (eV)	Compatibility with reference value
CIT	27939.0 ± 0.1	0.9
GSH	27939.8 ± 0.1	0.14
Na ₂ S (CIS in solution)	27938.6 ± 0.1	1.4

Table 3.15: E_0 of In in the synthesis without CuCl₂ and compatibility with reference value for In(III)



(a) Stacked XANES spectra with the found values of E_0 displayed



(b) Overlaid XANES spectra

Figure 3.20: XANES spectra at In K-edge for the synthesis without CuCl_2

3.2 Feasibility study of pump & probe XAS experiments

3.2.1 Estimation of the excited-state population

The feasibility of a pump–probe XAS experiment critically depends on the fraction of molecules that can be promoted to the excited state by the pump pulse. As a first step, an estimate of the excited-state population was therefore carried out under the experimental conditions available at the LISA beamline.

The number of photons contained in a single laser pulse, n_{ph} , can be obtained from the pulse energy E_{pulse} and the energy of an individual photon E_{ph} according to

$$n_{ph} = \frac{E_{pulse}}{E_{ph}}. \quad (3.2)$$

The total number of molecules contained within the excited volume of the sample can instead be estimated from the solute concentration c and the illuminated volume V as

$$n_{mol}^{tot} = c V N_A, \quad (3.3)$$

where N_A is Avogadro’s constant.

Assuming that each absorbed photon generates one excited molecule, the number of excited molecules can be estimated from the fraction of absorbed photons. This quantity is related to the absorbance of the sample through the Beer–Lambert law,

$$A = \epsilon c d, \quad (3.4)$$

where ϵ is the molar absorptivity and d is the optical path length. Since the absorbance is related to the transmittance T by

$$A = -\log_{10}(T), \quad (3.5)$$

the fraction of absorbed photons can be expressed as $1 - 10^{-A}$. Consequently, the number of excited molecules is given by

$$n_{mol}^{abs} = n_{mol}^{tot} (1 - 10^{-A}) = n_{mol}^{tot} (1 - 10^{-\epsilon c d}). \quad (3.6)$$

Equation 3.6 highlights the parameters governing the excited-state population. On the excitation side, increasing the pulse energy or reducing the illuminated area leads to a larger photon density. On the sample side, the fraction of excited molecules can be enhanced by increasing the optical absorption at the pump

wavelength. The concentration, however, must be chosen as a compromise: while lower concentrations favour a larger excitation fraction, excessively dilute solutions would ultimately result in XAS signals that are too weak to be detected.

The only laser source available at the LISA beamline was a PiLas picosecond diode laser operating at a wavelength of $\lambda_{laser} = 404$ nm and delivering a pulse energy of $E_{pulse} = 100$ pJ. The energy of a single photon was calculated from

$$E_{ph} = \frac{hc}{\lambda}, \quad (3.7)$$

yielding $E_{ph} = 4.9 \times 10^{-19}$ J. The corresponding number of photons per pulse is therefore approximately $n_{ph} \simeq 2 \times 10^8$

The effective excitation area was assumed to be limited by the X-ray beam footprint, which was smaller than the laser spot and corresponded to approximately 0.25 mm^2 . Assuming a solute concentration of 10^{-3} M and a molar absorptivity of $\epsilon = 10^5 \text{ M}^{-1}\text{cm}^{-1}$, representative of strongly absorbing chromophores at the laser wavelength, the fraction of excited molecules was estimated to be of the order of 10^{-7} . This outcome alone is already a warning sign, since this value is approximately four orders of magnitude below the value ($\sim 10^{-3}$), that it is the expected target value required to generate a detectable XAS signal.

3.2.2 Estimation of the fluorescence and transmission signals

The estimate of the excited-state population discussed in the previous section provides only a preliminary indication of the feasibility of a pump-probe XAS experiment. A complete assessment also requires an evaluation of the expected fluorescence and transmission signals, in order to determine whether the photo-induced changes could be detected with the instrumentation available at the LISA beamline.

To this end, a simplified model of the sample was developed. The metal centers were assumed to be concentrated within a thin layer located at the center of the capillary and characterized by the density of the corresponding pure metal. Under this assumption, an equivalent thickness d_{eq} can be defined as the thickness of a cylindrical layer having the same cross-sectional area as the beam footprint and containing the entire mass of metal present in the illuminated sample volume. This approach allows the absorption and transmission of X-rays through the different components of the system to be estimated using the Beer-Lambert law.

