

Enhancing Elastic Scattering via Transient Resonances

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Daniele Ronchetti

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Gutachter/innen der Dissertation:	Prof. Dr. Nina Rohringer Prof. Dr. Henry Chapman
Zusammensetzung der Prüfungskommission:	Prof. Dr. Henry Chapman Prof. Dr. Markus Gühr Prof. Dr. Markus Ilchen Prof. Dr. Jochen Liske Prof. Dr. Nina Rohringer
Vorsitzende/r der Prüfungskommission:	Prof. Dr. Jochen Liske
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Vorsitzender des Fach-Promotionsausschusses PHYSIK:	Prof. Dr. Johannes Haller
Leiter des Fachbereichs PHYSIK:	Prof. Dr. Markus Drescher
Dekan der Fakultät MIN:	Prof. Dr.-Ing. Norbert Ritter



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Dr. rer. nat. in Physics, Universität Hamburg.

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Fachbereich Physik:

<https://www.physik.uni-hamburg.de/>

Theoretical Ultrafast X-ray Science (FS-TUXS at DESY):

<https://tuxs.desy.de/>

*“Vero è che, come forma non s'accorda
molte fiata a l'intenzion de l'arte,
perchà risponder la materia è sorda”*

Dante Alighieri,
Divina Commedia, Paradiso, Canto I, vv. 127-129

*“True is it, that as oftentimes the form
accords not with the intention of the art,
because in answering is matter deaf”*

Zusammenfassung

In den letzten Jahren hat sich die Leistungsfähigkeit von Röntgen-Freie-Elektronen-Lasern enorm verbessert. Röntgenpulse mit Pulsdauern, die die Femtosekundengrenze unterschreiten – und damit in den Attosekundenbereich vordringen – sowie Intensitäten im Bereich von $10^{20} \text{ W cm}^{-2}$ sind mittlerweile verfügbar und vor allem zu einem zuverlässigen Werkzeug für die Wissenschaft geworden. Aufbauend auf diesen Möglichkeiten ist das Gebiet der nichtlinearen und ultraschnellen Röntgenphysik stark gewachsen, wobei eine Vielzahl neuartiger Phänomene beobachtet und untersucht wird. Bei Bestrahlung mit ultrakurzen und intensiven Röntgenlaserpulsen tritt ein charakteristisches Merkmal der nichtlinearen Röntgenphysik zutage: die Fähigkeit, Atome vorübergehend in Nichtgleichgewichts Konfigurationen der inneren Schalen anzuregen, die andernfalls verbotene Übergänge eröffnen. Unter bestimmten Umständen können diese vorübergehenden Resonanzen zusätzliche Streukanäle bereitstellen und den Atomstreufaktor erheblich erhöhen.

In dieser Arbeit zeigen wir, dass der L_α -Übergang bei 929.7 eV den elastischen Streufaktor von Kupferatomen vorübergehend verstärkt. Der Prozess wird durch $2p$ Photoionisation eingeleitet, gefolgt von einem Auger-Zerfall, der eine Kaskade von interatomaren Elektronenstoßionisationen auslöst und schließlich metastabile Zustände mit mehreren $3d$ -Lücken besetzt. Unter Verwendung von 15 fs Pulsen, die von einer Kupferhaltigen [SiC/Cu/B₄C] Multischicht reflektiert werden, beobachten wir einen intensitätsabhängigen Höchstwert um die L_α -Energie, dessen Amplitude und Breite nichtlinear von der Anregungsintensität abhängen. Ein selbstkonsistentes theoretisches Modell, das die transiente Elektronenbesetzung mit der Streuantwort verknüpft, reproduziert das beobachtete Verhalten. Eine einfache Zwei-Niveau-Beschreibung quantifiziert hingegen eine 12-fache Verstärkung des Imaginärteils des Atomstreufaktors f_2 .

Unsere Ergebnisse bestätigen die Rolle transienter Resonanzen bei der elastischen

Streuung und ebnen den Weg für innovative Methoden zur Verbesserung von Kontrast und Auflösung in der ultraschnellen Röntgenbildgebung.

Abstract

In recent years, X-ray Free Electron Lasers (XFELs) sources have seen a tremendous increase in their performance. X-ray pulses with durations breaching the femtosecond frontier – entering the attosecond domain – and intensities reaching the $10^{20} \text{ W cm}^{-2}$ regime have become available and, most importantly, a reliable tool for scientific exploration. Growing on the backbone of these capabilities, the field of nonlinear and ultrafast X-ray science has expanded, with a plethora of novel phenomena being observed and investigated. Upon irradiation with ultrashort and intense pulses, a defining feature of nonlinear X-ray science emerges: the ability to transiently excite atoms into non-equilibrium core-excited configurations opens otherwise forbidden transitions. Under particular circumstances, these transient resonances can provide additional scattering channels and substantially increase the atomic scattering factor.

In this thesis, we demonstrate that the L_α ($2p_{3/2} - 3d$) transition at 929.7 eV transiently enhances the elastic scattering factor of copper atoms. The process is initiated by $2p$ photo-ionization, followed by Auger decay that triggers a cascade of inter-atomic electron-impact ionizations, ultimately populating metastable states with multiple $3d$ holes. Using 15 fs pulses reflected from a Cu-containing [SiC/Cu/B₄C] multilayer, we observe an intensity-dependent peak around the L_α energy whose amplitude and width evolve non-linearly with excitation intensity. Theoretically, a self-consistent model linking the transient electronic population to the scattering response reproduces the observed behavior. A minimal two-level description quantifies a 12-fold enhancement of the imaginary scattering factor f_2 .

Our findings confirm the role of transient resonances in elastic scattering and establish a route towards innovative methods for improved contrast and resolution in ultrafast X-ray imaging.

Outline of the thesis

As a guide for the reader, we report a brief outline of the thesis. Chapter 1 is an extended introduction bridging between technological advances and applications of XFELs, to the main idea of the thesis. In chapter 2 on page 11 we introduce the theoretical framework that we use to interpret our measurements. The description of the experiment, data analysis procedures, and results are presented in chapter 3 on page 21. Finally, we summarize our findings and present an outlook in chapter 4 on page 47.

Throughout the thesis, we decided to keep the main body of the text focused on a streamlined discussion. For this reason, some information, which is relevant but not essential for the main narrative, is collected in the appendices. Whenever the consultation of an appendix is recommended, a reference to the specific appendix will be made in the main text.

List of Publications

The results of this thesis are collected in a publication which is currently in submission, and preliminary published as a preprint at:

1. Ronchetti, D., *et al.* “Spectrally resolved elastic scattering enhancement of copper atoms via transient resonances created by an X-ray free-electron laser”. Preprint forthcoming on arXiv.

In the broader scope of the doctoral work, the author contributed to the following publications:

2. Linker, T., *et al.* “Attosecond inner-shell lasing at ångström wavelengths”, in *Nature*, vol. 642, no. 8069, pp. 934–940, 2025. DOI: [10.1038/s41586-025-09105-9](https://doi.org/10.1038/s41586-025-09105-9)
3. Miedaner, P., *et al.* “Spin Waves Excited by Hard X-Ray Transient Gratings”, in *Phys. Rev. Lett.*, vol. 136, pp. 176701, 2026. DOI: [10.1103/zybx-dqfc](https://doi.org/10.1103/zybx-dqfc)

Several other publications are in preparation, an updated list can be found at the author’s Google scholar page: scholar.google.com/daniele.ronchetti.

The contributions of the author to the publications listed above are as follows:

1. D.R. closely followed the life-cycle of the project, from the initial experimental proposal to the final manuscript. He took a major role in the design of the experiment, the data acquisition and analysis, and the interpretation of the results. He wrote the manuscript with feedbacks from the co-authors.
2. D.R. participated in the experiment that led to the publication, contributing in operation of the instrument, data acquisition and analysis.
3. D.R. participated in the experiment that led to the publication, he occupied a major role in the online data analysis during the experiment.

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Chapter 1

Status of XFELs' science

In this introductory chapter, we will briefly review the state of the art of XFEL science. We do not discuss the physics of XFELs, since it is now an established topic; interested readers may find a tutorial at [1]. In particular, we will focus on recent technological advances (section 1.1) and applications of such technologies to the field of ultrafast and nonlinear optics (section 1.2). Later, we will introduce the idea of enhancing the scattering cross-section by means of transient resonances (section 1.3). Finally, we will present the motivation for this thesis and a brief overview of our work.

1.1 Current progress in XFEL technology

The generation of hard¹ X-ray pulses via the Self Amplified Spontaneous Emission (SASE) process was proposed at the beginning of the 1980s [2, 3]. Almost 30 years had to pass for the first hard XFEL to be built and produce the first lasing in 2009 [4]. After this milestone – as it often happens in the history of science – progress evolved exponentially, reaching levels of performance that were only present in the dreams of the early pioneers. The XFEL technology is now mature enough to be considered a standard tool for scientific research. Several facilities around the world routinely deliver femtosecond

¹In the context of X-ray generation, the boundary between “soft” and “hard” X-rays is often set around 100 eV. This value is chosen as it marks the limit of operation of conventional cavity optics, thus requiring the SASE process to generate intense radiation. In this document, we adopt the convention mainly used by the XFEL community, which sets the boundary between the two different regimes at 1 keV. Therefore, the reader should not be surprised when we will use the term “soft” to refer to wavelengths of about 950 eV. Notably, this specific region is sometimes also referred to as “tender”.

X-ray pulses with energies in the hundreds of microjoules to millijoules level [5], and a few more are in construction or planning stages [6].

The current development of XFEL technology is focused on reducing the duration of the pulses to the attosecond regime and increasing their intensity above the $10^{22} \text{ W cm}^{-2}$ mark [7, 8]. The former goal is motivated by the desire to capture the fastest processes in nature, such as electron dynamics in atoms and molecules [9], while the latter is driven by the quest to explore new regimes of matter under extreme conditions, such as those found in astrophysical objects or in inertial confinement fusion experiments [10].

1.1.1 Towards ultrashort duration...

The generation of attosecond pulses in the soft X-ray region has been pioneered by a team of researchers at the Linac Coherent Light Source (LCLS). They achieved the first production of sub-femtosecond X-ray pulses via the Enhanced Self Amplified Spontaneous Emission (ESASE) method [11]. In this scheme, a portion of the electron bunch is energy-modulated by an infrared laser in a wiggler magnet. Upon propagation through a magnetic chicane, the energy-modulation creates a high-current spike in the electron bunch. The lasing of this spike leads to the generation of attosecond pulses in the subsequent undulator. The resulting pulses were characterized by the infrared streaking method [12], confirming a median 280 as duration. The limit of this technique is the fact that the lasing process starts from noise, thus leading to a large shot-to-shot fluctuation in the pulse duration and intensity.

The same team moved forward and realized the production of attosecond pulses by means of the so-called fresh-slice cascade process [13]. In this case, an X-ray pulse is initially generated in a first undulator block; the electron bunch is then delayed by a magnetic chicane. In the second undulator, the X-ray pulse is now overlapped with a fresh-slice – a portion of the electron bunch that did not participate in the original lasing – and acts as the seed for the generation of the attosecond pulse. With the fresh-slice cascade method the authors achieved a median pulse duration of 440 as with a much higher peak power, improving from the gigawatt to the terawatt scale.

Moving to the hard X-ray region ($E_{ph} > 1 \text{ keV}$), the task of producing attosecond pulses becomes more difficult. Based on a known 1D model of Free Electron Lasers (FELs) [3], the shortest achievable pulse duration scales with the square root of the pho-

ton energy $E_{ph}^{1/2}$. In this spectral region, a common approach to produce attosecond pulses is by reducing the duration of the electron bunch that undergoes the lasing process. A first way to achieve this is by spoiling most of the electron bunch via a slotted foil [14]. Using this method, the authors managed to produce pulses with an estimated average duration of 400 as. The intrinsic limitation of this technique is the fact that a low charge bunch cannot create a high intensity pulse, thus not suitable for applications requiring high peak power.

Another approach for creating hard X-ray attosecond pulses involves creating a high-current spike in the electron bunch, similar to what is done in the ESASE method. This can be done by a strong nonlinear compression of the electron bunch right before the undulator section. In [15], the authors achieved an average pulse duration of 326 as with improved stability compared to the slotted foil method. A final technique employs a compression mode that induces self-chirping in the electron bunch to create the high-current spike [16]. In this case, the authors were able to produce pulses with an estimated average duration of 197 as and energy of 184 μ J.

It is clear that in the past years several techniques have emerged to produce attosecond pulses. While none of them have yet become a routine operational mode, the use of attosecond X-rays has become exponentially more reliable and researchers can now more easily employ them for a wide range of applications.

1.1.2 ...and ultrahigh intensity

XFELs possess an ultralow emittance, namely a small size of the radiation source and a low angular divergence. These two characteristics offer great advantages for producing ultrasmall focal spots. The small source size allows for the creation of a small focus by constructing an optical system capable of forming a demagnified image of the source. Furthermore, thanks to the reduced angular divergence a finite acceptance optical system can focus the beam without consistent loss of X-ray photons. The most common way to focus hard X-ray radiation to nanometer scale spot size is by using X-ray mirrors in the Kirkpatrick-Baez (KB) configuration [17]. The KB system consists of two orthogonal grazing-incidence mirrors with a spherical or elliptical surface, such setup provides high-reflectivity, high radiation damage threshold and broad spectral and spatial acceptances. With this system, X-ray pulses can be effectively focused down to 50 nm, reaching in-

tensities in the $10^{20} \text{ W cm}^{-2}$ range. Trying to reach smaller spot size – and thus higher intensity – would require an alignment precision which is unrealistic to manage.

Tackling this problem, a team of researchers from Osaka University and the SPring-8 center in Japan introduced the so-called advanced KB system. This configuration is based on a double reflection by the hyperbola and the ellipse, effectively increasing to 4 the number of reflecting surfaces. With their advanced KB system, the team managed to focus hard X-ray pulses down to 7 nm breaching the $10^{22} \text{ W cm}^{-2}$ intensity barrier [18]. Using a similar advanced KB system, it has been recently demonstrated the focusing to the nanometer scale of attosecond hard X-ray pulses [19]. The authors focused to 160 nm by 230 nm pulses with an estimated duration of 90 as and a photon energy around 9150 eV, thus reaching an intensity of $2.7 \times 10^{19} \text{ W cm}^{-2}$. This last result nicely bridges between the ultrashort duration and ultrahigh intensity regimes, opening the way to the exploration of new nonlinear phenomena in the interaction of matter with intense X-ray fields.

1.2 Nonlinear X-ray optics and transient resonances

Harnessing the extreme pulses described so far has opened, and continues to expand, the frontier of nonlinear X-ray science. One defining feature of this regime is the possibility of driving isolated atoms into highly-ionized, non-equilibrium states by sequential inner-shell photoionization and cascaded electronic decays. This idea was already studied theoretically [20] before the advent of XFELs, and the first signatures were observed in 2010 at the LCLS [21]. Such processes create a rich landscape of transient states with core-level excitations, revealing so-called *hidden resonances*. A hidden resonance is an atomic state in which a transition between two bound levels – previously forbidden by the Pauli exclusion principle – becomes allowed through the removal of one or more electrons from either level. Given that the lifetime of core electronic excitations is typically on the order of a few femtoseconds and is governed by further ionization or decay processes, such states are also referred to as *transient resonances*.

1.2.1 Evidence of nonlinear effects driven by transient resonances

The emergence and effects of transient resonances have been studied since the early days of XFEL science in different contexts. One example is provided by studies of nonlinear absorption in neon atoms [22, 23]. After irradiating neon atoms with intense ultrashort X-ray pulses, the authors observed a quadratic growth of the ionization cross-section of Ne^{8+} with fluence. This nonlinear behavior has been confirmed to arise from two distinct channels: the direct two-photon ionization of a single electron and a sequence of excitations between transient states that can outcompete the Auger decay. The latter process is a direct manifestation of the hidden resonances, which are transiently populated during the ionization cascade.

Another early example of the role of transient resonances is found in the study of resonant Auger effect in neon [24, 25]. In this experiment, after a similar intense irradiation with a pulse resonant to the $1s - 2p$ transition, the authors observed a modified Auger lineshape. This was attributed to the intense field driving Rabi cycling between the $1s$ and $2p$ levels. In the ground state this would be forbidden by the Pauli principle – being both levels fully occupied – but becomes allowed after the first ionization step, which unveils the transient $1s - 2p^+$ resonance. At this moment, the Rabi cycling between the two levels can occur, outcompeting the Auger decay, leading to the observed lineshape modification.

Building on these pioneering efforts, hidden resonances have been confirmed to play a central role in different nonlinear effects. One case is self-induced transparency [26], the increase in the transmission of an intense pulse through a medium due to the saturation of absorption channels. Another notable example is the introduction of stimulated X-ray Raman scattering [27, 28]. In this effect, one photon excites an inner-shell transient resonance, while a second photon dumps another electron into the short-lived core hole. The stimulated pathway results in a cross-section of the process that grows orders of magnitude larger than the resonant inelastic X-ray scattering counterpart, which relies on the spontaneous decay. When used as a tool, transient resonances can create opportunities for novel methods aimed at measuring previously inaccessible properties. For instance, transient resonances enable Resonant X-ray Scattering (RXS) [29, 30], X-ray elastic scattering of a pulse resonant to an inner-shell resonance. This approach allows probing interatomic electron currents in crystals [31] or plasma formation in nanopar-

ticles [32].

1.2.2 Atomic X-ray lasing

A notable effect in the field of nonlinear X-ray optics is the possibility of achieving atomic lasing in the X-ray regime, called Amplified Spontaneous Emission (ASE). In short, when an intense pulse with a photon energy above the $1s$ ionization threshold propagates through a dense medium – gas, liquid or solid all work equally well – it creates a massive population of core-ionized atoms. Eventually, one atom decays emitting a K_α photon ($1s^+2p \rightarrow 1s2p^+$). In the case that the photon is emitted in the forward direction, it will travel in an inverted medium, thus it can stimulate the emission of another photon. The process can now be repeated, leading to an exponential growth of the number of emitted photons. If sufficient conditions in terms of gain length are met, the cascade can lead to the generation of a laser X-ray beam.

