



DEPARTMENT OF
PHYSICS

PRECISION BENCHMARKING OF ATOMIC DATA OF HIGHLY CHARGED IONS

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Master in Physics Engineering

DOCTORATE IN ATOMIC AND MOLECULAR PHYSICS

NOVA University Lisbon

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To my wife.

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ABSTRACT

Highly Charged Ions (HCI) play an essential role in astrophysics, plasma physics, and fusion research, as their emissions are used as key diagnostic tools for evaluating the physical conditions of a plasma. This thesis is devoted to advance and refine the atomic data of HCI for these interdisciplinary areas. From the experimental side, an Electron Beam Ion Trap (EBIT) was used to produce, confine, and probe several charge states of different HCI specimens, observing their emissions in the Extreme-Ultraviolet (EUV) and X-Ray energy ranges. All the observations benchmark previously non-measured theoretical data and new calculations developed on the theoretical side of this thesis.

Oxygen is a ubiquitous element in astrophysical observations. Its $K\alpha$ emissions near the collisional excitation threshold, as well as the Dielectronic Recombination (DR) KLn satellite structure of its He-like charge state, were measured for the first time. A time-dependent Collisional Radiative Model (CRM) was developed to model the experimental observations. This model was shown to correctly describe the dynamics of the $1s2s\ ^3S_1$ metastable state, and its results were used to extract the z-line emissions from the total $K\alpha$ emission. The dielectronic recombination and excitation structures near the excitation threshold were benchmarked against both literature and new state-of-the-art configuration-interaction calculations. A similar setup was also employed in He-like calcium. For this case, both the cross-sections of the collisional processes and the line positions of the DR satellites were tabulated. The latter could be essential for future high-resolution X-Ray space missions, as He-like calcium lines can be used as an alternative to Ne-like iron lines.

Emissions lines of Ne-like krypton for both DR and excitation structures were also studied and benchmarked. The Non-Negative Matrix Factorization (NNMF) technique was shown to be viable for decomposing unresolved emission structures. Moreover, the $n = 5$ intrashell emissions of open $4f$ -shell ions of tungsten were also studied. Observations were made for W^{10-27+} . The NNMF technique was used to obtain individual spectra of every charge state, and the respective emissions were tabulated, and compared with new calculations. Emissions of these elements are vital in the development of X-ray diagnostics for tokamak plasmas, as both krypton and tungsten constitute contamination with charge state distributions given by the plasma local conditions.

RESUMO

Iões Altamente Carregados (HCI) desempenham um papel essencial em astrofísica, física de plasmas e fusão nuclear, uma vez que as respectivas emissões são utilizadas como ferramentas de diagnóstico para avaliar as condições físicas de um plasma. Esta tese é dedicada ao avanço e refinamento dos dados atômicos dos HCI nestas áreas interdisciplinares. Do ponto de vista experimental, foi utilizado um EBIT (do inglês *Electron Beam Ion Trap*) para produzir, confinar e analisar vários estados de carga de diferentes elementos, observando as suas emissões nas gamas de energia do Extremo Ultravioleta (EUV) e dos Raios-X. Todas as observações serviram para validar teorias previamente não medidas e novos cálculos desenvolvidos nesta tese.

Oxigênio é um elemento fundamental em observações astrofísicas. As suas emissões $K\alpha$ próximas do limiar de excitação colisional, bem como a estrutura dos satélites DR KLn do seu estado de carga do tipo hélio, foram medidas pela primeira vez. Foi desenvolvido um modelo de colisão radiativa (CRM) dependente do tempo para modelar as observações experimentais. Demonstrou-se que este modelo descreve corretamente a dinâmica do estado metastável $1s2s\ ^3S_1$, sendo os seus resultados utilizados para dissociar as emissões da linha z das restantes transições $K\alpha$. As estruturas de DR e excitação próximas do limiar foram comparadas tanto com a literatura como com novos cálculos de interação de configuração. Uma configuração experimental semelhante foi também aplicada ao cálcio do tipo hélio. Para este caso, foram tabeladas tanto as secções eficazes dos processos colisionais como as posições das linhas dos satélites DR. Estas últimas poderão ser essenciais para futuras missões espaciais de Raios-X de alta resolução, uma vez que as linhas de cálcio do tipo hélio podem servir como alternativa às linhas de ferro do tipo néon.

Foram também estudadas e comparadas as emissões de criptón do tipo néon, tanto para as estruturas de DR como para as de excitação. Nesta experiência, demonstrou-se a viabilidade da utilização da técnica de Non-Negative Matrix Factorization (NNMF) para decompor estruturas de emissão não resolvidas. Além disso, foram estudadas as emissões intrashell de $n = 5$ dos iões de camada $4f$ aberta de tungsténio. As observações foram realizadas para todos os estados de carga entre W^{10+} e W^{27+} . A técnica NNMF foi utilizada para obter os espectros individuais de cada estado de carga, sendo depois as respectivas

emissões tabeladas e comparadas com novos cálculos. As emissões destes elementos são fundamentais para o desenvolvimento de diagnósticos de Raios-X para plasmas de tokamak, uma vez que tanto o criptón como o tungsténio constituem impurezas cuja distribuição de estados de carga é determinada pelas condições locais do plasma.