The illuminated sample volume was calculated from the capillary diameter ($d = 1.6 \text{ mm}$) and the beam footprint ($A = 5 \times 10^{-3} \text{ mm}^2$), yielding

$$V_{exc} \simeq 8 \times 10^{-3} \text{ mm}^3. \quad (3.8)$$

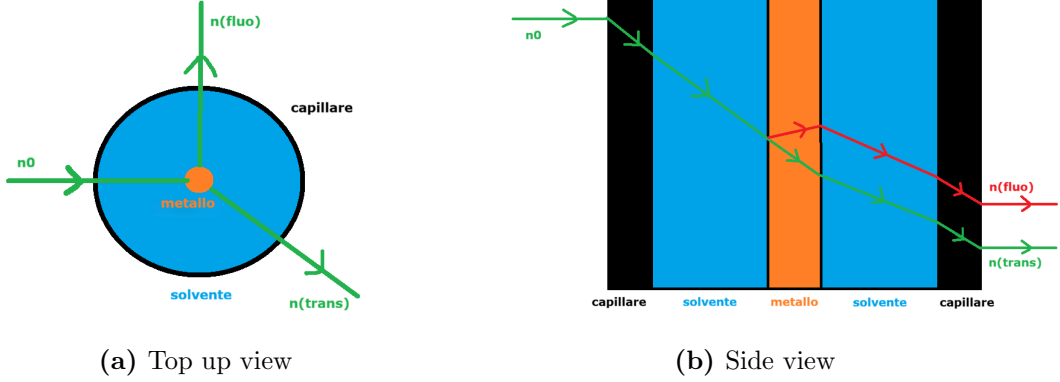


Figure 3.21: Scheme of the pump-probe system model

Assuming a solute concentration of 10^{-3} M, the number of molecules contained within this volume is found to be of the order of 10^{12} . By further assuming one metal atom per molecule, the total mass of metal present in the illuminated region can be estimated. Combining this quantity with the density of the corresponding metal yields an equivalent thickness d_{eq} of approximately $0.1 \mu\text{m}$ for representative cases such as Ag, Ni, and Co.

The propagation of X-rays through the sample was then modelled using the Beer–Lambert law in the form

$$n_T = n_0 \cdot e^{-\mu(\lambda)d}, \quad (3.9)$$

where n_0 and n_T denote the incident and transmitted photon fluxes, respectively, $\mu(\lambda)$ is the linear attenuation coefficient at the photon energy of interest, and d is the thickness of the material crossed by the beam.

With the modelization performed the sample was represented as three concentric regions corresponding to the capillary wall, the solvent, and the metal-containing layer. The attenuation of the X-ray beam was calculated sequentially across these regions, allowing the transmitted intensity to be estimated. In parallel, the fluorescence signal was evaluated by considering the photons absorbed within the metal layer,

$$n_{\text{abs}} = n_0 (1 - e^{-\mu(\lambda)d}), \quad (3.10)$$

and assuming, as a first approximation, that each absorbed photon generates one fluorescence photon. The attenuation experienced by the emitted fluorescence photons while exiting the sample was then taken into account by applying Eq. 3.9 to the remaining layers.

Calculations were performed for the K-edges of Ag, Ni, and Co, considering DMF ($\text{C}_3\text{H}_7\text{NO}$) as solvent and Teflon as the capillary material. Under these assumptions, the detectable fluorescence signal was estimated to be of the order of 10^6 photons s^{-1} , while the transmission ratio $n * \text{trans}/n_0$ was found to be approximately 0.9 for Ag and of the order of 10^{-1} for Ni and Co.

These values indicate that the expected signal variations induced by photoexcitation would remain below the detection limit of the experimental setup. Furthermore, although Ag provides the most favorable transmission conditions, its K-edge lies above 20 keV, where the increased contribution of Compton scattering results in a substantial background signal. Consequently, even the most promising scenario considered within this study does not appear compatible with reliable pump-probe XAS measurements at the LISA beamline.

3.2.3 Assessment of experimental feasibility

The analysis presented above indicates that the principal limitation of the proposed pump-probe experiment is the low fraction of photoexcited molecules achievable with the laser system available at the LISA beamline. Even under the most favourable assumptions regarding sample concentration, optical absorption and beam geometry, the estimated excited-state population remains several orders of magnitude below the threshold required for reliable detection.