ASE was first observed in neon atoms [33]. Later, the stimulated lasing – where the cascaded emission is started by a seed beam – was demonstrated in copper [34]. More recently the seeded emission has been observed also in manganese solutions [35]. The large experimental interest around the lasing effect has led to the development of *ad hoc* theories that treat the process with a stochastic formalism [36, 37]. Finally, by combining experimental observation and theoretical modelling, it has been demonstrated that depending on the particular pump pulse temporal structure, the lasing process can produce pulses with duration below 100 as and high coherence properties [38].

The X-ray lasing effect, both in its spontaneous and seeded version, is a striking example of the role of transient resonances in nonlinear X-ray optics. From the study of this effect, one of the key motivating questions for this work arose: *what would we observe if, instead of looking at the forward emitted photons, we point our detector in the elastic scattering direction?* In other words, what would be the signature of the massively populated transient state in the elastic scattering signal? This question is at the core of the work presented in this thesis, and will be further explored in the next chapters.

1.2.3 The case of Warm Dense Matter

The same extreme pulse properties that enable hidden resonances can also drive solids into the regime of Warm Dense Matter (WDM). At sufficiently high intensities

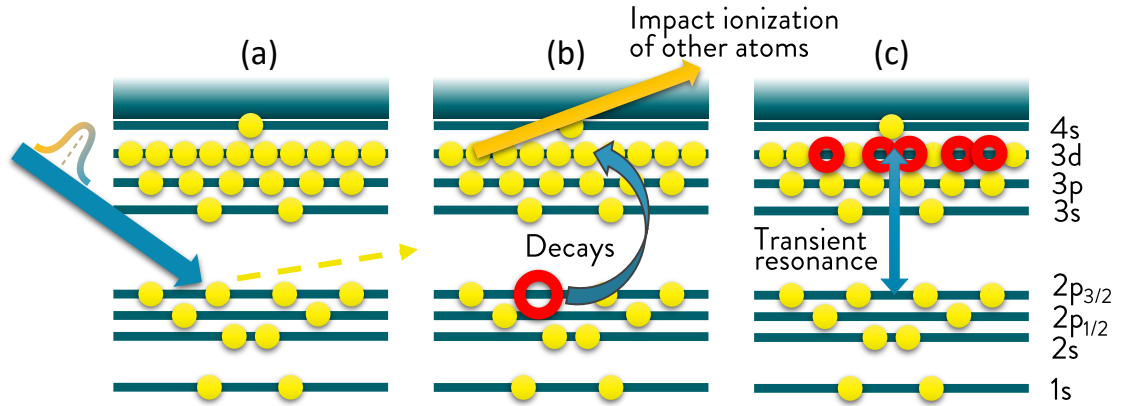


Figure 1.1: Mechanism that leads to the creation of the $2p_{3/2} - 3d$ transient resonance. (a) A $2p$ electron is photo-ionized by the X-ray pulse. (b) The created hole rapidly decays into the $3d$ level by Auger decay. This decay creates secondary electrons capable of impact-ionizing $3d$ electrons of neighboring atoms. (c) A cascade of electron impact ionization processes establishes a metastable state with abundance of holes in the $3d$ level. These holes open the transient resonance with the $2p_{3/2}$ level.

($> 10^{14} \text{ W cm}^{-2}$), irradiation by a strong XFEL pulse and subsequent electron collisions create transient, strongly out-of-equilibrium electronic states that verge on WDM conditions. WDM is a state in between plasma and solid, and is abundant in astrophysical objects and as a transient state in inertial-confinement fusion reactions. This regime is notoriously difficult to describe theoretically [39, 40]. The interplay of Coulomb coupling, thermal excitations, and fermionic exchange effects creates a state where the density is too high for weakly coupled plasma physics, yet too loosely bound for a condensed-matter description.

The transition of a solid into WDM is accompanied by a modification of its optical properties [41]. Mercadier *et al.* recently demonstrated how transient resonances can alter the absorption coefficient of XFEL-created WDM [42]. They showed that the absorption of a photon by a $2p_{3/2}$ electron, followed by Auger decay and subsequent cascades of inter-atomic electron-impact ionization, creates metastable vacancies in the $3d$ shell, see fig. 1.1. Such vacancies open additional transient absorption channels for further resonant excitation of a $2p_{3/2}$ electron. This process effectively amplifies the absorption cross-section in the spectral region of the resonance, an effect called Reverse Saturable Absorption (RSA). In addition, they introduced a theoretical framework capable of capturing this behavior, coupling a plasma description of XFEL-driven copper excitation

[43–45] with density functional theory calculations of the absorption spectrum [46].

The results of Mercadier *et al.* laid an important foundation for this work. They demonstrated that the $2p_{3/2} - 3d$ transient resonance can be massively populated in XFEL-irradiated copper. Furthermore, they showed that such a state is metastable, thereby relaxing the need for sub-femtosecond pulses, which at the time – just 4 years ago² – were not available. These findings motivated us to investigate the signature of this transient state in the elastic scattering signal. In addition, their theoretical framework provided a starting point for our modelling efforts, which we further developed – see chapter 2 on page 11 – to include the calculation of the elastic scattering signal.

1.3 The Enhanced Resonant Elastic Scattering effect

Absorption and scattering are intrinsically connected, as the absorption coefficient μ is proportional to the imaginary part of the atomic scattering factor f_2 , via $\mu = 2r_e\lambda N f_2$. Here r_e is the classical electron radius, λ the wavelength and N the atomic density. This relation implies that any effect which modifies the absorption coefficient will also directly modify the scattering properties of the material. One manifestation is what we call Enhanced Resonant Elastic Scattering (ERES), a process in which the elastic scattering factor of individual atoms is transiently enhanced by resonances that open additional scattering channels.

An early indication of ERES was reported by Bostedt *et al.* [47], who observed a nonlinear increase in the brightness of xenon clusters scattering patterns with increasing pulse intensity. Single xenon clusters were irradiated with femtosecond pulses of 13.7 nm wavelength and $10^{14} \text{ W cm}^{-2}$ intensity. The photoionization induces several transient electronic changes, which result in a tenfold increase of the absorption. The modification of the optical properties is associated with the increasing population of Xe^{4+} ions. Such ions have a larger cross-section than neutral xenon, and their increased density is further confirmed by ion time-of-flight spectroscopy.

A systematic study by Ho *et al.* [48] explored the role of transient resonances in ultrafast diffractive imaging of sucrose nanoclusters. The authors combined single-shot diffraction experiments with simulations that explicitly track the time-dependent elec-

²Our experiment was done in November 2022. The proposal was written in December 2021.

tron and nuclear dynamics during the intense X-ray pulses. Experimentally, diffraction patterns were recorded over photon energies from the water window (530 eV) up to 1.5 keV. The main finding was that the scattering signal is strongly suppressed near the oxygen K-edge, deviating significantly from conventional linear scaling laws. The direct cause of this reduction is the rapid formation of an expanding nanoplasma, where highly charged ions with reduced scattering strength are abundant. This plasma is itself created by an avalanche mechanism: after the first $2p$ ionization of oxygen, one $1s$ electron can be resonantly excited to the $2p$ level. The created $1s$ hole then decays via Auger decay, leaving other $2p$ holes that can be resonantly refilled, and so on. This cascade of resonant excitations and Auger decays leads to a rapid increase in the number of free electrons and highly charged ions that create the plasma. The study demonstrates that pulse duration and photon energy critically control imaging quality, with shorter (few-femtosecond) pulses mitigating damage, and that optimal imaging conditions require either detuning from absorption edges or exploiting transient resonances with ultrashort pulses.

Most recently, Kuschel *et al.* [49] deepened the study of Bostedt [47] by investigating coherent diffractive imaging of xenon clusters. They collected a large dataset of single-shot diffraction patterns varying the photon energy across the xenon M-edge, the pulse duration from hundreds of femtoseconds to sub-femtosecond, and the intensity of the incoming pulses. By analyzing the dataset, the authors found that pulses with duration between 5 and 10 fs are optimal for imaging, as they are short enough to mitigate the damage caused by the plasma formation, but long enough to allow the transient resonances to enhance the scattering signal.

1.3.1 This work

All the aforementioned studies provided evidence of the ERES principle, but they remain limited to core-to-valence resonances – which yield only modest enhancements – and to spectrally integrated measurements, which preclude identifying the specific transitions that drive the scattering process. In this thesis, we will employ the excitation pathway identified by Mercadier *et al.* [42] – in which $2p_{3/2}$ photoabsorption, Auger decay, and subsequent electron-impact cascades generate metastable $3d$ vacancies in copper – and probe its manifestation in elastic scattering rather than absorption.

Specifically, we demonstrate spectrally resolved ERES exploiting the transition from

the core $2p_{3/2}$ level into the $3d$ part of the conduction band of copper. Here, we call this a core-to-core transition as a shorthand notation, in analogy to the atomic copper L_α transition ($2p_{3/2} - 3d$). We exploit the transiently modified electronic structure of the $3d$ level that opens an additional scattering channel (fig. 1.1), and ultimately increases the scattering strength in the resonant region of the spectrum. To interpret the measurements, we follow two paths: as a predictive model, we adapt – to treat elastic scattering – the self-consistent theory of Mercadier *et al.* that forecasts the electronic excitation of the atomic ensemble. To quantify the excess scattering factor introduced by the transient resonance, we introduce a simplified model based on a two-level approximation of the excitation.

By combining spectrally resolved measurements, predictive modeling, and quantification of the scattering factor modification, we demonstrate and characterize the enhancement of elastic scattering by transient resonances, providing a basis for applications that benefit from stronger or spectrally controlled scattering signals.

Chapter 2

Modeling the Enhanced Resonant Elastic Scattering effect

In this chapter, we develop a theoretical framework to model the ERES effect, particularly focusing on the case using soft X-ray radiation. The ingredients that are required to simulate the effect are just two: the simulation of the scattering response of the particular system at hand to the incoming radiation, and a way to describe how the transient resonance contributes to the atomic scattering factor of individual atoms.

The first ingredient is clearly specific to the particular system under study; in our case – as we will see in the next chapter – copper-containing nanostructured multilayers. The easiest way to simulate the scattering response of such a system is to use the Parratt formalism [50], which is a well-known method to calculate the reflectivity of X-rays from layered structures, based on a recursive algorithm. Most importantly, we need to confirm that our approach can faithfully reproduce the scattering response of the system in the absence of the transient resonance. This is a necessary step before we can include the contribution of the transient resonance to the scattering factor. We do this by comparing the simulation to high resolution measurements of the soft X-ray Reflectivity (XRR) curve of the sample.

The description of how the transient resonance affects the atomic scattering factor is instead more general and could be applied to any atomic species and any resonance in the electronic levels of said atom. We will model how the atomic scattering factor of individual atoms are modified by the X-ray irradiation, and then we will use the modified

scattering factor to simulate the scattering response of the whole system. Two different models to describe the contribution of the transient resonance are presented, one based on a simple two-level approximation and another based on a self-consistent simulation of the X-ray driven excitation.

We begin the chapter by recalling fundamental notions about the atomic scattering factor in section 2.1. We move on in section 2.2 to describe the contribution of the transient resonance to the atomic scattering factor approximating the resonance as a two-level system. In section 2.3 on page 16 we briefly introduce the self-consistent model based on a full simulation of the X-ray driven excitation. Finally, in section 2.4 on page 17 we describe the procedure to validate our Parratt's approach.

2.1 Basic notions on the atomic scattering factor

The atomic scattering factor plays a major role in the theory of X-ray scattering. This quantity describes how an individual atom scatters incoming X-ray radiation. Comprehensive descriptions of X-ray scattering theory can be found in multiple textbooks. For a basic introduction, see [51]; for an advanced treatment of crystallography, see [52]. We also refer to [53] for a derivation, based on nonrelativistic quantum electrodynamics, of the theory describing X-ray processes. In [53], the authors start from the minimal-coupling Hamiltonian and through perturbation theory describe several X-ray induced processes, including the scattering of X-rays by atoms. In doing so, the definition of the elastic atomic scattering factor naturally arises as:

$$f^0(\mathbf{Q}) = \int d^3x \rho^{(el)}(\mathbf{x}) e^{i\mathbf{Q} \cdot \mathbf{x}}, \quad (2.1)$$

where $\rho^{(el)}$ is the ground-state electronic density of the system. Following the derivation in [53], the main quantity governing elastic X-ray scattering is the differential scattering cross-section, which is given by:

$$\frac{d\sigma(\mathbf{Q})}{d\Omega} = \left(\frac{d\sigma(\mathbf{Q})}{d\Omega} \right)_T |f^0(\mathbf{Q})|^2. \quad (2.2)$$

Here, the Thomson scattering cross-section $(d\sigma(\mathbf{Q})/d\Omega)_T$ – scattering of X-rays by a free electron with negligible momentum transfer – is not relevant for the rest of the discus-

sion, thus we decide to omit its expression. The interested reader may find it in eq. (80) of [53]. These relations are derived under the assumption of no multiple scattering of the detected X-ray photon (the kinematic regime) and in the absence of resonant scattering effects. The central point is that the scattering cross-section is proportional to the square of the atomic scattering factor, thus making it one of the main quantities governing the scattering process.

In the following, we limit ourselves to introduce the dispersion corrections to the elastic atomic scattering factor, and to recall the notation that we will use in the rest of the chapter. The total elastic atomic scattering factor of an atom depends on the photon energy ω and is given by:

$$f(\omega) = f_0 + f'(\omega) + if''(\omega), \quad (2.3)$$

where f_0 is the elastic scattering term as described above. The two terms f' and f'' are the correction terms that take into account the effect of absorption processes on the scattering, called the anomalous dispersion correction [53]. For instance, f'' increases when the incoming photon energy approaches an absorption edge, as the atom becomes capable of absorbing the incoming X-ray photons. All terms in equation eq. (2.3) can be taken from tabulated data, [54] contains an online database, while [55] incorporates the data in a Python library. Typically, the atomic scattering factor is expressed in terms of its real (f_1) and imaginary (f_2) part using the substitution¹:

$$\begin{aligned} f_1(\omega) &= f_0 + f'(\omega) \\ f_2(\omega) &= f''(\omega). \end{aligned} \quad (2.4)$$

Substituting equation eq. (2.4) into equation eq. (2.3) yields the common expression for the atomic scattering factor:

$$f(\omega) = f_1(\omega) + if_2(\omega). \quad (2.5)$$

It is useful to define the scattering factor as in eq. (2.5) because the real and imaginary part of the scattering factor have a clear physical meaning. The real part f_1 represents

¹We note that some textbooks and articles use instead the substitution $f_2(\omega) = -f''(\omega)$. While this different convention does not change the final result, the reader used to it might be confused.

the amplitude of elastic scattering by the atom's electronic cloud, including the correction for anomalous dispersion near elemental edges. The imaginary part f_2 accounts for inelastic processes, mainly the absorption of X-rays by the atom, as well as the emission of secondary radiation. Indeed, the absorption coefficient μ is directly proportional to f_2 via:

$$\mu = 2r_e\lambda N f_2. \quad (2.6)$$

Here r_e is the classical electron radius, λ the wavelength of the radiation and N the atomic density. Finally, it is important to note that f_1 and f_2 are not independent quantities, but they are related by the Kramers-Kronig relations, ensuring causality in the scattering process.

2.2 Transient resonance as a two-level system

The most straightforward way to account for a transient resonance in the scattering process is to recognize its final effect. Once a transient resonance is present, it can significantly alter the scattering behavior. Physically, we can think for example, of a process where one incoming X-ray photon is absorbed by the resonance, which then decays emitting a secondary photon in the scattering direction. After this, the resonance is back in the ground state and can absorb another incoming photon, thus repeating the process until ultimately decaying by a mechanism that fills both levels, for example by Auger decay. The process just described is similar to the absorption and re-emission of a photon via an electron that gets excited into a valence or unoccupied level. However, this latter process, which is accounted for in f_2 , is inelastic, meaning that the energy of the incoming photon is not the same as the energy of the outgoing photon. On the other hand, the transient resonance can inherently only resonantly absorb or emit photons, thus making the pathway elastic. The final effect of the transient resonance is therefore to open an additional elastic scattering channel, from here the name of the ERES effect.

Following this reasoning, to model the ERES effect, we have to include the contribution of the transient resonance, described as a two-level system, to the scattering process. For a two-level system characterized by a resonant energy ω_0 between the ground state $|g\rangle$ and the excited state $|e\rangle$, a spontaneous decay rate Γ_{sp} , a total decay rate γ_2 , and incoming monochromatic radiation with wavelength λ (photon energy ω), the scattering

factor is:

$$f_T(\omega) = -\frac{3}{8\pi} \frac{\lambda}{r_e} \Gamma_{sp}(\rho_{ee} - \rho_{gg}) \frac{(\omega - \omega_0) - i\gamma_2/2}{(\omega - \omega_0)^2 + (\gamma_2/2)^2}. \quad (2.7)$$

A complete derivation of eq. (2.7) is reported in appendix A. In the previous equation ρ is the density matrix of the two-level system, thus ρ_{ee} and ρ_{gg} are the population of the excited and ground state. We can re-write eq. (2.7) in a simpler form substituting:

$$A = -\frac{3}{8\pi} \frac{\lambda}{r_e} \Gamma_{sp}(\rho_{ee} - \rho_{gg}), \quad (2.8)$$

thus, resulting in the following expression for the scattering factor of the transient resonance:

$$f_T(\omega) = A \frac{(\omega - \omega_0) - i\gamma_2/2}{(\omega - \omega_0)^2 + (\gamma_2/2)^2}. \quad (2.9)$$

Following eq. (2.9) the maximum value of the imaginary part of the transient scattering factor is $A \frac{2}{\gamma_2}$.

As previously explained, eq. (2.9) is an additional contribution to the atomic scattering factor of atoms that develop the transient resonance. This means the total atomic scattering factor is then given by:

$$f(\omega) = f_1(\omega) + if_2(\omega) + f_T(\omega). \quad (2.10)$$

We can finally use eq. (2.10) in our code to simulate the soft XRR spectrum, see section 2.4. Our approach is to leave the amplitude (A), resonant energy (ω_0), and energy width (γ_2) of the two-level system as free parameters to be fitted against experimental data. In this way, the two-level model allows us to extract the parameters of the transient resonance directly from the measurements, without making any assumptions about the underlying physical mechanism that leads to the formation of the transient resonance. This point, which is an advantage if we are interested only in the final outcome of the effect, is also a limitation of the model. Indeed, the approximation of the transient resonance as a two-level system does not provide any insight on the physical mechanism that leads to its formation, thus it cannot be used to predict how the parameters of the transient resonance will evolve with the experimental conditions. We surpass this limitation by using a different theoretical model, explained in the next section.