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ACRONYMS

ADC	Analog to Digital Converter (<i>pp.</i> 70 , 75)
AFG	Arbitrary Function Generators (<i>p.</i> 74)
ASD	Atomic Structure Database (<i>p.</i> 80)
BMP	Beam Position Monitors (<i>p.</i> 58)
CC	Close-Coupling (<i>p.</i> 37)
CCD	Charge Coupled Device (<i>p.</i> 7)
CE	Collisional Excitation (<i>p.</i> 10)
CEQ	Coronal Equilibrium (<i>p.</i> 5)
CI	Collisional Ionization (<i>p.</i> 10)
CRM	Collisional Radiative Model (<i>p.</i> 4)
CSF	Configuration State Function (<i>p.</i> 21)
CW	Coulomb-Wave (<i>p.</i> 36)
CX	Charge Exchange (<i>p.</i> 10)
DC	Dielectronic Capture (<i>p.</i> 29)
DR	Dielectronic Recombination (<i>p.</i> 10)
DW	Distorted-wave (<i>p.</i> 36)
EA	Excitation-Autoionization (<i>p.</i> 35)
EBIS	Electron Beam Ion Source (<i>p.</i> 57)
EBIT	Electron Beam Ion Trap (<i>p.</i> 1)
ECRIS	Electron Cyclotron Resonance Ion Source (<i>p.</i> 57)
EUV	Extreme Ultraviolet (<i>p.</i> 11)
FAC	Flexible Atomic Code (<i>p.</i> 38)
GRASP	General Relativistic Atomic Structure Package (<i>p.</i> 40)

HCI	Highly Charged Ion (<i>p. 1</i>)
ITER	International Thermonuclear Experimental Reactor (<i>p. 11</i>)
LTE	Local Thermodynamical Equilibrium (<i>p. 5</i>)
MBPT	Many Body Perturbation Theory (<i>p. 22</i>)
MCDF	Multiconfiguration Dirac-Fock (<i>p. 22</i>)
MCDFGME	Multiconfiguration Dirac-Fock General Matrix Elements (<i>p. 40</i>)
MCHF	Multiconfiguration Hartree-Fock (<i>p. 22</i>)
MCP	Microchannel Plate (<i>p. 58</i>)
NNMF	Non-Negative Matrix Factorization (<i>p. 121</i>)
PHA	Pulse-Height-Analysis (<i>p. 75</i>)
PW	Plane-wave (<i>p. 36</i>)
QED	Quantum Electrodynamics (<i>p. 38</i>)
RE	Resonant Excitation (<i>p. 10</i>)
REDA	Resonant-Excitation Double-Autoionization (<i>p. 35</i>)
RF	Radio Frequency (<i>p. 57</i>)
RK4	Fourth order Runge-Kutta (<i>p. 48</i>)
RM	R-Matrix (<i>p. 37</i>)
ROI	Region Of Interest (<i>p. 78</i>)
RR	Radiative Recombination (<i>p. 10</i>)
SDD	Silicon Drift Detector (<i>pp. 8, 69</i>)
SOSA	Spin-Orbit Split Array (<i>pp. 39, 144</i>)
TDC	Time-Delay-Converters (<i>p. 75</i>)
TES	Transition Edge Spectrometer (<i>p. 8</i>)
TSR	Test Storage Ring (<i>p. 32</i>)
UHV	Ultra-High Vacuum (<i>p. 35</i>)
UTA	Unresolved Transition Array (<i>pp. 39, 144</i>)

INTRODUCTION

The cornerstone of this PhD project is centered on the study of Highly Charged Ion (HCI), both from the theoretical and experimental standpoints. The aim is to benchmark state-of-the-art atomic calculations experimentally, while also providing atomic data that is valuable for other scientific areas like astrophysics, plasma physics, nuclear physics or material science. The thesis is organized as follows: first I give an introduction to HCI physics, and describe modern applications of HCI, highlighting the importance of precise atomic data for each case. Then, Chapter 2 contains the current theoretical formalisms that are used to predict its proprieties. The following Chapter 3 describes the modern experimental methods that are used to produce, trap and probe them, giving emphasis to the instrument employed here that is the Electron Beam Ion Trap (EBIT). The contributions of this thesis to each scientific areas are presented in the final chapters.

1.1 Highly Charged Ions

Most of the observable matter in a universe is in the hot plasma state, consisting of highly ionized ions. This is due to the extreme energetic conditions present, for example, in stars, accretion disks and supernova remnants. These ions, often referred to as HCI, are atoms stripped to a few electrons due to collisions with other ions, photons, or free electron. Since mostly neutral or lowly ionized matter exists on Earth naturally, such atomic systems can only exist through laboratory setups. Moreover, although photon emissions of HCI are ubiquitous in the universe, its wavelengths are mainly in X-ray region, which is absorbed in the atmosphere. Therefore, the study of these atomic systems is intrinsically connected with the technological development for ionizing and storage these ions.

Before fully understand the importance of HCI, we need to describe its nomenclature [2]. An ion is defined by its atomic number Z and its electric charge $Q = Z - N_e$, where N_e is the number of electrons. Additionally, its isotopic species may also be required to specify the atomic system. Sometimes the charge state of an ion is indicated with roman numerals. For example, oxygen I corresponds to neutral oxygen, while oxygen II and oxygen III correspond to oxygen with one and two less electrons, respectively. While

studying the ion properties, e.g. transition energies, is common to change both Z and Q . Evaluating an ion propriety over Z , maintaining the number of electrons constant, is referred to as studying an isoelectronic sequence, while studying the proprieties with the change in Q by maintaining a constant value of Z is referred to a studying an isonuclear sequence. A schematic representation of this concept is represented in Figure 1.1. From the theoretical point of view, it is often convenient to study isoelectronic sequences, as changing the value of Z only changes the overall nuclear potential, while change N_e results in different electronic structures. Yet, from the experimental point of view, it is easier to study isonuclear sequences, as it can be done by probing a specific element and peeling its electrons layer by layer.