Although the use of more powerful laser systems could in principle overcome this limitation, their implementation would require substantial modifications to the beamline infrastructure and compliance with additional ESRF safety requirements, because they entail the implementation of an interlock for the use of too powerful lasers. For these reasons, pump-probe measurements were deemed impractical within the scope of the present work. The experimental effort was therefore redirected towards the investigation of CuInS_2 nanocrystal synthesis by means of *in situ* X-ray absorption spectroscopy, which constitutes the main focus of this thesis.

Upon varying the controllable parameters of the experiment, it ultimately becomes clear that the limiting factor is the fraction of excited molecules out of the total present in the sample, which is determined by the power of the laser used. As seen earlier, this was found to be of the order of 10^{-7} , but the target for obtaining detectable signals is set at around 10^{-3} , a value that cannot be achieved with the laser power available in the LISA laboratories, even setting the values of the other controllable parameters to the most convenient values. This problem proved critical, as using more powerful lasers poses a practical and logistical challenge, since ESRF safety regulations require the installation of an interlock should a certain power threshold be exceeded, thereby entailing a financial and structural cost that is unsustainable for the beamline. For this reason, it was decided to abandon the prospect of pump-probe measurements within the scope of this thesis and to focus

exclusively on the study of the synthesis of CIS nanocrystals.

Conclusions

This thesis presents the experimental work carried out at the N-REX laboratories of the University of Bologna and during the subsequent synchrotron campaigns performed at the LISA beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble.

The overall aim of this work was to investigate processes occurring on different timescales by exploiting synchrotron-radiation-based techniques.

Two complementary research activities were pursued: an in situ investigation of the growth mechanism of CuInS_2 nanocrystals by means of X-ray Absorption Spectroscopy and a feasibility study aimed at assessing the possibility of performing pump & probe experiments at the LISA beamline. Unlike the pump & probe experiments, the experimental campaign related to the former activity was successfully completed during the beamtimes granted at the ESRF between May and July 2025, yielding a comprehensive set of static and time-resolved XAS measurements.

The EXAFS analysis at the Cu K-edge provided detailed information on the evolution of the local environment around copper throughout the synthesis. During the first three reaction steps, copper remained coordinated by oxygen atoms in a configuration consistent with hydrated Cu(II) . Following the addition of citrate, a carbon contribution became detectable in the second coordination shell, providing evidence for the coordination of citrate around the hydrated copper complex. The addition of glutathione marked the transition to a sulphur-coordinated first shell, consistent with the formation of Cu(I) -thiolate species. Finally, after the addition of sodium sulphide, the fitted first-shell parameters became fully consistent with those expected for CuInS_2 nanocrystals. In addition, a second-shell contribution attributable to indium was detected. Although this signal remained relatively weak in the colloidal samples, it became significantly more evident in the purified CIS pellet measured at low temperature, where thermal and structural disorder were minimised, providing direct structural evidence consistent with the chalcopyrite local arrangement.

The XANES analysis complemented the EXAFS results by following the evolution of the copper oxidation state during the synthesis. The edge shift observed

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after the addition of glutathione, together with the calibration analysis performed using reference compounds, demonstrated that glutathione is responsible for the reduction of copper from Cu(II) to Cu(I), confirming its key role in activating the precursor prior to nanocrystal formation.

The EXAFS investigation at the In K-edge revealed an analogous evolution of the indium local environment during the early stages of the synthesis. Indium remained coordinated by oxygen atoms before sulphide addition, while a second-shell carbon contribution became detectable after citrate addition, consistent with the formation of indium–citrate complexes. Following the addition of sodium sulphide, oxygen ligands were replaced by sulphur atoms in the first coordination shell. In contrast with the copper analysis, however, no second-shell copper contribution could be reliably detected, even in the purified CIS pellets measured at low temperature. This most likely reflects the intrinsically weaker scattering contribution of copper in the indium EXAFS signal, which prevents its unambiguous observation despite the successful formation of the nanocrystals.

The control syntheses performed in the absence of one of the two metal precursors did not provide direct spectroscopic evidence for the absence of nanocrystal formation. Nevertheless, both the EXAFS analysis and the macroscopic observations consistently provided indirect indications that the synthesis pathway was substantially altered when either copper or indium was omitted from the reaction.

Overall, this work demonstrates that synchrotron-based XAS is a powerful tool for following both the structural and electronic evolution of multicomponent nanomaterial syntheses in real time. By combining EXAFS and XANES analyses with time-resolved measurements, it was possible to reconstruct the sequence of chemical transformations leading to CuInS₂ nanocrystal formation and to identify the distinct roles played by citrate, glutathione and sulphide during the reaction.