2.3 Self-consistent model

We introduce here a self-consistent theoretical model that directly accounts for the XFEL-driven excitation of the atomic ensemble and allows us to compute the transient atomic scattering factors.

Let us start by stating a common problem in condensed matter XFEL science. The irradiation by a strong XFEL pulse drives matter in transient strongly out-of-equilibrium states, even crossing in the regime of WDM. This state is notoriously difficult to model, lying at the interface between plasma and condensed matter physics, not allowing a complete description by either theory. Some progress has been made in understanding the steady state properties of WDM [56, 57]. Nevertheless, until recently there was no general approach that could be used to simulate the non-equilibrium electron dynamics and structural changes of WDM induced by XFEL excitation. In [42], Mercadier *et al.* solved this problem by disentangling the description of XFEL excitation – treated by plasma physics – from the calculation of the absorption coefficient via finite-temperature extensions of Density Functional Theory (DFT). With this approach, the authors were able to calculate the photon-energy-resolved absorption coefficient $\mu(x, y, t, \omega)$ for every time (t) and space point (x, y) during the evolution of the system.

Making use of the same results², we can compute the transient atomic scattering factor $f(x, y, t, \omega)$, which is the key quantity to simulate the transient reflectivity spectrum. The imaginary part of the atomic scattering factor (f_2) is directly related to the absorption coefficient, as recalled in eq. (2.6) on page 14. The real part of the scattering factor is simply obtained via the Kramers-Kronig transformation of f_2 . The resulting atomic scattering factor is used in the code to simulate the reflectivity curve, see section 2.4. Finally, the total reflectivity spectrum is computed as the average of all time and space points, each weighted by the XFEL field intensity $I(x, y, t, \omega)$. For a detailed description of the simulation methods and results relative to the excitation of the system, we refer the reader to the original publication [42]; all considerations reported there are also valid in the present case. In section 3.4 on page 41 we will discuss the merits and drawbacks of this self-consistent model when compared to the experimental data.

²The author thanks Dr. Andrei Benediktovitch for his help in using the results from [42] to compute the transient atomic scattering factors.

2.4 Simulation of the soft X-ray ERES effect

As mentioned in the introduction to the chapter, the final ingredient needed to simulate the ERES effect is the scattering response of the sample to an incoming X-ray pulse. In the case of our soft X-ray experiment – fully described in the next chapter, see page 21 – the samples used are nanostructured multilayers. The natural method to simulate the scattering response of such a sample is to use Parratt’s formalism [50]. In the following, we do not focus on describing the details of the formalism, which can be found in various textbooks (see, for example, [58]). Rather, we explain how the forward simulation of the low intensity (cold) soft XRR spectrum is built and checked against calibrated data measured at the Physikalisch-Technische Bundesanstalt (PTB).

In summary, the multilayer is firstly characterized by a hard XRR measurement. Then, based on the obtained sample parameters, the Parratt approach is used to calculate the expected soft XRR spectrum. This result is finally compared to a high-resolution measurement to confirm the validity of our simulation.

2.4.1 Characterization of the multilayer

Right after production, a hard XRR measurement in a laboratory setup using a Cu- K_α X-ray tube is performed on the sample to confirm its quality. The measured curve is then fitted with the GenX software [59]. The model for the multilayer structure is the one shown in fig. 3.2 on page 24. In this way, the thickness, density, and surface roughness of every layer are obtained. In fig. 2.1 we show an example of the result of this procedure.

2.4.2 Reflectivity calculation and comparison to high resolution measurement

Based on the parameters obtained from the hard XRR fit we then employ the Parratt’s recursive formalism to simulate the reflectivity curve. We developed an in-house code for the Parratt simulation to ensure the flexibility needed for modifying the atomic scattering factor of Cu atoms.

The soft XRR measurement was done at the PTB soft X-ray beamline of the BESSY II synchrotron using a high-resolution reflectivity setup in a two-step procedure. Firstly, the sample is rocked to find the maximum of the relevant peak. This measurement is done

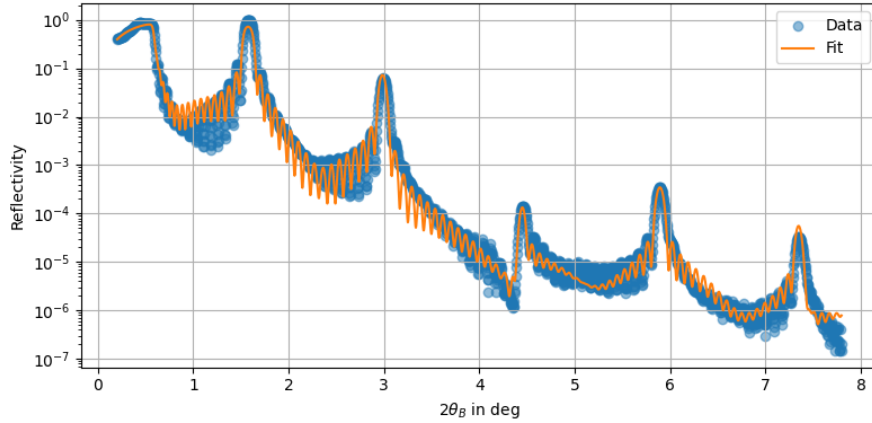


Figure 2.1: Hard X-ray Reflectivity. Measurement (blue dots) and fit (orange line) of the hard XRR of the multilayer sample.

using a constant photon energy of 932.2 eV (1.33 nm). Once the maximum is found, the sample angle is fixed and the reflectivity spectrum is measured by scanning the incoming wavelength.

Similarly, we first simulate the soft XRR curve for the same fixed wavelength as used in the experiment and select the angle where the fifth-order peak is maximum, as shown in panel (a) of fig. 2.2. We then re-run the code for a number of energies and select the slice corresponding to the angle previously found, as shown in panel (b) of the same figure. The final result of this procedure is the soft XRR spectrum presented in fig. 2.3, together with the high-resolution measurement. We applied a scaling factor of 0.41 to the simulation to rescale it to match the experimental curve, which indicates that the simulation overestimates the result. Such behavior is expected since there may be effects not accounted for in the model. For example, the signal-to-noise ratio of the hard XRR data is not sufficiently high to rule out the possibility of errors in the initial fit, especially at the more critical larger angles. Furthermore, a period of a few months elapsed between the hard and soft XRR measurements. During this time, the sample may have acquired an oxidation capping layer responsible for the lower signal. A lower reflectivity also arises from unavoidable sample imperfections such as interface roughness and layer interdiffusion. These shortcomings are not critical as the data measured at the European XFEL has to be normalized – see section 3.3 – to account for the involved measurement procedure. More importantly, the position and width of the overall feature are correctly reproduced

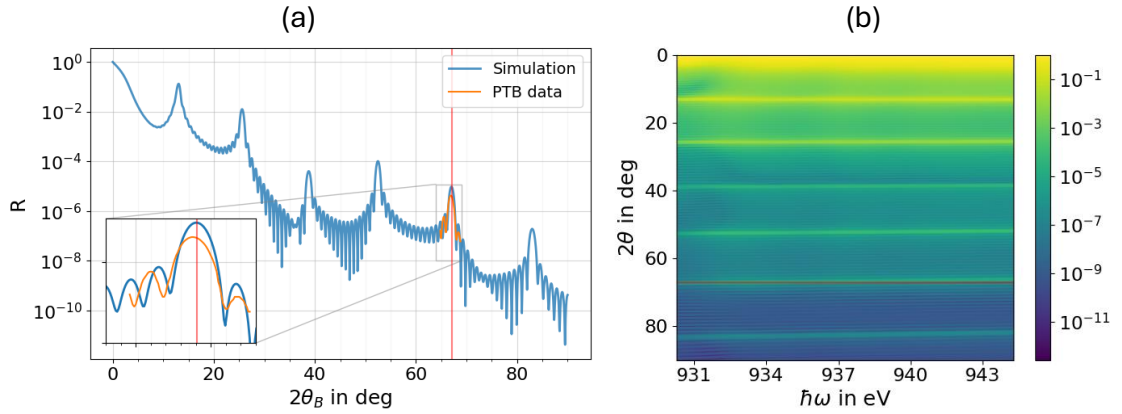


Figure 2.2: Soft X-ray Reflectivity curve and 2D map. (a) Simulation of the soft XRR curve for a wavelength of 932.2 eV (1.33 nm) based on Parratt's formalism. The simulation (blue) is compared to the measurements done at the PTB (orange). (b) Two dimensional map of the soft XRR. In both panels the red line corresponds to the maximum of the fifth super-lattice peak.

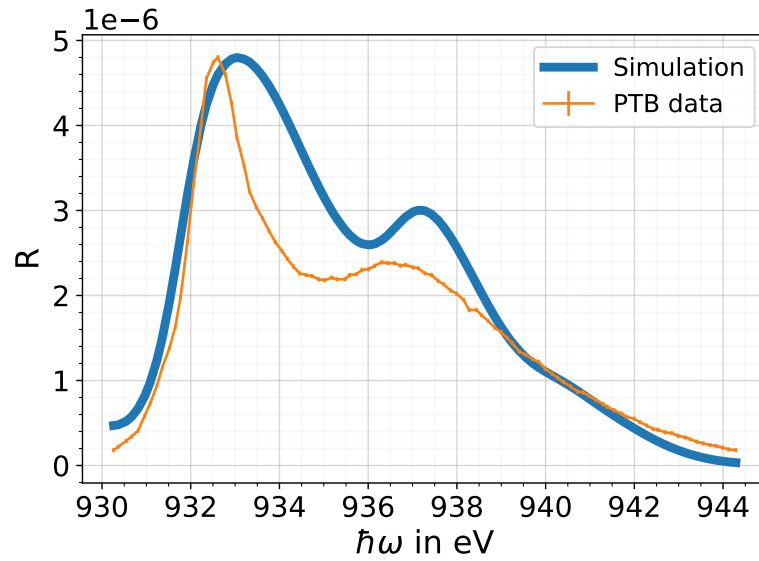


Figure 2.3: Soft X-ray Reflectivity spectrum. Simulation (blue) and measurement (orange) of the soft XRR spectrum. A scaling factor of 0.41 has been applied to the simulated curves to re-scale it to the same amplitude as the experimental one.

by the model, which indicates that all wavelength-dependent physical properties, such as the scattering factors, are treated accurately. Considering all these arguments we can confirm that the forward model faithfully reproduces the cold scattering properties of the samples.

To fully reproduce the XFEL measurement, we must account for the spectral shape of the beam and introduce the modified scattering factors for the pumped case. Unlike the measurement at PTB, where the spectral signature of the reflectivity curve was measured via a wavelength scan of the incoming beam (with every spectral point equally weighted), In the measurement at the European XFEL we have to account for the fixed spectral shape of the incoming SASE beam. The average of many SASE pulses results in a Gaussian envelope, therefore we can simply multiply the calculated soft XRR curve by a Gaussian with the same parameters as the average beam from the XFEL.

We introduce the modified scattering factors that result from either the two-level model or the self-consistent model, as described in the previous sections. We should point out here that the modification of the scattering factor is calculated only for copper atoms. This is justified by the fact that all other elements in the multilayer (Si, C, and B) are much lighter than Cu, and their absorption edges and emission lines are not resonant with the wavelength used, so there is no transient modification of their scattering properties aside from a small reduction due to photo-ionization. Furthermore, we assume that the lattice structure of the multilayer remains fixed. This is justified by the fact that radiation damage evolves on a much longer timescale (ps) compared to the pulse duration of 15 fs used in the experiment. This assumption is corroborated by the theoretical modeling reported in appendix B.

Combining all these components, we are able to reliably simulate the transiently modified reflectivity spectrum. An approximate model is available that we can use to fit the experimental data and extract effective values for the transient scattering factors. We can also employ the more rigorous self-consistent model to directly compare the simulated spectrum to the measurement without any free parameters. In the next chapter, we will guide the reader through the details of the experimental realization, and we will conclude by comparing the models introduced here with the measured data (see section 3.4 on page 41).

Chapter 3

Experimental observation of the ERES effect in the soft X-rays domain

This chapter contains a thorough description of the experimental results obtained from the ERES measurements in the soft X-ray domain performed at the Spectroscopy and Coherent Scattering (SCS) instrument of the European XFEL facility in Hamburg. We start by describing in section 3.1 the experimental setup and samples used to perform the measurements. This section also includes a description of the particular procedure adopted, which is instrumental in understanding the data analysis pipeline explained in section 3.2 on page 30. We then present the results obtained from the experiment in section 3.3. Finally, in section 3.4 on page 41, we compare the experimental measurements with the theoretical models previously described in chapter 2.

3.1 Experimental setup

The experiment was performed at the SCS instrument of the European XFEL facility [60]. In fig. 3.1, we present a scheme of the main devices used in the experiment. The accelerator and undulators were operated in two-color split-undulator mode [61] producing a pump beam at 945 eV, bandwidth 10 eV, and a probe beam at 929 eV with bandwidth 5 eV. The probe beam was produced upstream by 11 undulators cells, for the pump beam 10 cells were allocated. This setting granted the possibility of suppressing the pump beam, by opening its undulator gaps, without affecting the probe beam, making it

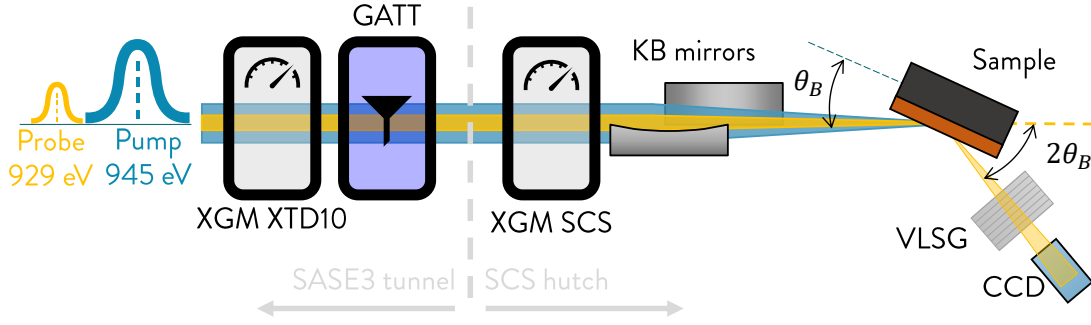


Figure 3.1: Schematic diagram of the experimental setup. The pump and probe pulses are generated in the SASE3 undulator line, their central wavelength are 929 eV and 945 eV respectively, and the bandwidths are roughly 5 eV and 10 eV. After generation they propagate through a X-ray Gas Monitor and a Gas ATTenuator to measure and/or reduce their intensity. Once arrived in the SCS hutch the intensity of the pulses is measured by another X-ray Gas Monitor. Then, the pump and probe beams are focused by the KB optics before impinging on the sample, which is rotated by the Bragg angle (θ_B). The scattered radiation is collected by the spectrometer arm, which is set to the corresponding $2\theta_B$ angle. A Variable Line Spacing Grating disperses the spectral components of the light which are then recorded by a CCD camera. (The scheme is not in scale).

possible to easily switch between single-color and two-color mode. In this configuration, the photon energy of the pump pulse is above the Cu- L_3 edge, and is therefore capable of ionizing electrons from the 2p shell. Concurrently, the probe pulse is resonant with the Cu- L_α transition, granting an efficient probing of the transient state. The capability of switching between single-color and two-color mode is crucial for the experiment, as it allowed us to collect two separate datasets. In one case we use a single pulse to both pump and probe the sample, exploiting the large bandwidth of the pulses to simultaneously excite and probe the transient resonance. In the other case, we use two distinct pulses, one for pumping and one for probing, which allows us to independently control the intensity of the pump and probe beams. We refer to these two datasets as single-color and two-color respectively.

Upon generation in the SASE3 undulator tunnel, the pulses propagated through a X-ray Gas Monitor (XGM); this device measured the total combined intensity of the pulses [62]. Following this, the pulses passed through a Gas ATTenuator (GATT); this device was used to reduce the pulses' intensity to a set percentage [63]. The GATT is a gas chamber, typically filled with N_2 , whose internal pressure can be controlled. By changing this value, the total transmission of the instrument is changed. Since during the experiment

a wide range of undulator configurations and GATT transmissions were explored, it was critical to correctly calibrate the XGMs for every different condition; a further discussion on this delicate topic is presented in appendix C. After that, the pulses were transported downstream to the SCS hutch.

In the SCS experimental hutch, the combined intensity of the pulses was measured by another XGM. Then, the pump and probe beams were focused to 20 μm diameter by the KB optics before impinging on the sample, which was rotated by the Bragg angle θ_B . Details on the samples follow in section 3.1.1. The sample itself was mounted on a sample holder inside the X-ray Resonant Diffraction (XRD) chamber, on a stage which allowed for linear movement in all 3 directions plus rotation around the vertical axis. The scattered probe pulse was collected by the Heisenberg-RIXS (hRIXS) spectrometer, which was positioned at the appropriate $2\theta_B$ angle. The hRIXS instrument is a spectrometer custom designed for Resonant Inelastic X-ray Scattering (RIXS) experiments in the soft X-ray range with high energy resolution, a thorough description of the device can be found in [64]. For the purpose of the present description, it is sufficient to note that the radiation was dispersed by a Variable Line Spacing Grating (VLSG) with 1000 lines mm^{-1} , resulting in a resolution of 0.27 eV. The spectrum was then recorded by a CCD camera (Princeton Instruments, Model PI-MT3) operating in accumulation mode. The energy axis was calibrated using the beamline monochromator [65], and the monochromator calibration was previously checked by a X-ray Emission Spectroscopy (XES) measurement at the Cu- L_3 edge energy.