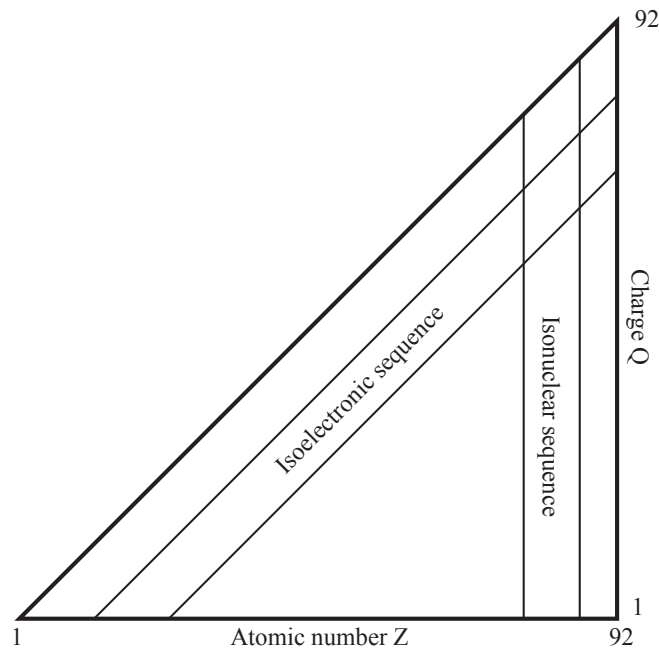


Figure 1.1: Representation of the isoelectronic sequence (constant number of electrons) and the isonuclear sequence (constant atomic number Z) as a function of the atomic number Z and the electric charge Q . Adapted from [2].

The most notable changes in atomic proprieties of HCl across the isoelectronic sequence are the size (or compression) and shape of the electronic wavefunctions. Following simple Bohr atomic theory, the isoelectronic scaling law of the Bohr radius R for an hydrogen-like ion is given by $1/Z$, meaning that the corresponding ion of uranium is around two orders of magnitude smaller than the than the hydrogen counterpart. The Coulomb potential of the nucleus also grows rapidly over the isoelectronic sequence according to $Z/R^2 \sim Z^2$. Looking into the isonuclear sequence, the possible ionization potential scaling law from the Coulomb potential, $\sim Q^2$, is broken down by jumps related to the change in electron orbital shells. While electrons within the stable shell have similar binding energies, the same cannot be said across different atomic electronic shells. This behavior is illustrated in Figure 1.2 for the isonuclear sequence tungsten ($Z = 74$).

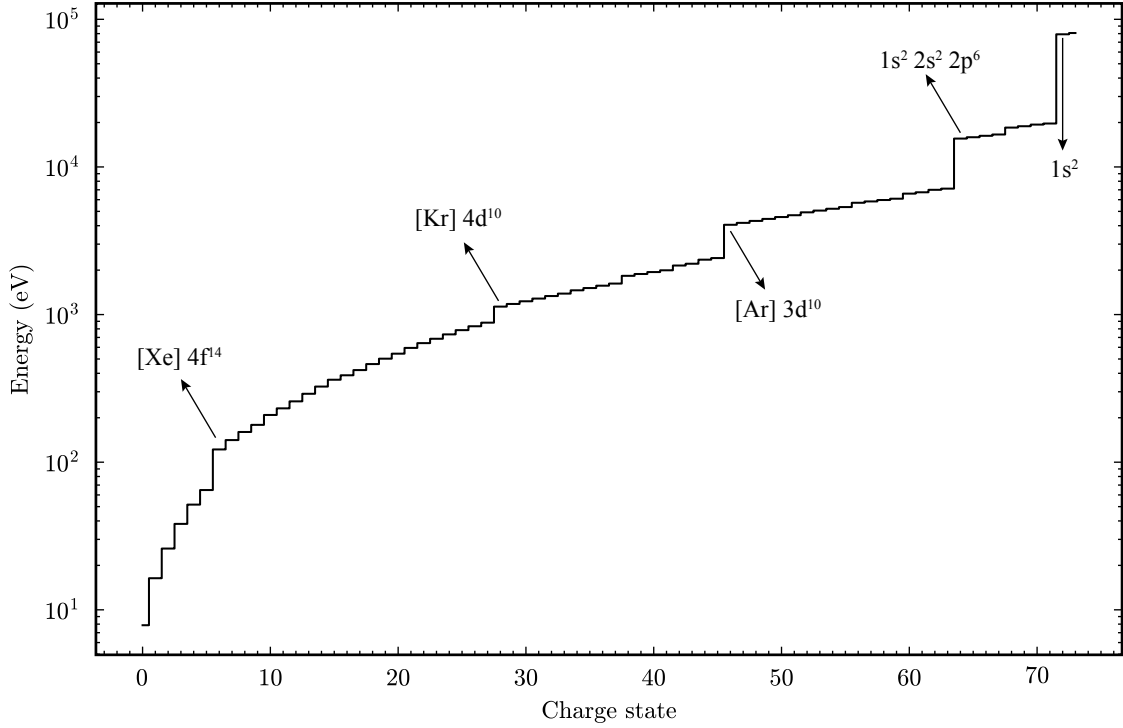


Figure 1.2: Ionization threshold of the ground state of each charge state of tungsten. The configurations of the most stable states, after a new ionization threshold jump, are represented.