Beyond providing a detailed structural description of the different synthesis stages around the metal centers, the time-resolved measurements yielded what is arguably the most significant outcome of this work. The different characteristic times measured at the Cu and In K-edges in the last step of the synthesis suggest that the incorporation of the two metal species does not occur simultaneously. Instead, the experimental evidence supports a reaction pathway involving the formation of an indium–sulphide intermediate immediately after the addition of sodium sulphide, followed by the slower incorporation of copper into the growing CuInS₂ nanocrystals. To the best of our knowledge, such an intermediate has not previously been proposed on the basis of in situ XAS measurements of this synthesis. Although further experimental and theoretical investigations will be required to confirm its detailed structure and role, the present results provide the first direct experimental indication of this reaction mechanism.

More broadly, the methodology developed in this work demonstrates the capa-

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bility of synchrotron XAS to resolve transient structural transformations occurring during colloidal nanocrystal synthesis and provides a framework for investigating reaction mechanisms that remain inaccessible to conventional ex situ characterisation techniques.

The second activity consisted, as mentioned before, of a feasibility study aimed at assessing the possibility of performing pump & probe experiments using the instrumentation available at the LISA beamline. This study showed that, under the available experimental conditions, the laser power was insufficient to perform meaningful pump & probe measurements.

Appendix

A.1: Synthesis Protocol for Aqueous CuInS₂ Quantum Dots

General Procedure

To improve the accuracy and reproducibility of reagent addition, stock solutions are prepared prior to the synthesis. The reagents are then added sequentially using micropipettes in the following order:

1. deionized water;
2. metal precursors (Cu²⁺ and In³⁺ stock solutions);
3. sodium citrate stock solution;
4. solid glutathione;
5. sodium sulfide stock solution.

After the addition of all reagents, the reaction mixture is allowed to react for 40 minutes. Although the most significant changes observed by UV–Vis spectroscopy occur within the first 10 minutes, the reaction is conventionally considered complete after approximately 40 minutes.

Note. If only a single synthesis is planned during a synchrotron experiment, the preparation of stock solutions can be omitted and the solid reagents can be added directly to 2 mL of bidistilled water. The required amounts of each precursor are reported in Section 3.2.3. Although this approach has not been routinely employed in the laboratory, no significant differences in the reaction outcome are expected.

Storage of Solid Precursors

- **CuCl₂**: no particular precautions are required. The batch currently available at the Department of Chemistry is likely partially hydrated but has not caused any issues during synthesis.
- **InCl₃**: strongly hygroscopic. It should preferably be stored in a desiccator and exposure to air should be minimized during weighing.
- **Na₃C₆H₅O₇** (sodium citrate): no specific precautions are required.
- **L-glutathione**: relatively stable, although gradual oxidation may occur over long storage times. Refrigerated storage is recommended when not in use.
- **Na₂S·9H₂O**: strongly hygroscopic. It should preferably be stored in a desiccator and exposure to air should be minimized during weighing.

Preparation of Stock Solutions

- **CuCl₂**, 0.01 M in bidistilled water. Stable for extended periods.
- **InCl₃**, 0.25 M in ethanol. Stable for approximately 10 days. After longer storage times, precipitation may occur (likely due to the formation of In(OH)₃), resulting in an inaccurate precursor concentration. Therefore, this solution should be prepared only in the quantity expected to be used within a short period.
- **Na₃C₆H₅O₇** (sodium citrate), 0.4 M in bidistilled water. Stable for extended periods.
- **Na₂S**, 1 M in bidistilled water. Sulfide ions gradually oxidize in air and a black precipitate may appear after approximately one week. Consequently, large volumes of this solution should be avoided unless they are expected to be consumed rapidly.

CuInS₂ Quantum Dot Synthesis Procedure

The following protocol yields approximately 2 mL of reaction mixture with an initial Cu²⁺ concentration of about 3 mM.

1. Add 1.5 mL of bidistilled water to the reaction vial.
2. Add 1.005 mL of the CuCl₂ stock solution.

3. Add 120 μL of the InCl_3 stock solution.
4. Add 300 μL of the sodium citrate stock solution and manually shake the vial. The solution should develop a blue coloration due to the formation of Cu-citrate complexes.
5. Add 27 mg of solid glutathione and manually shake the vial. The blue colour should disappear almost immediately. At this stage, the solution typically becomes turbid due to the formation of a white, milky precipitate. This intermediate species, generally described as a Cu-GSH cluster/polymeric complex, exhibits orange-red photoluminescence under UV illumination.
6. Under continuous stirring, add 144 μL of 1 M Na_2S solution. The precipitate formed in the previous step should dissolve completely and the solution should immediately turn orange, gradually darkening during the course of the reaction. This stage corresponds to the formation and growth of the CuInS_2 quantum dots.