3.1.1 Samples

The samples are nano-structured multilayer mirrors. The substrate is Si, a SiO_2 layer naturally grows on top of the substrate, and the multilayer itself is composed of 17 repetitions of the tri-layer $[\text{SiC}/\text{Cu}/\text{B}_4\text{C}]$, as shown in fig. 3.2 both by a Scanning Electron Microscope (SEM) image and a sketch. The thickness of each individual layer is 2 nm, resulting in a total multilayer thickness of about 100 nm. Two different stacking sequences were prepared: in the first one, the order of the layers starting from the substrate is Si/- SiO_2 /[$\text{SiC}/\text{Cu}/\text{B}_4\text{C}$]; this is referred to as “direct sequence”. In the second one, called “inverse sequence”, the order is Si/ SiO_2 /[$\text{B}_4\text{C}/\text{Cu}/\text{SiC}$]. The naming stems from the fact that in the direct sample we expect to observe the resonant enhancement of the scattering,

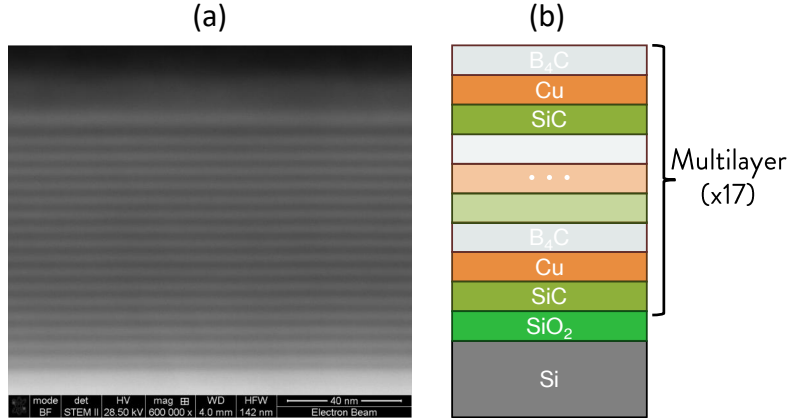


Figure 3.2: SEM image and sketch of the multilayer samples. The sample is a nano-structured [SiC/Cu/B₄C] multilayer, having 17 repetitions, grown on a Si substrate with a naturally occurring SiO₂ interface layer (b). SEM image of the lateral section of the sample (a). The thick white bottom layer is the Si substrate, the light lines are the B₄C and SiC layers, which are indistinguishable due to similar density, the dark lines are the Cu layers.

while in the inverse sequence, due to geometrical reasons, the resonant scattering should be suppressed. This is a manifestation of the so-called Bijvoet effect [66] – a difference in the diffracted intensity of two reflections (hkl) and ($\bar{h}\bar{k}\bar{l}$) – which is commonly exploited in crystallography to determine absolute configurations of molecules [67, 68].

The choice of these materials is motivated by several factors. First, Cu has a strong absorption edge at 932.7 eV (Cu- L_3 edge) and a prominent resonance at 929.7 eV (Cu- L_α), making it suitable for resonant scattering experiments in the soft X-ray range. Second, both SiC and B₄C have low absorption at these energies, ensuring that the multilayer structure can effectively reflect X-rays at the desired wavelengths. Third, these materials are commonly used for the production of multilayer mirrors in the soft X-ray range; therefore, their growth processes are well established [69].

Finally, we note that it is necessary to use a multilayer sample because the Cu lattice does not have any Bragg peak at a wavelength of 929 eV. Conversely, by growing every individual layer with a thickness of 2 nm, the fifth-order superlattice peak falls at the Bragg angle $\theta_B = 34$ deg. An example of a sample before irradiation is shown in fig. 3.2(a), where a SEM picture of the lateral section is displayed. The difference between the Cu and the other layers is clearly visible; however, the SiC and B₄C layers are indistinguishable, having too similar density.

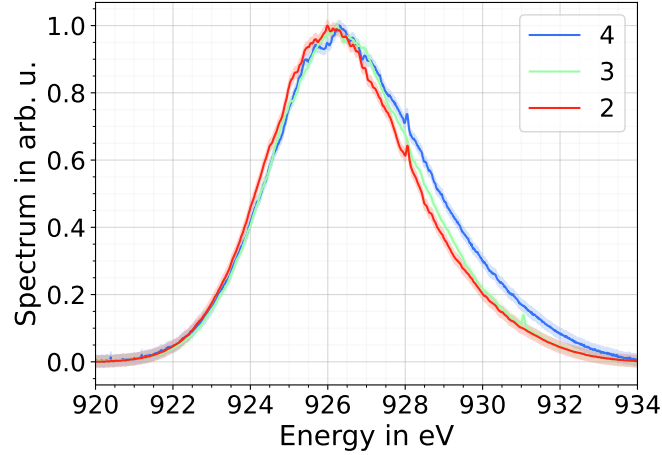


Figure 3.3: I_0 average probe spectra for different undulators' configurations. Average probe spectra measured in the tunnel, generated using a different number of undulators' cells. The blue, green and red spectra are produced, respectively, leaving 4, 3 and 2 undulators' cells open. The total number of available cells is 11. The solid line marks the average of more than 1000 spectra, while the shaded area is the 99.9% confidence interval. All spectra are normalized to unitary amplitude.

Table 3.1: Gaussian fit parameters of the I_0 probe spectra shown in fig. 3.3. The amplitude is not shown since the spectra have been normalized before fitting.

Open cells	Central wavelength in eV	Sigma in eV
4	926.6	2.038
3	926.5	1.887
2	926.3	1.861

3.1.2 Analysis of the probe beam spectra

In collecting the different datasets we often changed the undulator configuration of the XFEL. In particular, the single-color dataset was acquired using all the 11 available undulator cells, while the two-color dataset used only 8 cells to produce the probe beam. Here, we report an analysis of the spectra of the probe beam upstream of the experimental hutch. The spectra were measured using a grating spectrometer in the SASE3 tunnel [65]. This spectrometer is invasive, meaning that it cannot be operated simultaneously with the experiment, since it completely blocks the XFEL beam. During idle times of the beamtime, the spectrometer was inserted to collect data.

In fig. 3.3, we show the average of more than 1000 single-shot spectra for 3 different

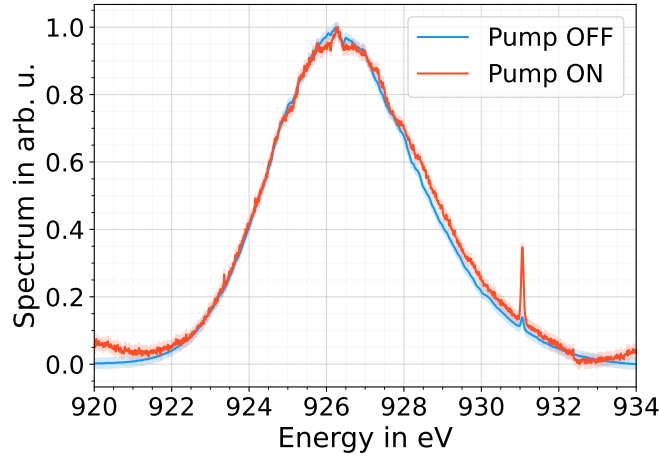


Figure 3.4: I_0 average probe spectra measured with (red) and without (blue) pump beam. In both cases the probe beam is generated using 8 of the 11 undulators' cells available, this condition is the same used during the collection of the two color dataset. The pump beam is either suppressed, by opening all undulators' gaps, or produced using the whole undulator. The solid line marks the average of more than 1000 spectra, while the shaded area is the 99.9% confidence interval. All spectra are normalized to unitary amplitude, this is necessary as the detector gain needs to be changed depending on whether the pump beam is present or not.

undulator configurations: opening 4, 3, or 2 gaps of the probe beam, while all the gaps of the pump beam are open (i.e., the pump beam is suppressed). To better understand the spectral properties, we can fit a Gaussian function to each average spectrum; the results are reported in table 3.1. The central photon energy remains the same for the 3 different conditions, while increasing the number of open gaps from 3 to 4 results in a spectral broadening of about 0.15 eV. This can be attributed to the poorer performance of the XFEL when too many undulator gaps are left open. Still, the spectral shape does not change greatly; we can therefore conclude that measurements acquired with different undulator conditions are comparable.

Finally, it is important to verify that, in the case of the two-color measurements, the spectrum of the probe beam is unaltered by the presence or absence of the pump beam. This is confirmed by the data in fig. 3.4, where the average probe spectrum is shown for both settings. The data are normalized to unitary amplitude to account for the gain switching of the detector. In fact, when the pump beam is present, the gain is lowered to avoid saturation of the detector, but this reduces the signal-to-noise ratio of the probe portion of the detector. This analysis confirms that the spectrum of the probe beam is

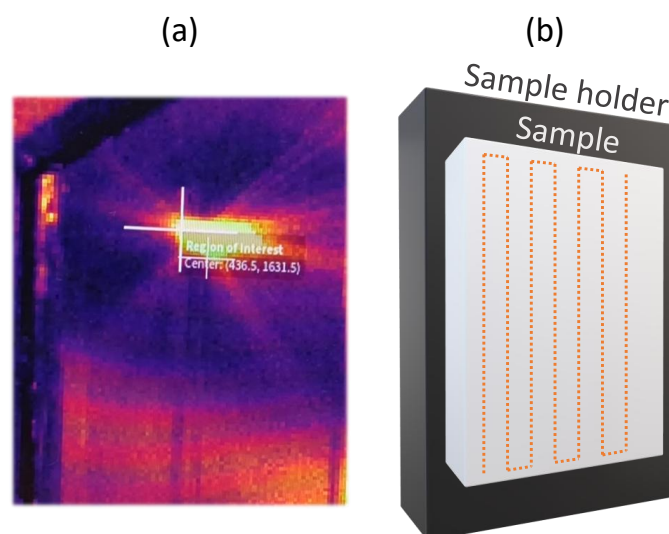


Figure 3.5: Snapshot and sketch of the measurement process. Snapshot of the multilayer sample being hit by the XFEL pulses (a). A plasma burst is created at the surface of the sample and the craters left by previous irradiation are visible as straight lines below the cross. Sketch of the rastering movement (orange line) used during the measurement, note that only vertical lines are measured (b).

stable throughout the experiment; even measurements taken with different undulator configurations can be, at least qualitatively, compared.

3.1.3 Measurement procedure

The XRD chamber of the hRIXS instrument is designed for static and non-destructive measurements of solid targets. This design choice is crucial because RIXS is an extremely photon-hungry technique, where collecting a single spectrum can require measurement times spanning several tens of minutes, even at a high repetition-rate XFELs. A typical RIXS measurement uses a large spot size and an attenuated beam to ensure that repeated irradiation does not degrade the sample quality. Once optimized settings are reached, they can be maintained for days, or even weeks, allowing measurement to begin. The CCD camera's readout rate is adjusted based on the type of signal under examination: if single photons can be detected, readout can occur every few seconds. Alternatively, the CCD camera can operate in accumulation mode, reading out an accumulated image over a period spanning from seconds to minutes.



Figure 3.6: Post-exposure optical microscope image of the surface of the sample. The interaction of the X-ray with the sample locally destroys the surface leaving a crater. The 3 vertical lines are measured at different intensities, which shows in the different sizes of the craters.

In our experiment, achieving a high photon flux ($>10^{12} \text{ W cm}^{-2}$) was essential to reach the non-linear interaction regime. However, this condition limited each sample exposure to a single destructive shot. Consequently, the irradiated spot on the sample had to be moved aside, and a fresh area was brought into the interaction region with each shot. This restriction required us to use the hRIXS spectrometer in an unconventional way. The XFEL repetition rate was set to a single pulse per train (10 Hz), allowing the stepper motor to renew the sample at the same rate. Using just two pulses per train would have increased the required renewing rate to over 1 kHz, which is beyond the capacity of conventional linear stages. The motor moved continuously within user-defined upper and lower sample limits – defining a “line” on the sample surface – which could range from a few mm to a few cm. The speed of the motor was fixed at 0.5 mm s^{-1} , allowing a distance between two consecutive shots of $50 \mu\text{m}$. The CCD camera operated in accumulation mode, with the integration time matched to the duration of a full line scan. In this way, each line on the sample provided a spectrum, and from one to an arbitrary number of lines could be measured during a single run¹, see panel (b) of fig. 3.5. In fig. 3.5, one can see evidence of the destructive interaction of X-rays with the sample: the plasma flare (bright yellow spot) and the craters left by previous irradiation (visible as lines directly

¹“Run” is the term which we use to identify a single measurement instance. In other words, a “run” represent a single measurement where, typically, the conditions are not changed. Note that, in a single run we can record from 1 to any number of spectra.

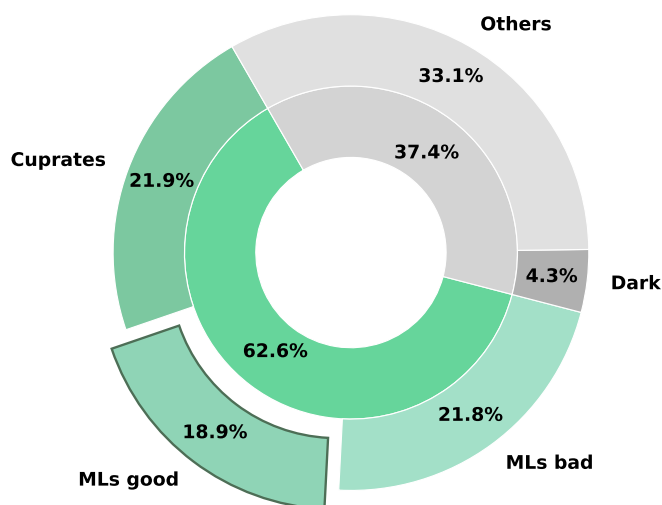


Figure 3.7: Statistical overview of all measurements. The green part refers to sample measurement, the sub-division highlights the different samples multilayer and cuprates). Furthermore, in the case of multilayers the division between good and bad runs is shown. The gray area is for non-measurement runs, this includes “darks” which are run with closed shutter and “other” which groups together alignment, calibration, signal optimization, and anything else.

below the plasma). Further proof is shown in fig. 3.6 as an optical microscope image of the sample surface after irradiation. The 3 vertical series of craters are left by pulses at different intensities. The terraces on the right side of the main crater are individual layer groups that are ablated, the same type of damage was previously observed in multilayers under similar conditions [70].

3.1.4 Overview of the measured data

During the experiment, several different types of measurement were conducted, and a total of 638 runs were recorded, amounting to 19.66 TB of data, all data from the experiment is available at [71]. The primary goal of the campaign is to maximize the number of runs containing high-quality, publishable data. Achieving this often requires significant time and resources to explore the experimental conditions. Unfortunately, the intrinsic stochasticity of XFELs poses a substantial challenge to the measurement process, compounded by sample inhomogeneity and potential machinery failures.

In fig. 3.7, we present a statistical overview regarding the measured data during the beamtime. The gray portion of the pie chart represents all the non-sample measurements.

These include dark runs – typically required for background correction of the signal – as well as other preparatory measurements such as alignment, calibration, signal optimization, and other non-repeatable procedures unpredictably needed during the experiment. The green section of the chart corresponds to the actual sample measurements, divided between the two different samples used: multilayers and cuprates². Throughout this document, unless explicitly stated otherwise, we focus on the highlighted slice of the chart, representing the good, usable multilayer measurements. The “Multilayers bad” slice includes all measurements that failed due to specific reasons, such as sample degradation, user errors, detector failures, and other issues. In section 3.2, we detail the checks that led to the classification of measurements as either good or bad.

The usable measurements (“MLs good”) are further categorized into two main groups: single-color and two-color measurements. Recall that for the single-color measurements, a single XFEL pulse serves as both pump and probe, thanks to the large bandwidth and the proximity in energy of the Cu- L_3 edge and the Cu- L_α transition. For this type of measurement, we have data available for both direct and inverse sequence multilayers. In the case of two-color measurements, two distinct pulses are used: one for ionizing the atoms and the other for probing the transient state. For these measurements, data is available only for the direct sequence samples. The results of the single-color experiment are discussed in section 3.3 on page 36, while the two-color experiment is detailed in appendix D.

3.2 Data analysis

In this section, we discuss how the data measured during the experiment is processed. Each run is first individually checked; this procedure discriminates between the usable and corrupted data, shown in fig. 3.7 on the preceding page. All runs undergo two distinct steps: raw data processing, to transform the raw images into valid spectra, and checks for data reliability, to ensure that the run is free of experimental or user errors. Subsequently, measurement series are grouped together to build the final result. While the cleaning step is identical for every run, we differentiate between single-color

²The cuprate samples were used as a backup. Unfortunately, the measurement on these samples has not produced any relevant results, therefore we avoid discussing them in this document. We deeply thank Emilio Bellingeri and Daniele Marrè for the realization of these samples.

and two-color measurements when constructing the final results, as the workflows for the two measurement types differ slightly. All steps of data ingestion and preprocessing utilize the SCS toolbox python module [72], while the main part of the data analysis is achieved with user written python scripts and jupyter notebooks, all available at [73].

3.2.1 Raw data processing

Following the measurement routine detailed in section 3.1.3 on page 27, each run consists of a series of raw images collected by the CCD camera. Each image corresponds to a single exposure of the camera, which integrates the incoming photons over a time window matched to the duration of a single line scan of the sample. In this way, our unit of data is the single exposure; however, artifacts and errors that occur at the level of a single shot are also accumulated during the exposure. The most evident artifacts are broken lines along the non-dispersive direction of the detector, which are caused by defects in the CCD sensor, evident in fig. 3.8a. Those are simply corrected by assigning to these lines the average value of neighboring pixels, resulting in the corrected images shown in fig. 3.8b. In the same figure we can see the diffracted signal (bright spot) superimposed with the Cu- L_α fluorescence line (faint vertical line). The Bragg spot is concentrated in a small area, while the fluorescence line spans across the detector, confirming that we are in Bragg condition and capable of analyzing the spectrum of the diffracted beam. Another feature appearing in the image is a non-uniform background caused by stray light from the beamline.

Each corrected image is then integrated along the non-dispersive (vertical) direction of the detector, resulting in a single spectrum as shown in the top panel of fig. 3.8c. Here, the background is clearly visible and a second degree polynomial baseline can be removed by fitting the regions outside the signal, as indicated by the green vertical lines in the figure. The resulting baseline corrected spectrum are shown in the bottom panel of fig. 3.8c. The blue vertical lines in this figure delimit the peak region. This part of the spectrum is integrated and used to discriminate the presence or absence of a peak based on thresholding. This filtering step is necessary to remove accidental dark images and low quality data coming from the sample edges. The filtered spectra are shown in fig. 3.8d, where the green region is the Cu- L_α resonance and the Cu- L_3 edge is highlighted by the red region.