The proprieties of HCI are highlighted in the photon energy of its respective energy level transitions. Different types of transitions have different scaling laws. Also from simple Bohr theory, the energy of transitions between different shells ($\Delta n \neq 0$) yield a scaling law of $E_\gamma \sim Z^2$ due to their dependence of the Coulomb potential. In intrashell transitions ($\Delta n = 0$), however, the energy shifts are dominated by relativistic effects. If we consider the expansion of the relativistic energy of a free particle with a velocity much lower than the speed of light c ,

$$E = \sqrt{p^2 c^2 + m_0^2 c^4} \approx m_0 c^2 + \frac{p^2}{2m_0} - \frac{p^4}{8m_0^3 c^2} + \dots, \quad (1.1)$$

the first order of the relativistic correction depends on the fourth power of the particle linear momentum p . For a definite value of angular momentum l , with $l = r \times p$, one can see that if the radius scales inversely with Z , p increases linearly with Z , resulting in a scaling law in the format of

$$E(Z) \approx Z^4. \quad (1.2)$$

Thus, the transition energies increase rapidly with increasing Z values for a given number of electrons. While most of neutral atoms emit photons in the infrared and visible energy ranges, most of the energy level transitions in HCI occur in the UV and X-ray energy ranges. This is demonstrated in Figure 1.3, where the wavelength of the transitions $1s^2 - 1s2s$ and $1s2s - 1s2p$ for He-like ions are represented across the entire range of Z . At these scales,

quantum-field theory effects become significant, since these effects scale with Z^4 (lowest order terms) [3], making heavy ions with a low number of electrons ideal test benches for quantum electron dynamics.

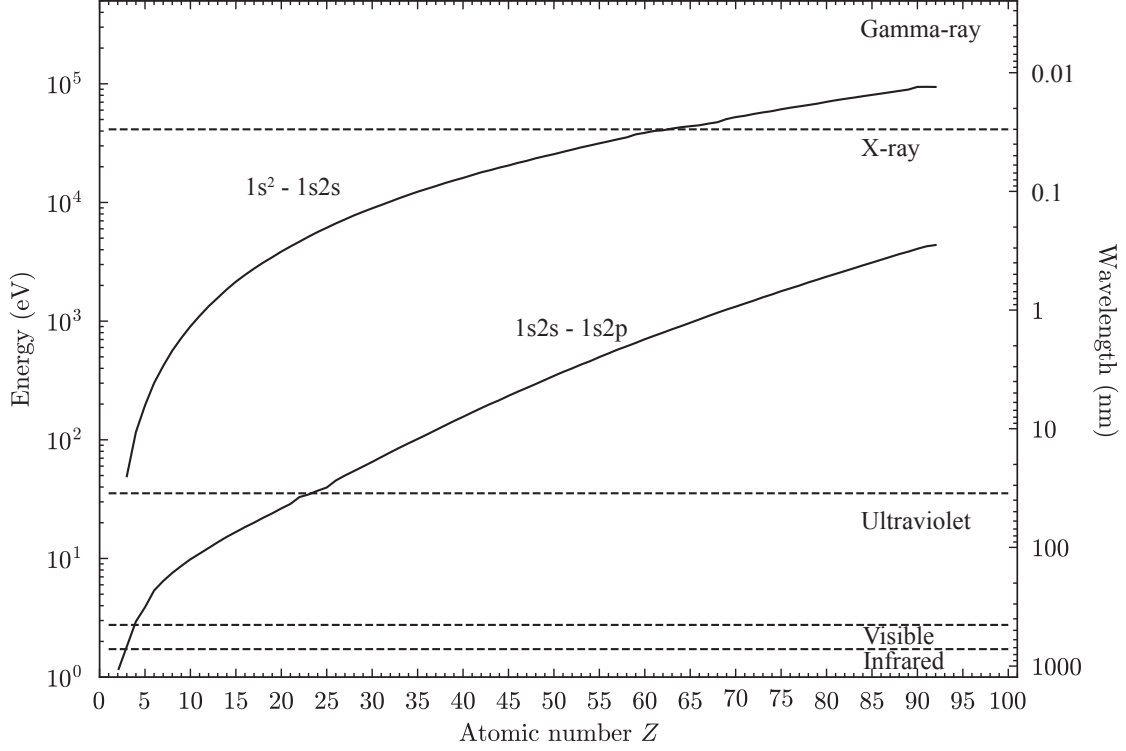


Figure 1.3: Typical wavelength for He-like ion transitions as a function of the atomic number Z . The ranges of the different categories of wavelength are also represented. Most of the He-like transitions are observed within the X-ray energy range.

1.2 Applications

Due to extreme plasma conditions and these scaling laws, HCI play fundamental roles in several topics of physics. In this thesis, the explored atomic systems and the respective atomic data have direct applications in areas such as astrophysics and nuclear fusion. These areas study the structure of the Universe and develop new ways to produce clean sustainable energy, respectively, thus have a great impact in the scientific community, and potentially in our everyday lives.

In the following, I specify the applications of HCI for each scientific area. As HCI are present in plasma environments, the basic concepts of plasma modeling with the known Collisional Radiative Model (CRM), as well as its brief history, will be described. Then, applications of HCI atomic data for plasma modeling and diagnostics for astrophysics and nuclear physics will be discussed.