Note. The volumes given here, which are those used in the syntheses carried out during the synchrotron measurements, have been recalculated on the basis of those provided by Dr. Bellatreccia, so as to obtain a total solution volume of 3 mL rather than 2 mL, whilst maintaining the same reagent concentrations.

Recommended Stock Solutions for Five Syntheses

- CuCl_2 : 6.73 mg dissolved in 5 mL of bidistilled water.
- InCl_3 : 27.7 mg dissolved in 0.5 mL of ethanol.
- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$: 141.1 mg dissolved in 1.2 mL of bidistilled water.
- Na_2S : 144.1 mg dissolved in 0.6 mL of bidistilled water.

Note. The Na_2S and InCl_3 stock solutions are not stable for prolonged exposure to air. Therefore, if fewer than five syntheses are planned within one week, the preparation volumes should be scaled accordingly to minimize reagent waste.

Required Amounts for a Single Synthesis

- CuCl_2 : 0.9 mg;
- InCl_3 : 4.4 mg;

- $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$: 20.6 mg;
- L-glutathione: 18 mg;
- Na_2S : 23.1 mg.

A.2: Estimation of the statistical errors via propagation

Estimation of E_0 's error

From the equation defining E_0 via integral method:

$$E_0 = E_1 + \frac{\int_{E_1}^{E_2} \mu_2 - \mu(E) dE}{\mu_2 - \mu_1} = E_1 + \frac{I}{\mu_2 - \mu_1}; \quad (3.11)$$

via error propagation:

$$\sigma_{E_0} = \sqrt{\frac{I^2}{(\mu_2 - \mu_1)^4} (\sigma_{\mu_1}^2 + \sigma_{\mu_2}^2) + \frac{\sigma_I^2}{(\mu_2 - \mu_1)^2} + \sigma_{E_1}^2} \quad (3.12)$$

Where $\sigma_{E_1} = 0.1$ eV,

while for the estimation of σ_μ it has been exploited the fact that the absorption coefficient μ is proportional to the normalised fluorescence signal: $\mu = \frac{I_f}{I_0}$, from which:

$$\sigma_\mu = \mu \sqrt{\left(\frac{\sigma_{I_f}}{I_f}\right)^2 + \left(\frac{\sigma_{I_0}}{I_0}\right)^2} \quad (3.13)$$

and for the estimation of the integral I 's error, via numerical error propagation:

$$\sigma_I = \sqrt{\sum_i (w_i^2 \cdot \sigma_{\mu_i}^2)}; \quad i \in [0, N] \quad (3.14)$$

with:

$$w_i = \begin{cases} -\frac{\Delta E_1}{2} & \text{if } i = 1 \\ -\frac{\Delta E_{i-1} + \Delta E_i}{2} & \forall i \in]1, N[\\ -\frac{\Delta E_{N-1}}{2} & \text{if } i = N \end{cases} \quad (3.15)$$

Estimation of oxidation number's error

From the equation:

$$o.n. = \frac{E_0^{exp} - A^{fit}}{B^{fit}} \quad (3.16)$$

(where: E_0^{exp} is the E_0 value found for a specific experimental spectrum, while A^{fit} and B^{fit} are the parameters of the calibration line);
error propagation yields:

$$\sigma_{o.n.} = \frac{1}{B^{fit}} \sqrt{\sigma_{E_0}^2 + \sigma_{A^{fit}}^2 + (E_0 - A^{fit})^2 \cdot \sigma_{B^{fit}}^2} \quad (3.17)$$

A.3: Miscellaneous

Compatibilty

If we have two measurements $x \pm \sigma_x$ and $y \pm \sigma_y$, the normalised deviation between the two is defined as:

$$\lambda_{x-y} = \frac{|\hat{x} - \hat{y}|}{\sqrt{\sigma_x^2 + \sigma_y^2}} \quad (3.18)$$

and it is the actual definition of compatibility. Since λ follows a gaussian distribution, we know that if $\lambda \in [0, 3]$, the probability that the two measurements belong to the same population is $\approx 98\%$. This is the critical value usually chosen as the upper limit for λ in order to consider the two measurements compatible and therefore estimation of the same physical quantity. If $\lambda < 1$ the measurements are said to be strongly compatible.

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