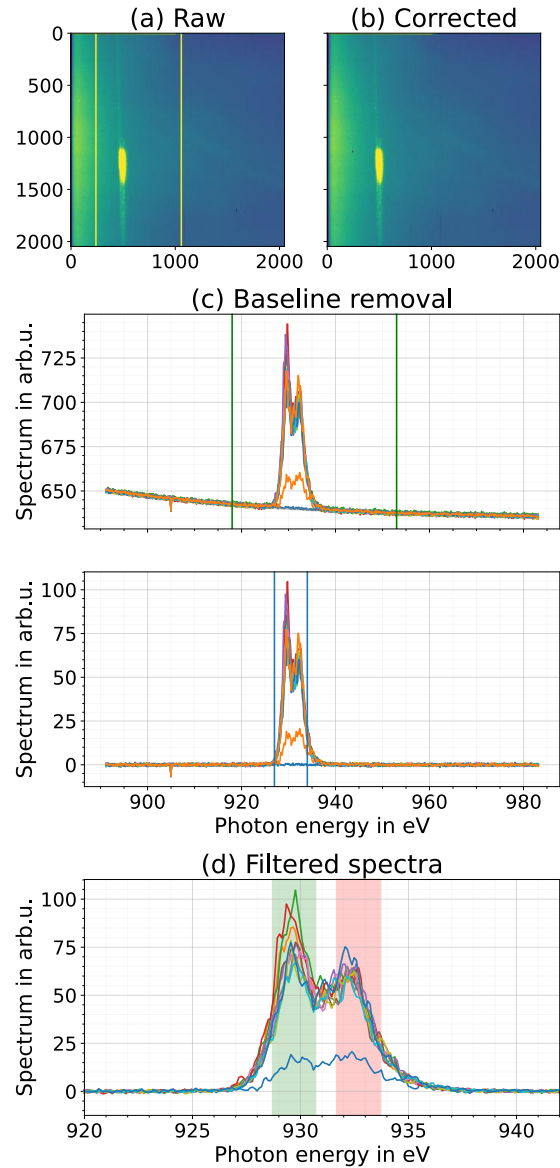


Figure 3.8: Processing from raw data to spectrum. The raw images collected by the CCD camera (a) are corrected for artifacts resulting in the corrected images (b). The images are integrated along the non-dispersive (vertical) direction and result in the single spectra. A second degree polynomial baseline is removed. The green vertical lines delimit the signal region, which is excluded for the baseline fit. The blue lines delimit the peak region, which is integrated and used to discriminate the presence or absence of a peak based on thresholding (c). The filtered spectra. The green region is the Cu-L_α resonance and the red region is the Cu-L_3 edge (d).

The steps outlined in this section are fundamental to convert the raw data into usable spectra. However, further checks are necessary to ensure the reliability of the data, meaning that no experimental or user errors have compromised the measurement. This is discussed in the next section.

3.2.2 Checks for data reliability

The measurement procedure is semi-automatic, meaning that user input is required to start and stop each line within a run. In details, it is the user input that enables the motor to move synchronized with the opening of the shutter. This procedure is prone to human errors, which can compromise the measurement. For example, if the user forgets to start the motor movement, the shutter will open while the sample is static, resulting in an exposure of the CCD camera without any line scan, as well as sample damage. The opposite can also happen, the sample starts moving while the shutter is not open. While the latter case does not damage the sample, both cases are problematic, as they introduce errors into the data, either in the form of a dark image or a corrupted spectrum. We note that at the time of the experiment, this was the best available procedure. The simple reason is that the hRIXS is an instrument designed for static measurements, therefore we had to adapt the existing control software to our dynamic measurement needs.

To identify and remove the problematic spectra, we analyze the motor position and shutter status logged during the measurement, as shown in fig. 3.9a. The colored points represent the shutter being open, and the gray points represent the shutter being closed. The blue line is the motor position. The shutter is open only when the sample is moving, confirming that the measurement procedure was correct.

Another possible error can be the irradiation of sample regions which are not properly prepared or damaged. The multilayer sample is not coating the entire substrate uniformly; instead, it gradually stops close to the edges. If the measurement is performed too close to the edges, the data quality can be compromised, to the point that, when irradiating the substrate no signal is detected. Furthermore, a second irradiation error can occur if the sample is damaged by previous exposures and re-irradiated. This can happen if the user accidentally repeats a line scan on the same region of the sample. To avoid this issue, we check for correlations between the measured spectra and the incoming pulse energy. In fig. 3.9b we plot the integrated intensity of the Cu- L_α (green) and Cu- L_3 edge

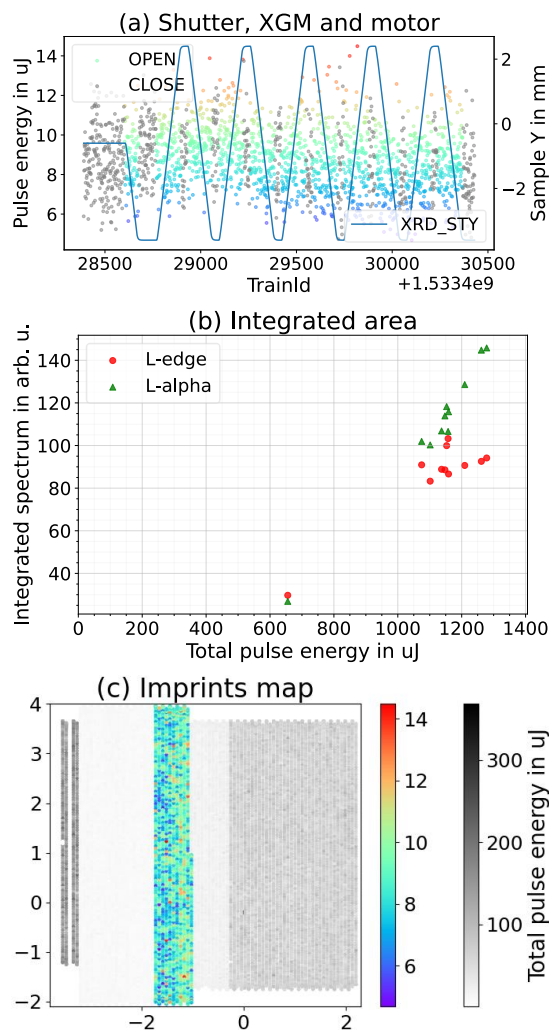


Figure 3.9: Checks for data reliability. Shutter position, XGM readout and motor movement (a). On the left axis is the single shot pulse energy. The shutter position is open for colored points and closed for gray points. On the right axis the blue curve is the sample position. The shutter is open only when the sample is moving, confirming that the measurement procedure was correct. One vertical slice with colored points and moving sample correspond to one exposure of the CCD camera. The integrated Cu- L_{α} and Cu- L_3 edge regions of the spectrum – as defined in fig. 3.8 – versus the total pulse energy measured in a single exposure (b). The imprints map of the sample. The current run (colored) is overlapped to the full map of the sample (grey) (c).

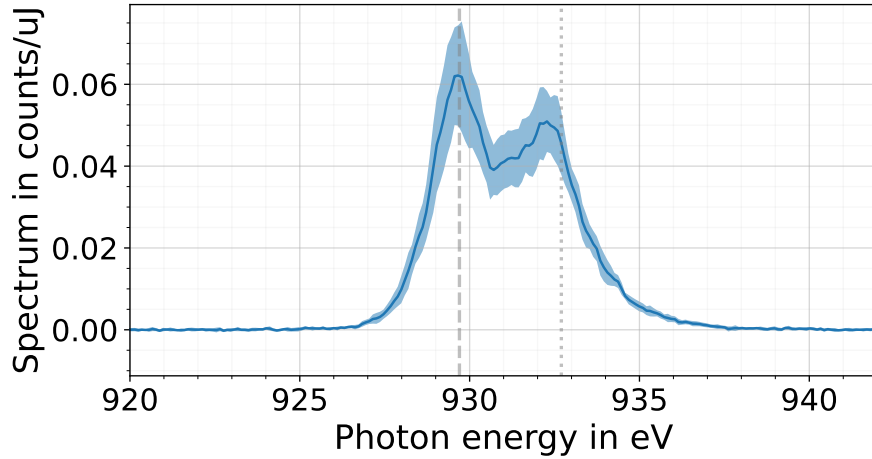


Figure 3.10: Average spectrum of a single run. Average spectrum of a single run after processing and reliability checks. Before averaging each spectrum is normalized by the total exposed pulse energy. The solid line is the average spectrum, the shaded region around is the error bar at 1 standard deviation. The dashed and dotted lines mark the position of the $\text{Cu-}L_\alpha$ resonance (929.7 eV) and the $\text{Cu-}L_3$ edge (932.7 eV) respectively, at low intensity.

(red) regions of the spectrum versus the total pulse energy measured in a single exposure. The $\text{Cu-}L_3$ edge should show no correlation with the pulse energy, as it is not related to resonant processes. While the $\text{Cu-}L_\alpha$ intensity should show a growth with pulse energy, if the sample is properly prepared and undamaged. This is indeed the case in our data, meaning that the sample is in good condition throughout the measurement.

Finally, to confirm that we are not re-irradiating damaged regions of the sample, we plot the irradiated spots during the current run on top of the full imprints map of the sample (fig. 3.9c). All the checks presented in this section confirm that the data collected during the measurement is reliable and free of experimental or user errors.

3.2.3 Creating the final spectrum

At this stage of the analysis we confirmed that the data measured in the run is reliable. The final step is to create the averaged spectrum and relative error bars. We start by normalizing each individual spectrum by the total pulse energy to which the sample is exposed during the corresponding line scan. This means dividing the intensity of each spectrum by the sum of the XGM readouts corresponding to each exposure composing the line scan, visually this quantity corresponds to a group of colored points in fig. 3.9a.

After the normalization each spectrum is then given in units of counts per unit of energy (counts/ μJ). The normalization by the incoming energy is crucial, as the XFEL output fluctuates significantly from shot to shot, and even more so when comparing different runs measured at different times. Furthermore, in our spectra, we have a region – the Cu- L_α resonance – which is expected to depend in a nonlinear way on the incoming intensity, and another region – the Cu- L_3 edge – which is expected to be linear with intensity. Therefore, normalizing by the intensity is necessary to compare different spectra and identify nonlinear effects.

During this step, we also remove images with a large variation of the total exposed energy, which indicate extremely large fluctuations in the XFEL operation. The criterion we use is to remove all images with a total energy larger than five standard deviations from the mean total energy of the run. This is done to prevent rare long-term drifts in the XFEL operation from affecting the final result.

The final averaged spectrum of a single run is shown in fig. 3.10. The solid line is the average spectrum, while the shaded region around it represents the error bars at 1 standard deviation. The dashed and dotted lines mark the position of the Cu- L_α resonance (929.7 eV) and the Cu- L_3 edge (932.7 eV) respectively, at low intensity.

During the experiment we visited the same conditions in different runs, to improve the statistics and ensure reproducibility of the results. Given the data analysis procedure outlined so far, we can now combine the data from different runs to create a high quality final spectrum for each measurement condition. The merging of different runs happens after the normalization and the averaging is applied to the full set of data. In this way, we create the final spectrum for each measurement condition, which is then used to analyze the nonlinear response of the system, as discussed in section 3.3.

3.3 Results

Here, we present the results of the single-color experiment. The results of the two-color experiment are not yet supported by a theoretical model. Therefore, we decided not to include them in this chapter, but rather to present them separately in appendix D.

We note that in every figure in this section, we decided to renormalize the data. The normalization we chose sets to unity the integral area of the spectrum above the Cu- L_3 edge, which is the region where the scattering is dominated by the nonreso-

nant, intensity-independent contribution. This normalization allows us to directly compare measurements across different samples, which without normalization would differ greatly due to differences in sample quality. Some samples display intrinsically higher reflectivity due to better layer separation and lower roughness, which results in a stronger signal. This is the case of the direct multilayer sample, which shows a much stronger signal compared to the inverse one, as we will see in the following. The inverse multilayer sample is of lower quality, with higher roughness and interdiffusion, which results in a weaker signal. The renormalization allows us to standardize the results. Moreover, this normalization allows us to directly compare the experimental results with the theoretical model, which is also normalized in the same way.

3.3.1 Single-color experiment on the direct multilayer

Recall that this type of sample is expected to show the nonlinear enhancement of the scattering strength – the ERES effect – which here manifests as an increase in reflectivity. The results of the measurement are presented in fig. 3.11. The low-intensity – henceforth referred to as “cold” – spectrum, recorded at $1.2 \times 10^{13} \text{ W cm}^{-2}$, exhibits the characteristic feature of anomalous dispersion near the Cu- L_3 edge at 932.7 eV. When the photon energy exceeds the ionization threshold, atoms can absorb X-rays; the associated change in absorption directly modifies the scattering factor, leading to enhanced signal near elemental edges [74]. As the excitation intensity increases beyond the cold value, additional scattering strength emerges in the pre-edge region, most prominently as a peak at the Cu- L_α ($2p_{3/2} - 3d$) resonance. This feature constitutes the signature of the transient resonance. The resonant contribution grows nonlinearly with intensity, reaching a maximum at $8 \times 10^{14} \text{ W cm}^{-2}$, where the peak amplitude is nearly six-fold relative to the cold spectrum at the same photon energy. A further increase in intensity reduces the peak amplitude. This is caused by the augmented number of ionized electrons, which in turn decreases the screening of the nuclear charge and shifts the resonance to higher energies, outside the observation window. Concurrently with this trend, the resonant peak spectrally broadens. This broadening is a consequence of the increasing number of atoms with 2 or more $3d$ vacancies, which have an intrinsically broader spectral profile. Both the shift and the broadening of the transient resonance have already been observed in a transient absorption experiment on copper foil by Mercadier *et al.* [42], which was

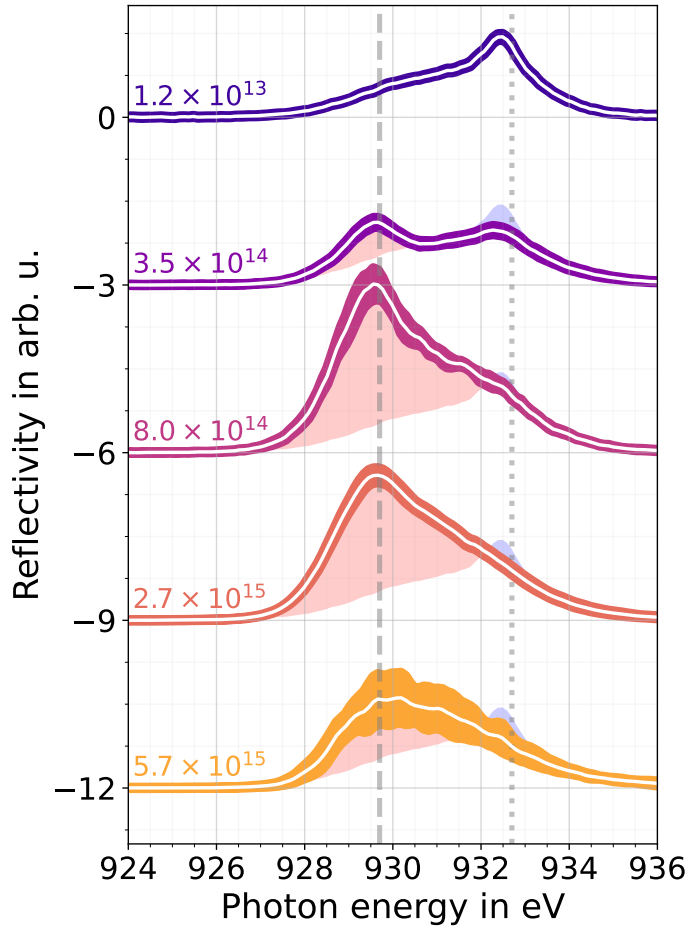


Figure 3.11: Spectrally resolved reflectivity of the direct multilayer sample. Experimental measurement of the spectrally resolved scattered radiation from the direct multilayer structures around the Cu- L_{α} resonance for different intensities (in W cm^{-2}). The different spectra are offset vertically by -3 arbitrary units for clarity. The colored region around each spectrum represents the 99% confidence interval. The shaded red (or blue) regions correspond to positive (or negative) difference with respect to the reference spectrum measured at the low intensity $8.0 \times 10^{12} \text{ W cm}^{-2}$. The dashed and dotted lines mark the position of the Cu- L_{α} resonance (929.7 eV) and the Cu- L_3 edge (932.7 eV) respectively, at low intensity.

performed at the same facility and with the same experimental conditions.

The results shown for the direct multilayer sample indeed confirm the presence of the ERES effect, as supported by the emergence of the transient resonance peak at the Cu- L_α energy. We can fully confirm this observation, thanks also to the high signal-to-noise ratio of the measurement, which allows us to clearly resolve the spectral features and their evolution with intensity. The error bars in the figure represent the 99% confidence interval. This is relatively narrow, indicating that the measurement is very precise and that the observed features are statistically significant. In section 3.4, we will compare these results with the theoretical model, which will further confirm the presence of the transient resonance and provide a quantification of the excess scattering factor achieved.

3.3.2 Single-color experiment on the inverse multilayer

We move on to discuss the results from the inverse multilayer sample; however, before analyzing the measured data, we should point out a few preliminary notes. First and foremost, the inverse multilayer sample is of lower quality compared to the direct multilayer, which results in a significantly weaker signal. It is well established that multilayer interfaces are asymmetric and depend on the deposition sequence. Experimental studies comparing A-on-B and B-on-A growth have shown significant differences in interfacial width, interdiffusion and roughness due to different nucleation and growth kinetics [75, 76]. We have directly observed the lower quality of the inverse sample during the experiment. In particular, we could not find the fifth-order superlattice peak in the reflectivity curve, which indicates that the layer roughness is higher in this case³.

To conclude the measurement, we chose to measure at the calculated optimal angle for the fifth-order superlattice peak, which is 34.6° , already expecting a much weaker signal. As shown in section 2.4 on page 17, the difference between the peak and the baseline is about 2 orders of magnitude. Furthermore, in the same section, we have demonstrated that the angle plays a significant role in the spectral shape of the reflectivity. Because of these two factors combined – the lack of the superlattice peak and the arbitrary angle chosen – we should not expect that the cold reflectivity of the inverse sample will show the same spectral features as the direct sample. Nevertheless, we are not interested in

³The search for the superlattice peak was done manually and, unfortunately, we do not have any saved data to show the angular reflectivity curve of this sample.