1.2.1 Plasma modeling

CRM are an essential tool to model and analyze plasmas in various physical conditions, from astrophysical objects, such as hot stellar coronae and supernova remnants [4, 5], to laboratory plasma applications, such as lithography [6, 7]. Such models combine comprehensive atomic data, like transition rates and collisional processes, with environmental conditions to simulate plasma characteristics, such as mean charge state, charge state distributions, collisional rates and emission spectra [8]. This is accomplished by solving a set of coupled inhomogeneous first-order differential equations that represents the balance kinetics of the atomic state populations, thereby determining the associated line emissivities. First introduced by [9] to describe the excitation, recombination, ionization and spontaneous transition rates in a plasma, this basic concept has been developed over the years to adapt it to different applications, connecting the pure theoretical side of atomic physics with experiments. A common approach of CRM is to consider steady-state conditions that are present in a variety of plasmas, such as hot corona [5] and nuclear fusion plasma observations [10–12]. Several approximations can be used in these steady-state conditions, such as the Coronal Equilibrium (CEQ) [13] and the Local Thermodynamical Equilibrium (LTE) [14] approximations, which can accurately simulate steady-state plasmas in low and high electron densities limits, respectively. In the CEQ framework, the line emissivities and ionization balance of an optically thin plasma ($\lesssim 10^{18} \text{ cm}^{-3}$) depend only on the collisional processes rather than the radiative decay rates. The LTE approximation works well in high density plasmas ($\gtrsim 10^{26} \text{ cm}^{-3}$), where the population distributions are given by Boltzmann statistics and Saha equations. While these approximations are valid for the for each extreme density condition, a fully detailed collisional radiative model is necessary to simulate plasmas in the intermediate regime. Fully detailed atomic systems can become complex with thousands to millions of linear equations [15], so different levels of sophistication have been introduced over the years to reduce the set of populations describing the plasma. Such procedures include the average atom approximation [16], the use of screened hydrogenic levels [17] or configuration-average models [18].

On the other hand, non-steady conditions in plasmas are more of a rule than an exception. Laboratory plasmas, such as high-Z and tokamak hot plasmas [19], are open systems that change their features using different dynamical mechanisms, such as entering or escaping material or radiation. For example, neutral tungsten populations in tokamak plasmas do not necessarily exist in steady state owing to wall sputtering, reaching equilibrium in milliseconds [20]. Non-steady conditions are also present for non-static radiation fields, such as ultra-short laser pulses [21–23] and XFEL laser pulses [24–26], where the excitation processes are time-dynamic. Metastable atomic states often play an important role in spectral emissivity [20], and their level population dynamics cannot be evaluated with a model designed for equilibrium conditions. Moreover, the time-dynamics presented in [27] described a rapid recombination process, where the recombination rate has an order of magnitude similar to what is found in allowed radiative transitions. Following

the early CRM developments, a generalized collisional radiative theory was developed to accommodate the role of metastable populations in dynamic systems [28, 29]. A local equilibrium is considered for non-metastable levels that are governed by fast rates. Following this principle, the solution of the linear equations addressing non-metastable levels is incorporated into the metastable differential rate equations while being integrated over time.

Time-dependent CRMs have been developed in the past with this principle, such as FLYCHK [30], TRANSPEC [31], NLTE [32], NOMAD [27]. While the first uses a faster model with hydrogenic levels for fast simulations, others use fully detailed atomic data. With exception of FLYCHK, these are in-house and not available to the general public. Other implementations of the local-equilibrium approach have been made public: ADAS [29, 33], AtomDB [34], CHIANTI [35] and SPEX [36]. Also based on this principle, the open-source ColRadPy code [37] was developed to provide a python implementation of a CRM that can be used in both steady-state and time-dependent modes. These codes have been developed with thermal plasma in mind, making extensive use of Maxwellian electron energy distributions. Other custom-made CRM simulations consider realistic non-Maxwellian distributions for specific plasmas, such as electron-cyclotron ions sources [38, 39], tokamak [19] and z-pinch [40].

1.2.2 Astrophysics

In the middle of the last century, photographic plates attached to V-2 rockets confirmed the presence of an X-ray source outside our atmosphere. The existence of the source had already been previously theorized, being appointed as the main reason for the ionization of the ionosphere [41]. These rockets were later upgraded with the ability to roll of its flight axis, allowing the confirmation of the X-ray source as the sun by comparing the X-ray signal with the orientation of the spacecraft [42]. Around 20 years later, an Aerobee rocket detected the first X-rays coming from outside of the solar system [43]. These discoveries, paired with developments of space exploration technology, marked the beginning of X-ray astronomy. Given the energy range of the emissions, these celestial bodies must be composed of HCl.

While optical astronomy has been done for centuries, from the discovery of the larger moons of Jupiter in the 17th century [44] to modern high-resolution observations of distant galaxies and nebulae with the Hubble telescope [45], X-ray astronomy has only become a viable astrophysical tool in the last decades. The observation of different energy regions allow the observation of emissions from different charge states. Optical wavelengths come from mostly neutral and lowly ionized ions and tend to come from relatively cool regions of matter. The opposite can be applied to higher energies, which allow the observation and study of hot environments, such the solar corona, black holes, supernovae, kilonovae, binary systems, ... As an example, different aspects of the crab nebula are represented in Figure 1.4. In this Figure, we see the same celestial body being represented by false images

taken at different photon energy ranges. The visible range allows the observation of the supernova remnant shock front, already cooling down and emitting light in the visible range. It was observed by the Hubble telescope and, being observed in the visible range, its image was recorded in high resolution. The UV and X-ray range observations were made with the XMM-Newton and the Chandra telescope, and allow the direct observation of the pulsar lying in the core of the nebula. As the this object is characterized by the presence of extremely hot plasmas, it mainly emits radiation with energies in the range of the X-ray and gamma-ray.