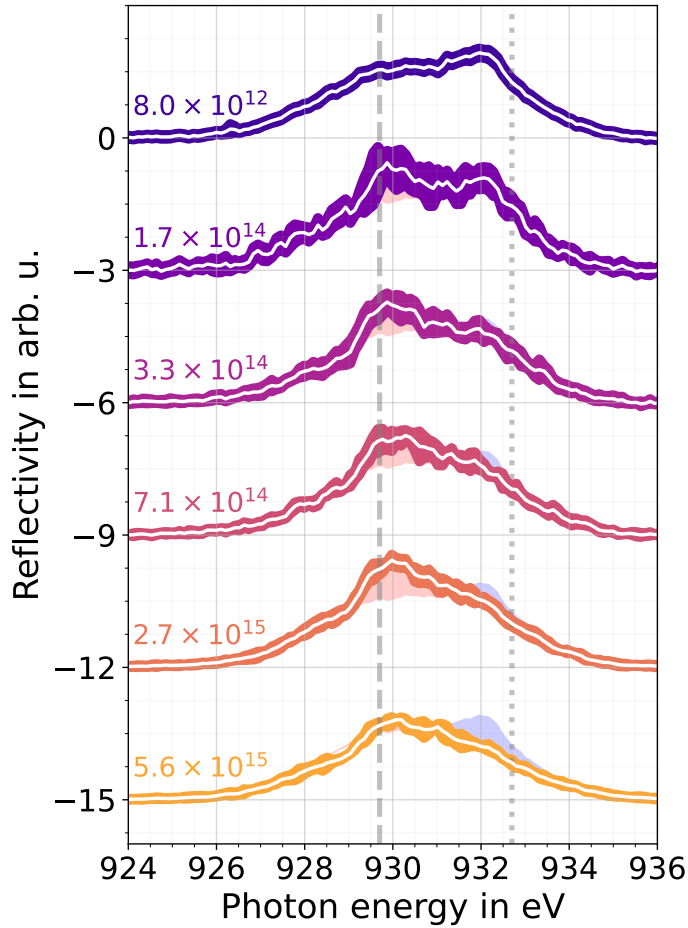


Figure 3.12: Spectrally resolved reflectivity of the inverse multilayer sample. Experimental measurement of the spectrally resolved scattered radiation from the inverse multilayer structures around the Cu-L_α resonance for different intensities (in W cm^{-2}). The different spectra are offset vertically by -3 arbitrary units for clarity. The colored region around each spectrum represents the 99% confidence interval. The shaded red (or blue) regions correspond to positive (or negative) difference with respect to the reference spectrum measured at the low intensity $8.0 \times 10^{12} \text{ W cm}^{-2}$. The dashed and dotted lines mark the position of the Cu-L_α resonance (929.7 eV) and the Cu-L_3 edge (932.7 eV) respectively, at low intensity.

how the direct and inverse multilayer curves differ at a given intensity, but rather in how the reflectivity spectra of a single sample evolve with intensity. In particular, having observed the emergence of the transient resonance in the direct multilayer sample, we are interested in whether this is suppressed in the inverse case. This would be an indication of the Bijvoet effect [66]. Lastly, we lack the hard XRR measurement of the inverse multilayer sample, which is the starting element of our simulation. This means that we cannot directly compare the experimental results with the theoretical model, as we will do for the direct multilayer sample.

The results of the intensity scan are collected in fig. 3.12. We can still observe the anomalous dispersion feature around the Cu- L_3 edge ; in this case, the anomalous peak slowly decreases with intensity, indicating strong sample degradation. This is to be expected given the lower quality of the inverse multilayer sample. Contrary to the direct multilayer, we do not observe a strong emergence of the transient resonance peak at the Cu- L_α energy. We see only a small increase in the reflectivity for intensities between $1.7 \times 10^{14} \text{ W cm}^{-2}$ and $2.7 \times 10^{15} \text{ W cm}^{-2}$. In particular, for the lower intensities – $1.7 \times 10^{14} \text{ W cm}^{-2}$ and $3.3 \times 10^{14} \text{ W cm}^{-2}$ – the change occurs almost completely within the confidence interval, which means that we cannot be certain that the observed modification is statistically significant. Furthermore, this slight increase in the reflectivity appears constant, showing no intensity dependence. This might indicate that we are observing the decoupled action of copper atoms, which should be suppressed in the ideal case of a perfect sample.

In summary, the results from the inverse multilayer sample do not show a strong transient resonant peak. However, the low signal-to-noise ratio of the measurement and the intrinsically low quality of the sample do not allow us to draw a definitive conclusion on the presence or absence of the Bijvoet effect. Ideally, future experiments on higher quality inverse multilayer samples will be necessary to clarify this point.

3.4 Comparison between results and theoretical models

In the following, we compare the experimental results of the single-color experiment on the direct multilayer sample with the theoretical models described in chapter 2 on page 11. To quantify the excess scattering factor introduced by the transient resonance, we fit the experimental data with a simplified model, see section 2.2 on page 14 for a

detailed description of the model. A self-consistent theory – introduced in section 2.3 on page 16 – that predicts the electronic excitation of the atomic ensemble allows us to interpret the measurements.

3.4.1 Fit with the two-level model

The results of the fitting procedure are shown in fig. 3.13. Panel (b) shows the final result of the simulation compared with experimental data in panel (a), while panel (c) displays the dependence of the parameters of the transient resonance (eq. (2.9)) on the pulse intensity. The fit captures the behavior of the transient scattering contribution well, with the appearance, growth, and broadening of the resonant peak. Furthermore, by analyzing the evolution of the fitting parameters against the pumping intensity, we can draw conclusions about the underlying transient mechanism. The peak value ($2A/\gamma_2$) of the imaginary part of the transient atomic scattering factor rapidly grows to its maximum value, approximately 25, for a pumping intensity of $8.0 \times 10^{14} \text{ W cm}^{-2}$, and then drops for higher intensity. The width (γ_2) of the peak has a similar behavior, rapidly growing past the natural width of the Cu- L_α emission line (0.5 eV) [77], reaching a maximum of almost 4 eV and then steadily decreasing at a slower rate than the peak value. Concurrently, the resonant energy (ω_0) of the effective transition initially jumps to lower values (red-shift), then gradually increases, shifting closer to the Cu- L_3 edge (932.7 eV).

These trends, which thanks to the two-level model become evident, are in agreement with the transient absorption measurements in [42]. With increasing ionization rates, which are a direct consequence of a higher pulse intensity, the increased number of ionized electrons reduces the screening of the nuclear charge. This directly affects the position of the transient resonance, which gets shifted towards higher energies. Since the photon energy of our incoming pulse is fixed at 931 eV, the transient resonance gradually slips out of the observable window, thus reducing its peak value. Similarly, the increased density of highly-charged Cu ions ($\text{Cu}^{7,8+}$), which accompanies the increased intensities, explains the broadening of the peak, since those ions have a broadened absorption profile. Extrapolating the trends observed in fig. 3.13 toward higher intensities ($>10^{16} \text{ W cm}^{-2}$), we can speculate that the resonant peak will eventually shift completely into the above-edge region and disappear.

Despite its simplicity, this two-level model provides valuable insights in the physics

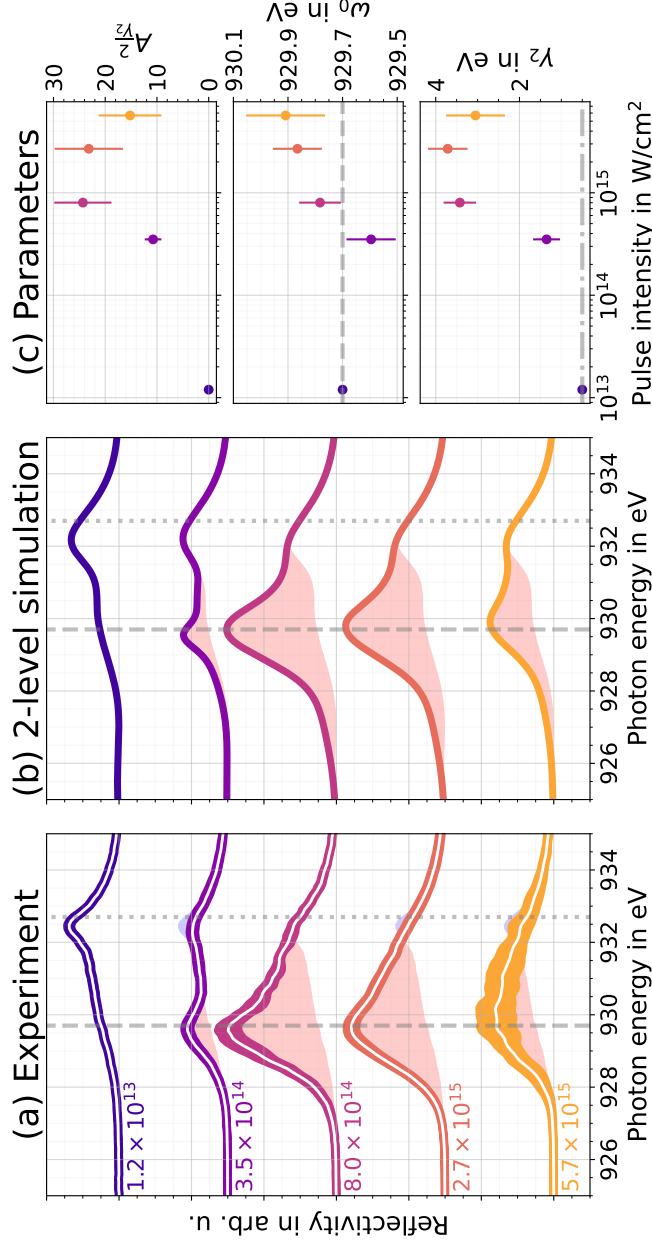


Figure 3.13: Comparison of experimental data and fit with the two-level model. (a) Experimental measurement of the spectrally resolved scattered radiation from the multilayer structures. (b) Corresponding simulation of the reflectivity spectrum with the two-level model. (c) Parameters of the Lorentzian representing the transient contribution to the scattering factor of Cu atoms (see eq. (2.9)). The error bars are standard deviation as resulting from the fit multiplied by 5. The parameters for the lowest intensity curve are not fitted, instead they are fixed to the case of zero enhancement ($A = 0$, $\omega_0 = 929.7$ and $\gamma_2 = 0.5$). The dashed line in the middle panel is the Cu- L_α resonance. The dash-dotted horizontal line in the bottom panel is the width of the Cu- L_α emission (0.5 eV) [77].

of the effect. It identifies the cause of the enhancement in the transient $2p_{3/2} - 3d$ resonance and yields its quantitative parameters – energy, width, and strength – that can be efficiently extracted from experimental measurements.

3.4.2 Simulation with the self-consistent model

In fig. 3.14, we show the measurement and the forward simulation done with the self-consistent model side by side. A general qualitative agreement between theory and experiment is evident, with the model capturing most spectral characteristics, in particular the position and structure of the peaks, as well as the formation, broadening, and fading of the resonance. Nevertheless, some discrepancies are noticeable, most prominently the amplitude of the peak at $3.5 \times 10^{14} \text{ W cm}^{-2}$ is overestimated by the model. A primary contributor is the error in the experimental characterization of the beam intensity, which can be as high as 50%. Furthermore, single-shot measurements are unavailable, and all data are accumulated over a few tens of shots, as previously described in section 3.1.3 on page 27. This, together with the absence of an in-line measurement of the incident spectrum, makes single-shot normalization not possible. In contrast, the theoretical model assumes an idealized Gaussian intensity profile, thus neglecting these fluctuations and the spectral variations of individual pulses.

Finally, the parameter with the strongest impact on the spectral profile is the Bragg angle. In a multilayer mirror, the Bragg angle critically shapes the spectral response, as even small angular deviations shift the reflected photon energies and alter the apparent line shape; see, for example, fig. 2.2 on page 19, where a soft XRR 2D map of angle versus energy is shown. In fig. 3.14, a single Bragg angle is used for all simulated curves – the one that minimizes the residuals between the measurement and the simulation of the lowest intensity curve – however, because each measurement probes a different region of the sample surface, local strain, layer-thickness variations, or slight misalignment of the sample as it is rastered may alter the effective Bragg angle between measurements. For reference, we show in fig. E.1 on page 66 a comparison between the experimental data and the self-consistent simulation, where the Bragg angle differs by 0.05 deg from the one used here. This figure shows how even a slight difference in angle has a strong impact on the spectral profile. Despite these limitations, the overall agreement between experiment and theory demonstrates that the model captures the essential physics with

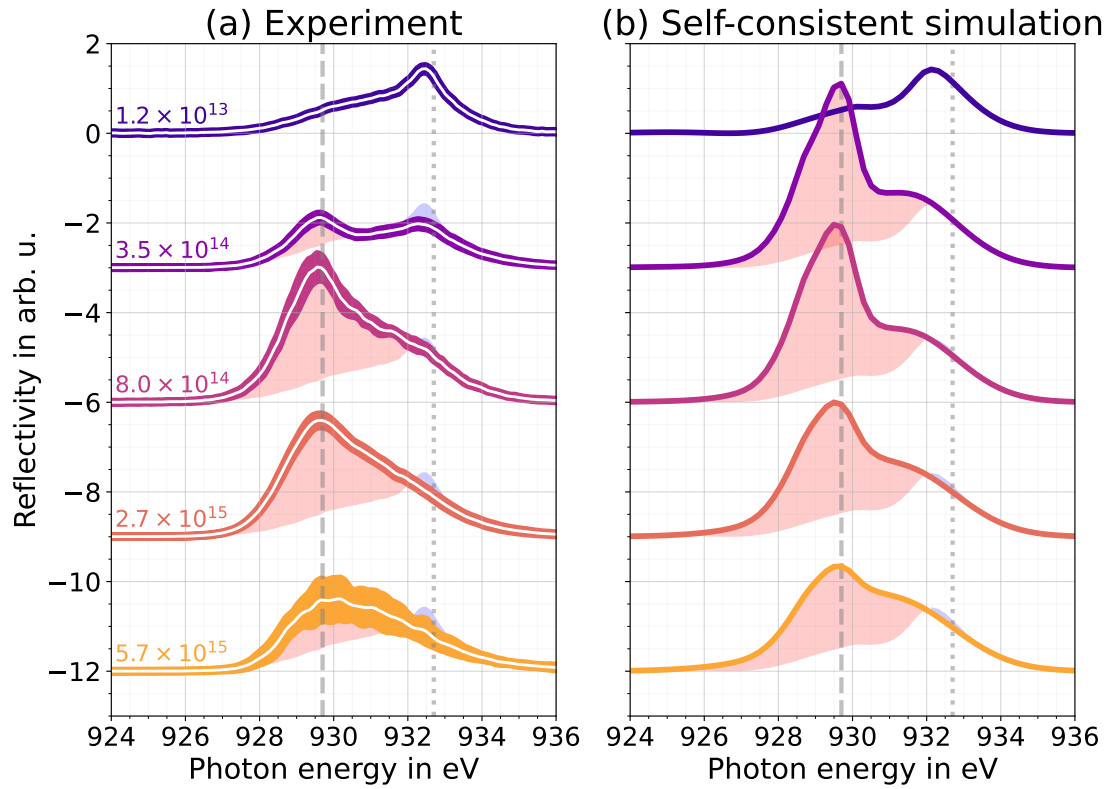


Figure 3.14: Comparison of experimental data and self-consistent simulation. (a) Experimental measurement of the spectrally resolved scattered radiation from the multilayer structures. (b) Corresponding simulation of the reflectivity spectrum with the self-consistent model.

fidelity.

Chapter 4

Summary and future directions

In this thesis, we have introduced the reader to the broader field of nonlinear X-ray science, and more specifically to the ERES effect. In this respect, we have presented a comprehensive study demonstrating the enhancement of the elastic scattering factor of copper atoms driven by the transient $2p_{3/2} - 3d$ resonance formed under intense XFEL irradiation. Our spectrally resolved measurements validate the idea that the transient resonance is the ultimate source of the observed enhancement. To further corroborate the hypothesis, we established a general interpretation by coupling a self-consistent framework with an effective two-level description. Quantitatively, the transient response yields $f_2 \approx 25$, to be compared with the equilibrium value of $f_2 \approx 2$, confirming a more than ten-fold enhancement. These results deliver a practical, physics-grounded route to extract transient atomic scattering factors from diffraction spectra and to validate them against a microscopic model that explicitly generates the required metastable $3d$ vacancy configurations.

We have also measured the same effect in a two-color X-ray pump X-ray probe experiment; details have been omitted in the main text, but are all collected in appendix D. At the maximum enhancement, the resonant part of the spectrum grows by almost a factor of 20 compared to the unperturbed value. The two-color experiment shows that decoupling the pump and probe beams enables a more efficient ionization of the $2p_{3/2}$ electrons and more effective probing of the transient state, ultimately yielding more accurate control of the scattering properties of the atoms.

Establishing a reliable way to control and enhance the scattering properties of atoms

could be of great benefit to the field of Single-Particle Imaging (SPI). The main aim of SPI is to reconstruct the 3D structure of non-crystalline objects such as single biomolecules or nanoparticles with atomic resolution. In this context, even with high-repetition-rate XFELs and advanced data analysis routines [78], the goal remains unreachable due to the weak diffraction signals [79]. In addition to the weak scattering signal, sample delivery techniques – combined with other noise sources – further compromise the signal-to-noise ratio [80, 81]. A typical delivery method for SPI is through a gas jet, which can cause significant background noise due to the scattering of the jet itself. Alternative methods, such as helium electrospray, have been developed to mitigate this issue, but they still introduce some level of background noise. The combination of weak scattering signals and background noise makes it extremely challenging to achieve high-resolution 3D reconstructions of randomly oriented objects [82], with the best currently achieved resolution on biological samples being 6 nm [79]. The prospect of exploiting transient resonances in scattering schemes to enhance the diffraction signal – and thereby improve the signal-to-noise ratio – in SPI has already been recognized by the community. Recent studies highlight this concept as a promising route to overcome current limitations and potentially yield considerable improvements in the achievable resolution [80].

The direct application of the ERES principle to SPI needs to overcome one main limitation. In this thesis, the enhancement of the scattering factors has been demonstrated in the soft X-ray regime, targeting the $2p_{3/2} - 3d$ resonance. The wavelength used here – 1.33 nm – is too long and therefore not suitable for crystallographic applications. However, the transient scattering enhancement mechanism is expected to operate in the hard X-ray regime, targeting K-edges, provided that few-femtosecond to attosecond pulses are available, needed to match the short lifetime of the relevant transient resonances. With these settings and leveraging two-color control, the effective enhancement could yield values of f_2 reaching the hundreds under favorable conditions. Such operation would open routes to resonance-assisted novel methods in SPI and to state-selective scattering schemes that exploit transient increases in f_2 for contrast and resolution.

Overall, the high-quality results presented in this work are a stepping stone towards the control of the scattering properties of matter at the atomic level. These capabilities open up exciting possibilities for future research in the field of nonlinear X-ray science and its applications in structural biology and materials science.

Appendix A

Scattering factor of a two-level system

Let us consider an ensemble of atoms with concentration n . Each atom is described as a two-level system with ground state $|g\rangle$ and excited state $|e\rangle$. The system has one resonant frequency ω_0 , a total decay rate γ_2 , and a spontaneous decay rate Γ_{sp} . If we consider the interaction with an external field of frequency ω – and corresponding wavelength λ – defined in terms of its Rabi frequency Ω_s , the evolution of the system is described by the optical Bloch equations [83]. In particular, the coherence element (ρ_{eg}) of the density matrix of a single atom evolves, in the retarded time frame τ , following:

$$\frac{\partial \rho_{eg}(\tau)}{\partial \tau} = -i\omega_0 \rho_{eg}(\tau) - i\Omega_s(\tau)(\rho_{ee} - \rho_{gg}) - \frac{\gamma_2}{2} \rho_{eg}(\tau). \quad (\text{A.1})$$

We assume that the population of the ground (ρ_{gg}) and excited state (ρ_{ee}) are stationary. We can then Fourier transform equation A.1 to obtain:

$$-i\omega \hat{\rho}_{eg}(\omega) = -i\omega_0 \hat{\rho}_{eg}(\omega) - i\hat{\Omega}_s(\omega)(\rho_{ee} - \rho_{gg}) - \frac{\gamma_2}{2} \hat{\rho}_{eg}(\omega). \quad (\text{A.2})$$

By simple algebra and defining the detuning parameter between the incoming field frequency and the resonant frequency of the two-level system $\Delta\omega = \omega - \omega_0$, one can obtain the expression for the coherence element:

$$\hat{\rho}_{eg}(\omega) = \frac{i(\rho_{ee} - \rho_{gg})}{i\Delta\omega - \frac{\gamma_2}{2}} \hat{\Omega}_s(\omega). \quad (\text{A.3})$$

On the other hand, the field propagates through the ensemble of atom and evolves

following Maxwell's equation:

$$\left[\frac{\partial}{\partial z} - i \frac{k_0}{2} \chi(\omega) \right] \hat{\Omega}_s(\omega) = \left(i \frac{3}{8\pi} \lambda^2 \Gamma_{sp} n \right) \hat{\rho}_{eg}(\omega) \quad (\text{A.4})$$

where $k_0 = 2\pi/\lambda$ is the wave vector of the field and χ the susceptibility of the material. We can now substitute $\hat{\rho}_{eg}$ in equation A.4 with equation A.3, obtaining:

$$\left[\frac{\partial}{\partial z} - i \frac{k_0}{2} \chi(\omega) \right] \hat{\Omega}_s(\omega) = -\frac{3}{8\pi} \lambda^2 \Gamma_{sp} n \frac{\rho_{ee} - \rho_{gg}}{i\Delta\omega - \frac{\gamma_2}{2}} \hat{\Omega}_s(\omega). \quad (\text{A.5})$$

The right side of equation A.5 is an extra source of radiation, thus can be expressed in terms of a new susceptibility term (χ_T). With this definition equation A.5 becomes:

$$\left[\frac{\partial}{\partial z} - i \frac{k_0}{2} \chi(\omega) - i \frac{k_0}{2} \chi_T(\omega) \right] \hat{\Omega}_s(\omega) = 0, \quad (\text{A.6})$$

with:

$$\chi_T(\omega) = \frac{3}{8\pi^2} \lambda^3 n \Gamma_{sp} \frac{-i(\rho_{ee} - \rho_{gg})}{i\Delta\omega - \frac{\gamma_2}{2}}. \quad (\text{A.7})$$

This last equation is the transient contribution to the susceptibility of every atom due to the interaction with the external field.

The atomic scattering factor (f) is intrinsically related to the susceptibility:

$$\chi = \frac{n r_e \lambda^2 f}{\pi}. \quad (\text{A.8})$$

Therefore, we can find the transient contribution to the atomic scattering factor (f_T) by substituting χ_T (equation A.7) in equation A.8, leading to:

$$f_T(\omega) = -\frac{3}{8\pi} \frac{\lambda}{r_e} \Gamma_{sp} (\rho_{ee} - \rho_{gg}) \frac{\Delta\omega - i\gamma_2/2}{\Delta\omega^2 + (\gamma_2/2)^2}. \quad (\text{A.9})$$

This last equation is the atomic scattering factor of an unbalanced two-level system, which we used in our simulation codes as mentioned in the main text.

Appendix B

Structural evolution of the multilayer¹

To verify that the multilayer structure remains unchanged during the pulse, we performed simulations with the hybrid code XTANT-3, which combines a Monte Carlo method for modeling photon-induced electron kinetics, the Boltzmann equation for low-energy electrons populating the valence and conduction bands, a transferable tight-binding method to calculate the transient electronic structure and interatomic forces, and molecular dynamics to trace atomic motion [84]. The Density Functional based Tight Binding (DFTB) parameterization matsci-0-3 is used to model Cu and Si atoms [85]. As a computationally tractable model that provides realistic insights, we employed a system consisting of a crystalline Cu layer (144 atoms in the fcc structure, 1.4 nm thick) and an amorphous Si layer (144 atoms, 2.4 nm thick) with periodic boundary conditions. The system was relaxed to the ground state, thermalized, and then irradiated with a 15 fs FWHM pulse at 950 eV photon energy with absorbed doses of 2 and 40 eV atom⁻¹—corresponding to pump pulse intensities of 2.5×10^{13} W cm⁻² and 5.0×10^{14} W cm⁻², respectively. A few snapshots of the structure evolution are shown in figure B.1.

Figure B.2 (a) shows the absolute mean displacement of atoms within the bulk of the layer, while figure B.2 (b) demonstrates the projections of the Mean Square Displacement (MSD). The projection on the Z axis identifies the motion of the interfacial layer. The displacements of Cu atoms are small, even though the interfacial layer moves as a whole (MSD of Cu atoms along Z is larger than along other axes). The displacements of Si atoms along all axes, including the direction normal to the interface, are larger, as

¹The author thanks Nikita Medvedev for his instrumental help in performing the simulations and providing the results presented in this appendix.

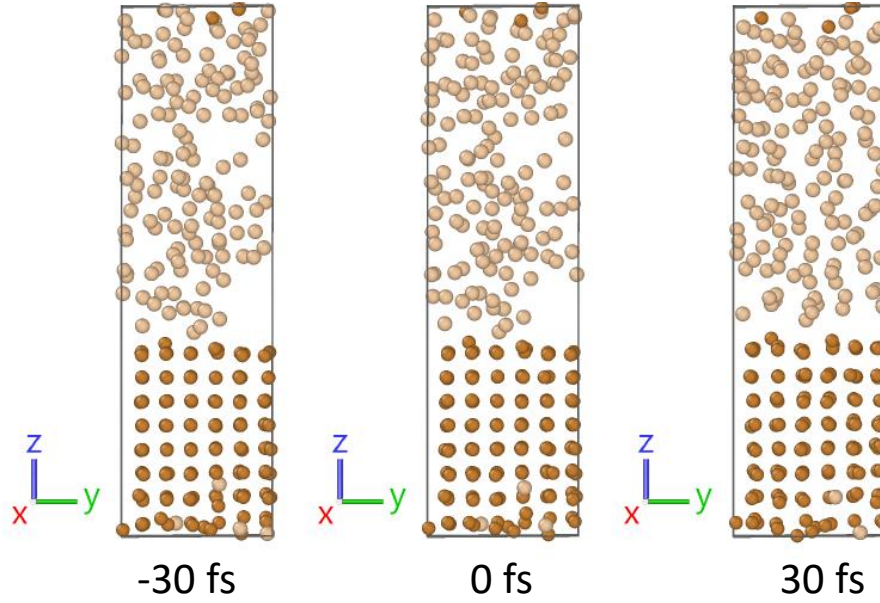


Figure B.1: Multilayer structure simulated with XTANT-3 code. Snapshots of the evolution for the case of irradiation with an FEL pulse with 950 eV photon energy, 15 fs FWHM, absorbed dose 40 eV atom^{-1} . Dark brown atoms are copper, light brown are silicon.

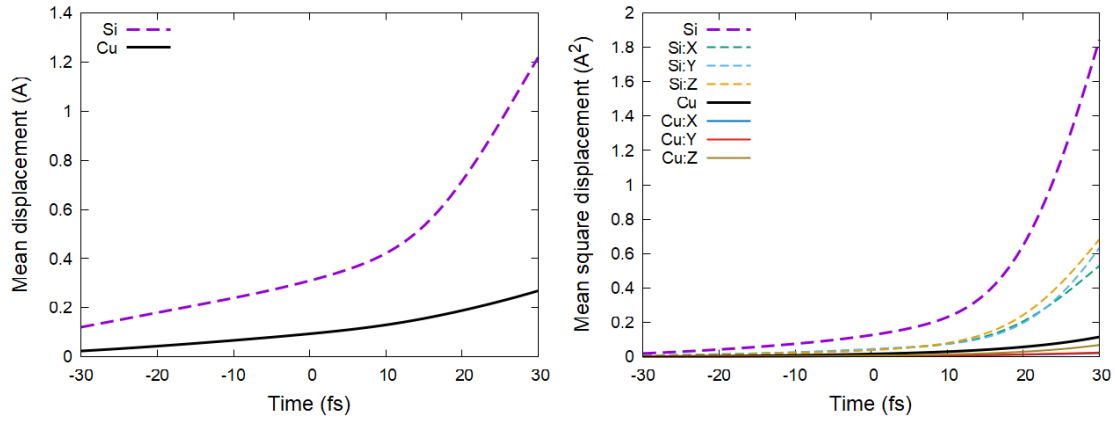


Figure B.2: Atomic displacements in Cu/Si multilayer. Atomic displacement in the Cu/Si multilayer when excited by an FEL pulse with 950 eV photon energy, absorbed dose 40 eV atom^{-1} . (a) Mean atomic displacements within the whole volume for Cu and Si subsystems. (b) Total and projected mean square displacements. Directions x, y, and z correspond to the axes displayed in figure B.1

it behaves more like a liquid. However, both the mean and mean square displacements within ± 30 fs—corresponding to when the FEL pulse interacts with the system—are only ≈ 1 Å for Si atoms, whereas for Cu atoms they are < 0.3 Å.

To estimate the behavior of the Cu/B₄C system, we use the following approximation: we employ the same tight-binding parameters and structure as for Cu/Si, but artificially set the mass of Si atoms equal to the mass of boron. This way, we can accelerate the dynamics (for lighter “boron” atoms versus silicon ones) and mimic the response of B₄C to irradiation. Then, we simulate the irradiation of this multilayer target with the same laser pulse as above. Lighter “boron” atoms move faster upon irradiation; however, the inter-layer surface does not appear significantly different from the previous case. We conclude that the interface roughness is mainly defined by the behavior of the heaviest component, copper. As the copper atoms’ movement during the FEL pulse at the studied absorbed doses (up to 40 eV atom⁻¹) is below 1 Å, we conclude that changes in the interface roughness of a multilayer system may be neglected.

Appendix C

X-ray Gas Monitors: set up and calibration

XGMs are devices used to determine the position and energy of the X-ray beam by exploiting photo-ionization processes of noble gases. The gas chamber is typically filled with Ne, Ar, or Kr at a low pressure of about 10^{-5} mbar. When the FEL beam propagates through the chamber, it ionizes the rare gas atoms. The products of this reaction—ions and electrons—are then accelerated by an electric field towards the detection plates, and the electric currents originating from the plates are outcoupled from the vacuum. In this way, the measured ion and electron currents are proportional to the energy of the FEL beam.

Two main units compose the XGMs installed at the European XFEL: the X-ray Gas Monitor Detector (XGMD) and the Huge Aperture Open Multiplier (HAMP). The XGMD is an upgrade of existing Gas Monitor Detectors (GMDs) typically working in the XUV range [86], adapted towards X-ray radiation. The HAMP is the most recent development, which allows single-shot resolution even when using extremely hard X-rays [62, 87]. The key difference between the two is that the HAMP amplifies the ion signal to an electronic signal via a multiplier stage. This stage is fundamental for correct operation at very short wavelengths, where the photo-ionization cross-section is greatly reduced, and to avoid secondary effects from photo-electrons, the gas pressure must be kept low. The combination of these two devices allows a high degree of flexibility, making it possible to measure the absolute intensity of largely different XFEL pulses.

During our transient scattering experiment, we explored a wide range of undulator configurations and GATT settings, resulting in XFEL pulse energies spanning more than one order of magnitude. Because of this, the inherent flexibility of the XGMs was a key factor in recording meaningful data at widely different pulse energy conditions. Nevertheless, to ensure the correctness, reproducibility, and comparability across different measurements, the XGMs needed to be properly set up and calibrated. The only parameter we adjusted was the voltage responsible for the accelerating electric field that pushes ions towards the detecting Faraday cups. This voltage had to be set proportionally to the pulse energy, so that for any beam energy, the XGM responds linearly. Once the voltage is set, if the beam energy changes significantly, the XGM might fall into a nonlinear regime, meaning that the reading for the new pulse energy would not be comparable with previous measurements.

Following these arguments, we established a precise routine for our measurements. First, the undulators and GATT were set to the required conditions. Then, the XGM voltage was tuned to an appropriate value. Subsequently, a measurement with the SCS hutch shutter closed was recorded. This measurement was later used in the offline data analysis to calibrate the XGM reading as explained in the next section. At this point, the actual measurement could be performed. The details are summarized in section 3.1.3 on page 27. Once we completed the data acquisition, we could move to the next condition and repeat the measurement routine step by step.

C.1 XGM calibration

To understand why the calibration of the XGMs is crucial, we must first understand their operational principle. The complete description of the XGMs at the European XFEL is reported in [62]; here, we present a brief summary. Let us recall that each XGM is composed of two units: the XGMD and the HAMP. The XGMD outputs two signals: the first is a slow photo-ion current, measured as a low-pass filtered average with a time constant of about tens of seconds. This signal is absolutely calibrated to the photon flux at the PTB. Therefore, the average photon flux can be determined in absolute terms, though not for single shots. The second signal is a fast, pulse-resolved photo-electron current, which is not absolutely calibrated. This fast signal is averaged to the same time scale as the slow ion current, allowing it to be cross-calibrated to the photon flux to obtain

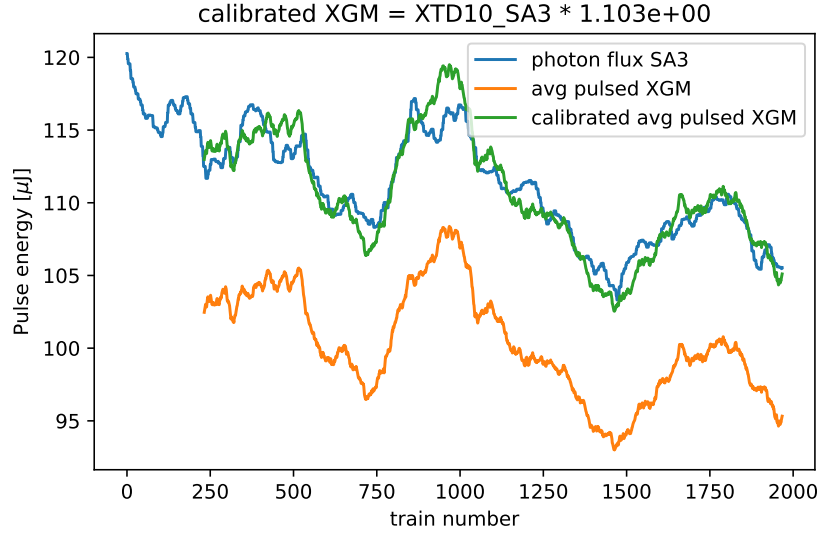


Figure C.1: Calibration of the XGM signal. The averaged pulse resolved fast signal (orange line) is multiplied by a factor F to match the absolutely calibrated slow signal (blue line). This results in the calibrated signal, which is here shown via its average (green line).

an absolutely calibrated, pulse-resolved signal. The HAMP measures only the photo-ion current, which is also a fast, pulse-resolved signal that can be calibrated to the slow photo-ion current of the XGMD in the same manner described above. An example of such calibration is shown in fig. C.1. The software-averaged fast signal (“avg pulsed XGM”) is multiplied by a constant factor, in this case $F = 1.103$, to match the absolutely calibrated slow signal (“photon flux SA3”). This operation yields the absolutely calibrated pulse-resolved signal (“calibrated avg pulsed XGM”), shown in the figure by its average.

During offline data analysis, we found that only the XTD10 XGM – see fig. 3.1 on page 22 – was fully reliable for the entire experiment. The reason is that this detector is upstream of the GATT; therefore, it required voltage adjustment and recalibration only when the undulator configuration changed, and those operations were correctly performed. In contrast, the XGM located in the SCS hutch required voltage adjustments every time the transmission value was modified; unfortunately, this was not done for all measurements. Moreover, under certain specific conditions (e.g., many undulator cells open and/or high attenuation), the signal was too weak to be detected. To maintain consistency in our choice of signals, we decided to rely solely on measurements from the XTD10 XGM and disregard the downstream detector. The final factors needed to obtain

the absolute energy for every pulse are the beamline transmission (approximately 0.33) and the GATT attenuation factor.