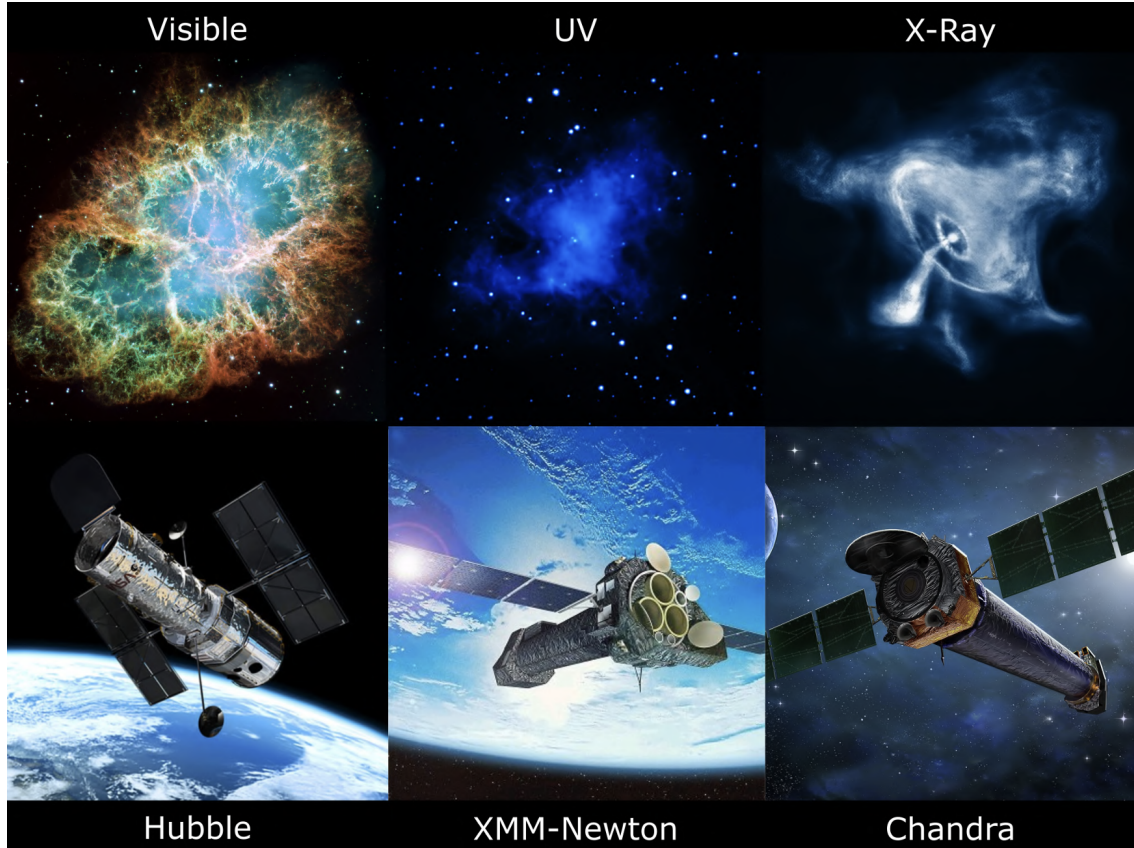


Figure 1.4: Crab nebula observed at different wavelengths. On the left is represented the cooler supernova remnant captured in the visible spectrum by the Hubble telescope. In the middle and on the right are represented the images of this nebula in the UV and X-ray energy ranges. These images show the hot pulsar in the heart of the nebula, captured by the XMM-Newton and the Chandra telescopes. Images adapted from [46]

While optical astronomy can be performed from the Earth surface, X-ray astronomy can only be done by launching the telescopes with spectrometers into space due to our atmosphere being optically thick. Telescopes like XMM-Newton, Chandra and Nu-star have been the standard X-ray observation instruments in the last few decades. They use flat-field crystal spectrometers to produce the X-ray emission spectra from the observation. With the development of advanced Charge Coupled Device (CCD) camera arrays, these telescopes can also produce X-ray images. Grating systems are used to select portions of

the X-ray spectrum and, although the created images are not photon energy completely differentiated, images with different energy ranges can be captured and compared to extract information about the astrophysical systems.