Appendix D

Two-color soft X-ray experiment

As briefly mentioned in the text, here we discuss the methods and results of the two-color X-ray pump X-ray probe measurements. The experimental setup does not change with respect to what is described in the main text. The key difference is that here we fully leverage the possibility of creating 2 distinct X-ray pulses with different central photon energies and a variable time-delay [61]. The probe beam has a central wavelength of 929 eV, a FWHM of 5 eV, and is produced using only 8 of the 11 available undulator cells. This adjustment is needed to limit the beam energy even at full GATT transmission. To probe only the dynamics induced by the pump beam, it is necessary that the intensity of the probe beam remains below the threshold of inducing the transient effect, even without attenuation. All 10 available undulator cells contribute to the generation of the pump beam, which has its central wavelength at 945 eV and a FWHM of about 10 eV. The time-delay between the two pulses is set to 0 fs. To normalize out the effect of the probe beam, each dataset is composed by a cold probe-only measurement, followed by a two-color pumped measurement. Each couple of measurements is taken at a fixed GATT transmission.

Before discussing the data, it is worth stressing that the two-color results are not a simple extension of the one-color measurements because the excitation and probing conditions differ. In the one-color experiment, the focal spot on the sample was adjusted to 20 μm . In the two-color configuration, the pump is also nominally focused to 20 μm , but its source is located downstream of the probe, so its waist lies closer to the sample and the probe has begun to diverge. Consequently, the probe beam is larger at the interaction re-

gion, and the signal contains contributions from both pumped and unpumped portions of the film. The effective fluence needed to produce a given enhancement is therefore considerably higher than in the one-color case. For this reason, we cannot quantitatively compare the one- and two-color datasets directly; we will simply point out similarities and differences between them.

D.1 Results

Figure D.1 collects the results of the measurement, panel (a) shows the cold (dashed) and pumped (solid) curves, while panel (b) shows the ratio between the two. Figure D.2 presents only the cold measurements, and confirms that all measurements are comparable. The marked intensity refers to the pump beam, deduced by the difference in pulse energy between the pumped and cold measurements. All spectra are measured in a single CCD camera accumulation (except for those at $4.7 \times 10^{14} \text{ W cm}^{-2}$ and $8.8 \times 10^{14} \text{ W cm}^{-2}$) and are averaged over a variable number of single pulses, ranging from 125 for the low intensities to 25 for the highest. For this reason, there are no error bars in figure D.1, except for the very tight ones at the two lowest intensities. Because of the limited quantity of available data resulting from scarce sample availability, one should not interpret the small features that give structure to the peak. To aid interpretation of the general trend, a Savitzky-Golay filter is applied to the right panel, which shows the ratio between the pumped and cold measurements. The filter uses a 2nd degree polynomial and a window size of 30, note that the total number of points in the figure is 77.

In the two lowest intensity curves, the enhancement is similar to what is measured in the one-color experiment at corresponding intensities. The measurement at $4.7 \times 10^{14} \text{ W cm}^{-2}$ presents an enhancement ratio of almost 2, whereas the measurement at a similar intensity ($3.5 \times 10^{14} \text{ W cm}^{-2}$) in the main text shows an increase of a factor of 2.4 compared to the lowest intensity. The measurement at $8.8 \times 10^{14} \text{ W cm}^{-2}$ in the two-color experiment presents an enhancement ratio of 4, whereas the similar intensity one-color measurement ($8.0 \times 10^{14} \text{ W cm}^{-2}$) shows an increase of a factor of 6. At higher intensities, the trend differs between the one-color and two-color experiments. Contrary to the one-color case, where the maximum enhancement is reached at $8.0 \times 10^{14} \text{ W cm}^{-2}$, the two-color measurement shows its highest growth at $8.1 \times 10^{15} \text{ W cm}^{-2}$. The optimal pumping intensity threshold is one order of magnitude larger in the two-color case.

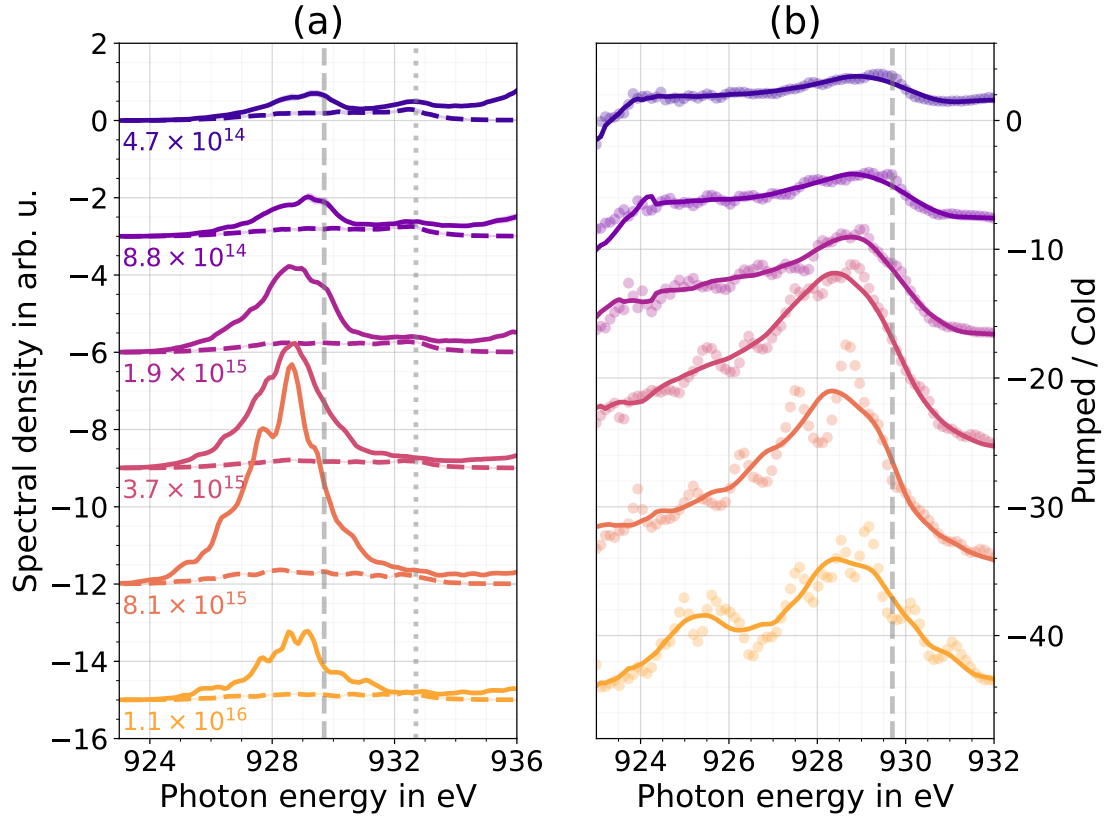


Figure D.1: Two-color measurement of the spectrally resolved transient enhancement of the scattering strength of Cu atoms. (a) Cold (dashed) and pumped (solid) experimental measurement of the spectrally resolved scattered radiation from the multilayer structures around the Cu- L_{α} resonance for different pumping intensities (in W cm⁻²). The different spectra are offset vertically by -3 arb. u. for clarity. (b) Corresponding ratio between the pumped and cold measurement. The dots are the data points, while the solid line is a Savitzky-Golay smoothing. The data are offset vertically by 9. The gray dashed and dotted lines mark the position of the Cu- L_{α} resonance (929.7 eV) and the Cu- L_3 edge (932.7 eV) respectively, at low intensity.

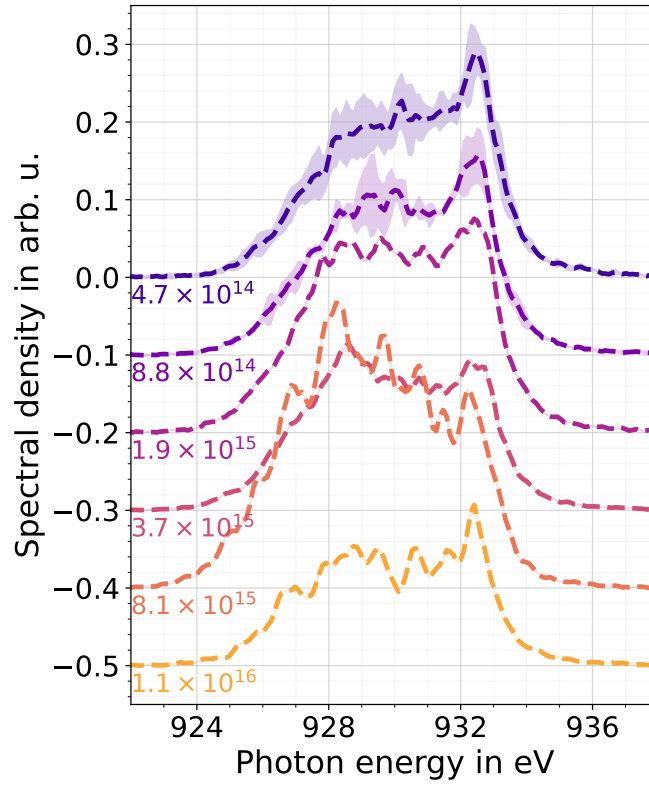


Figure D.2: Zoom in of the cold measurements from the two-color dataset. Cold experimental measurement of the spectrally resolved scattered radiation from the multilayer structures around the $\text{Cu-}L_{\alpha}$ resonance for different pumping intensities (in W cm^{-2}). The different spectra are offset vertically by -3 arb. u. for clarity. The data is the same as the dashed lines in figure D.1.

Beyond this value, the peak decreases and broadens, similar to the one-color trend.

D.2 Discussion

Currently, we do not have a complete theoretical model for simulating the two-color experiment; therefore, we cannot investigate the origins of the differences between the two datasets quantitatively. We will limit ourselves to reporting a few hypotheses and effects that might be at play in the two-color case.

A main difference between the one-color and two-color experiments is the photon energy of the pump pulse. In the one-color case, the pumping is realized by the spectral window of the beam above the Cu- L_3 edge (932.7 eV), where the absorption cross-section is maximum, ensuring the most efficient ionization. In the two-color case, the pump beam has its central wavelength at 945 eV and a bandwidth of about 10 eV; here, the absorption cross-section is already decreased by about 16% [88].

Let us start by analyzing the low intensity case ($I < 10^{15} \text{ W cm}^{-2}$). In this regime, only low charged states are present. In [42], the authors show that almost 70% of atoms are not ionized, whereas roughly 30% are singly ionized. This means the enhancement is dictated by the number of ionized atoms; therefore, the difference in absorption cross-section is the crucial factor determining how many atoms develop a transient resonance. A higher absorption cross-section leads to a larger population of ionized atoms, resulting in a more pronounced transient modification of the scattering factor. In other words, in the low intensity limit, the transient enhancement is ultimately governed by the number of Cu atoms with holes in the $3d$ shell, generated from the decay of the ionized $2p_{3/2}$ electrons and the subsequent cascade mechanism. Therefore, a higher ionization cross-section will yield a stronger enhancement. This explanation might partially account for the small reduction in enhancement ratio at low intensities.

The case at higher intensities ($I > 10^{15} \text{ W cm}^{-2}$) is more complicated to analyze because nonlinear effects become more relevant. Without a defined theoretical model, it is difficult to identify the main mechanisms at play. We note that the difference in pumping conditions—probe beam waist being larger than the pump beam waist, thus probing a mixture of pumped and unpumped regions—might be responsible for the shift of optimal pumping intensity to higher values.

Finally, it is unsurprising that the two-color experiment produces a stronger atomic

scattering factor enhancement. Using two different pulses—one to prepare the transient state and one to probe it—enables more precise control of the experimental conditions. To understand why, consider the one-color experiment. Due to the stochastic nature of the SASE process and the proximity in energy of the spectrum above and below the Cu- L_3 edge, situations can arise in which a single pulse comprises strong components above the edge but lacks components below, or conversely, lacks components above the edge. Both scenarios are not observable in our measurement: in one case, the transient state is not probed, and in the other, it is not created. Such instances reduce the overall signal, which comes from accumulation over many shots, as described in the main text. When considering the two-color experiment, these limiting scenarios are less probable. In particular, the case where there is no component above the edge is completely avoided. These arguments explain why the measured enhancement is higher in the two-color experiment and confirm that decoupling the pump and probe pulses is advantageous.

Appendix E

Supplementary figures

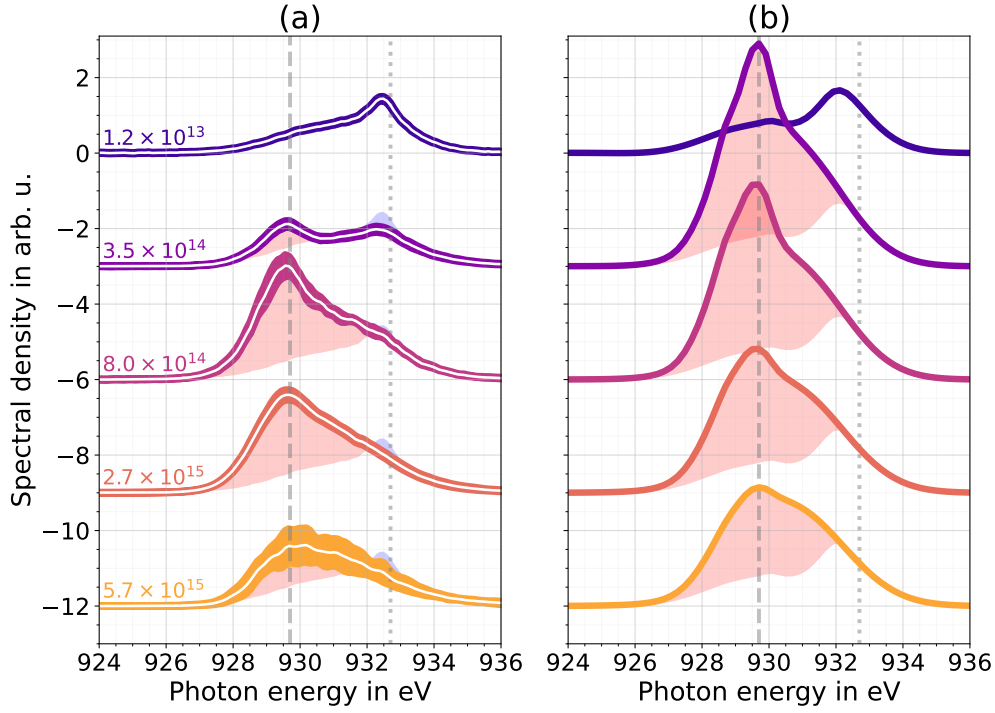


Figure E.1: Comparison of experimental data and self-consistent simulation with shifted Bragg angle. (a) Experimental measurement of the spectrally resolved scattered radiation from the multilayer structures around the Cu- L_α resonance for different intensities (in W cm⁻²). The different spectra are offset vertically by -3 arb. u. for clarity. The colored region around each spectrum represents the 99% confidence interval. The shaded red (or blue) regions correspond to stronger (or weaker) scattered intensity with respect to the cold reference spectrum measured at the low intensity 1.2×10^{13} W cm⁻². The dashed and dotted lines mark the position of the Cu- L_α resonance (929.7 eV) and the Cu- L_3 edge (932.7 eV) respectively, at low intensity. (b) Corresponding forward simulation of the reflectivity spectrum. The Bragg angle fixed in the simulation is shifted by 0.05 deg with respect to the results presented in the main text (fig. 3.14 on page 45).

Acknowledgments

Let me start by expressing my gratitude to my supervisor, Prof. Dr. Nina Rohringer. From our first virtual meeting I had a great impression of her, her positive attitude, and her enthusiasm for science. Such expectations were always fulfilled. My doctoral journey started as a theoretical project, but she soon realized that my bread and butter is experimental work, and she did not hesitate a second to pivot my project towards hands-on work, of this I will always be grateful. She has been always encouraging and supportive, granting me the freedom to explore my ideas, participate in many experiments – even not directly connected with my research – and travel to many conferences to share my findings and build a strong network. She has taught me also outside the scientific realm, thanks to her, I have jumped back on skies for the first time in many, many years. Looking back at my journey, starting from day one she has been very welcoming, and she has not stopped to be so until now. Thank you Nina.

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experiments. Tae and Doaa, we shared our journey only for a brief period, I could only wish to have met you way before, but I am grateful for the time we had together. Last, but not least, I want to thank Nicola. Her support and friendship have been a fundamental part of this journey. Every bureaucratic challenge become just a 10-minute task with her. I would need another 100 pages to thank her for all the phone calls that she has kindly done on my behalf. I will always remember her signature “Schön guten tag! Hier spricht Nicola Baark”.

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D. R.

Acronyms

ASE	Amplified Spontaneous Emission.
DFT	Density Functional Theory.
DFTB	Density Functional based Tight Binding.
ERES	Enhanced Resonant Elastic Scattering.
ESASE	Enhanced Self Amplified Spontaneous Emission.
FEL	Free Electron Laser.
GATT	Gas ATTenuator.
GMD	Gas Monitor Detector.
HAMP	Huge Aperture Open Multiplier.
hRIXS	Heisenberg-RIXS.
KB	Kirkpatrick-Baez.
LCLS	Linac Coherent Light Source.
MSD	Mean Square Displacement.
PTB	Physikalisch-Technische Bundesanstalt.
RIXS	Resonant Inelastic X-ray Scattering.
RXS	Resonant X-ray Scattering.

RSA Reverse Saturable Absorption.

SEM Scanning Electron Microscope.

SASE Self Amplified Spontaneous Emission.

SPI Single-Particle Imaging.

SCS Spectroscopy and Coherent Scattering.

VLSG Variable Line Spacing Grating.

WDM Warm Dense Matter.

XES X-ray Emission Spectroscopy.

XFEL X-ray Free Electron Laser.

XGM X-ray Gas Monitor.

XGMD X-ray Gas Monitor Detector.

XRD X-ray Resonant Diffraction.

XRR X-ray Reflectivity.

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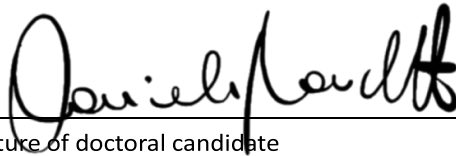
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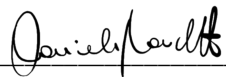
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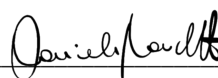
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