The next generation of X-ray space telescopes use a microcalorimeter as a detector of the Transition Edge Spectrometer (TES) type. In these devices, a group of pixels is cooled down and maintained in a temperature in the middle of the transition edge between normal and superconducting. As a pixel observes an X-ray photon, its temperature rises just enough for the change in resistivity to be measured. The change in resistivity is proportional to the photon energy, making this device a non-dispersive spectrometer, similar to a solid state detector, like a Silicon Drift Detector (SDD). Unlike the SDD, the TES has a photon energy resolution that can reach levels comparable to dispersive crystal spectrometers without the need of the dispersive element. With this, the new generation of telescopes has the potential of improving the overall observed spectrum resolution more than 10-fold, allowing the observation of features that were previously blended. Unfortunately, the deployment of these telescopes has been troublesome. In 2005, a microcalorimeter was launched on board of the Suzaku telescope, along with several other X-ray imaging instruments. Due to a malfunction in the cooling system 29 days after launch, a loss of liquid He rendered the microcalorimeter inoperable. From then on, this telescope was only used for X-ray imaging and low resolution spectroscopy. In 2016, The HITOMI telescope was successfully launched with a variety of X-ray and gamma-ray instruments, namely a microcalorimeter. This telescope was operational for two months, during which time it proved the capabilities of microcalorimeter based spectroscopy. After this period, an error in the attitude control system led to an uncontrolled spin of the spacecraft, resulting in the breakage of the weaker mechanical elements and loss of contact with the ground control station. In 2023, the XRISM (successor of HITOMI) was launched into space and remains operational to this day. Its microcalorimeter based spectrometer has an unparalleled resolution in the soft X-ray region, being able to observe up to 12 keV. While the lower observable energy limit was targeted to be a few hundreds of eV, the beryllium window that protected the detector opening during launch failed to open in space, covering the detector line-of-sight and effectively cutting off the all the emissions below 3 keV. This means that a few astrophysically important lines, such as oxygen $K\alpha$ and iron $L\alpha$ cannot be observed. Nevertheless, this telescope will contribute to the advancement of studies of hot celestial bodies, such as black holes, supernovae and binary systems. A comparison of the first XRISM spectrum compared with a similar observation from Suzaku is presented in Figure 1.5. The Athena mission will succeed the XRISM mission by using a detector with a higher number of pixels, making it possible to produce high resolution images while also making high resolution spectroscopy in each pixel. This mission is currently planned to launch around 2035.

With the development of the high resolution X-ray spectrometers, a new generation of experimental data will be available for X-ray astrophysics. In this field, the observations are routinely compared complex theoretical plasma models that ultimately rely on the

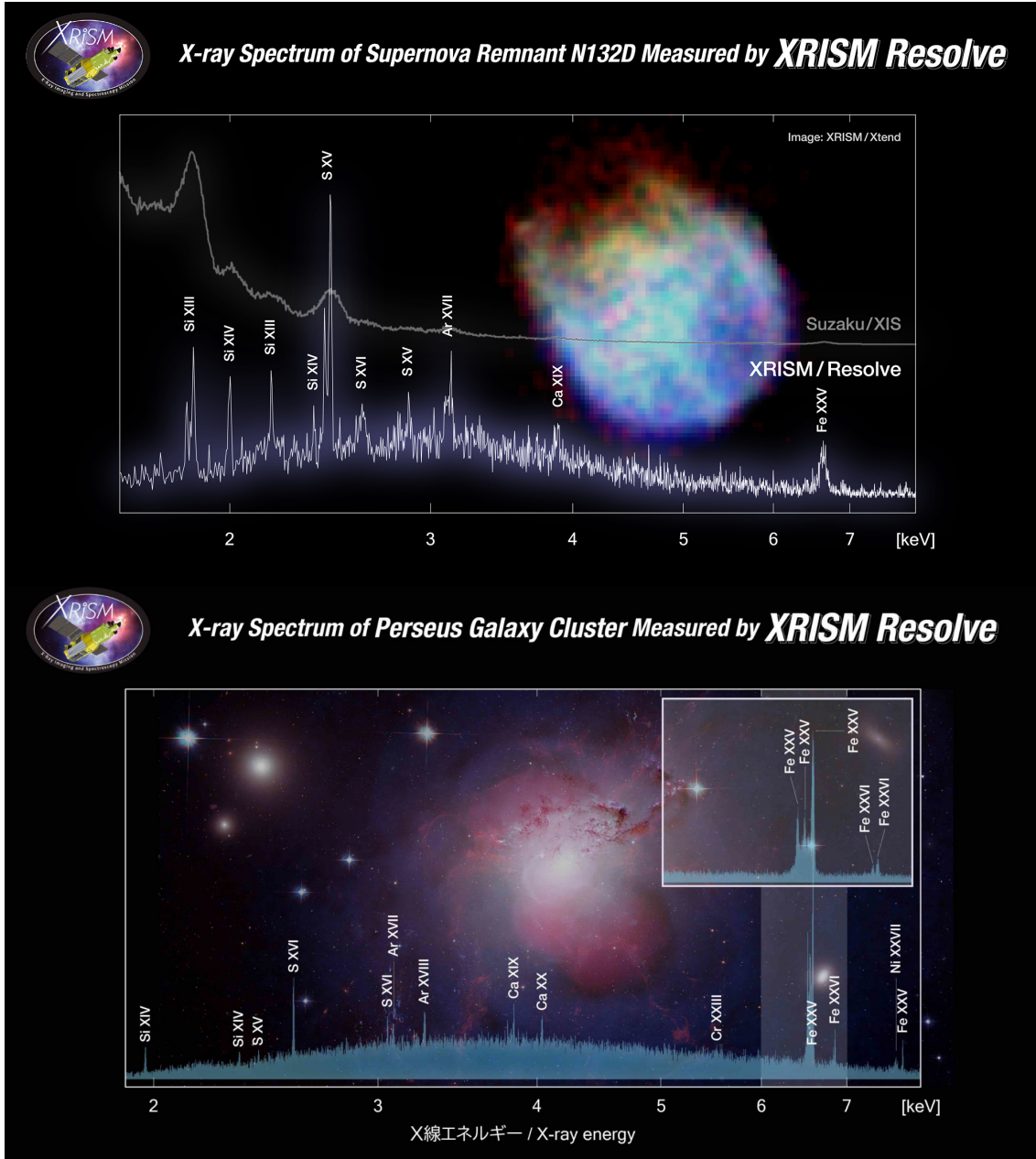


Figure 1.5: Spectra captures by the XRISM telescope. On the top, an observation of the supernova remnant N132D is represented, with the observation of lines from Si, S, Ar, Ca and Fe. A lower resolution spectrum of the same object captured by the Suzaku telescope is also represented. On the bottom, a spectrum of the Perseus galaxy cluster is represented, along with a zoom around the $K\alpha$ Fe lines. Figure adapted from [47, 48]

accuracy of the underlying atomic data. This atomic data generally consists in the electronic structure, radiative and non-radiative transitions rates and excitation, recombination and ionization cross-sections. As an example, line ratios are used as diagnostics to infer the macroscopic conditions of a plasma, as the intensity of this line is highly dependent on the plasma conditions that affect the population of the energy levels of the ions present.

Due to the abundance and stability of He-like ions in a wide range of hot astrophysical

plasmas, their bright $K\alpha$ emission lines are essential for the diagnostics of such sources, in particular when relatively high-resolution grating spectrometers onboard Chandra [49, 50] and XMM-Newton [51] are used. The simple closed-shell He-like structure favors $n = 2 \rightarrow n = 1$ transitions, often referred to, following the Gabriel notation [52], as the resonance line w ($1s2p\ ^1P_1 - 1s^2\ ^1S_0$), the intercombination line—composed of two transitions, x ($1s2p\ ^3P_2 - 1s^2\ ^1S_0$) and y ($1s2p\ ^3P_1 - 1s^2\ ^1S_0$)—as well as the forbidden line z ($1s2s^3S_1 - 1s^2\ ^1S_0$). Their intensity is governed by a combination of atomic processes, such as Radiative Recombination (RR) and Dielectronic Recombination (DR), Collisional Ionization (CI), Collisional Excitation (CE), Resonant Excitation (RE), Charge Exchange (CX), as well as their subsequent Auger and radiative cascades. Contributions from these processes are differently influenced by macroscopic plasma parameters such as temperature and density, as well as by other conditions, e. g., being in local thermal equilibrium or a transient state. A brief theoretical description of each of the mentioned atomic processes will be made in the next Chapter.

By studying these lines, astronomers gain insight into the composition and structure of the emitting plasma [53, 54]. As an example, their intensity ratios are sensitive to the local electron density ($R = z/(x + y)$) and temperature ($G = (x + y + z)/w$) of the plasma (see reviews from Refs. [4, 55, 56]), and their Doppler shifts, to plasma velocity [57, 58]. This diagnostic method is applied to a great variety of plasmas: hot stellar coronae [54, 59–62], accretion disks around pulsars [63]; cool active galactic nuclei [64, 65]; out-of-equilibrium-plasmas present in the winds of X-ray binaries [66, 67], supernova remnants [53, 68, 69], and many extra-solar objects [70–74].

Moreover, the Soft X-ray Spectrometer (SXS) microcalorimeter onboard the ill-fated Hitomi satellite acquired high-resolution spectra of the Perseus cluster, allowing to characterize the turbulent motion at its center [75] based on the broadening and Doppler shift of their He-like lines. However, differences in theoretical atomic data result in large discrepancies of up to 17% [5] for the metallicity of iron derived from the z/w intensity ratio by the spectral codes AtomDB/APEC [76], SPEX [77], and CHIANTI [35]. Since this problem arises from differences in the theory sources, experiments are required to assess the quality of the theoretical atomic data.

Over the last few decades, measurements in EBITs [78–92] and ion-storage rings [93–99] have been used to benchmark various cross-sections of aforementioned line formation mechanisms. In EBIT measurements, the electron-beam energy is swept to extract energy-differential cross-sections of various processes, such as DR, RE, and DE. The sweep time is usually a few to tens of milliseconds in order to keep it shorter than ionization and recombination times scales typical for EBITs. In this thesis, the $K\alpha$ line formation of He-like oxygen was studied using an EBIT setup. Oxygen was chosen due to its easy of use in the laboratory, as well as its prominent presence in astronomical observations [100]. As its main metastable state has a known lifetime of around 1 ms [101], its population dynamics make the retrieve of useful atomic data challenging for typical EBIT setups. The observation of this line complex, analysis of the results and modeling of the observed

phenomena are one of the subject of this work. Moreover, experiments were also carried in He-like calcium. As an He-like ion, its atomic data is always useful for astrophysics. Furthermore, the energy range limitation of the XRISM mission means that alternatives must be found to the popular iron lines to make new diagnostics. Some of such lines, which were already observed with the telescope, are the He-like $K\alpha$ lines of calcium, which will be explored in this work. The respective $K\alpha$ complex can be observed in the Figure 1.5 with a photon energy around 3.8 keV. It is worth to note that this set of lines seems to be accompanied by the less intense satellite lines, likely from dielectronic recombination. The main DR satellite lines, as well as the main $K\alpha$ complex are the object of study of one the experiments presented in this thesis, mainly motivated by the general lack of published accurate atomic data for this charge state in the literature.

1.2.3 Nuclear fusion

The tokamak is the leading device in the pursuit of sustainable nuclear fusion energy production. The International Thermonuclear Experimental Reactor (ITER), being built in France, aims to be the first magnetic confinement fusion device operating with a positive return of power, estimated to output 500 MW of fusion power with a 50 MW heat input [102].

A tokamak, which is the Russian acronym for toroidal chamber with magnetic coils, is a doughnut-shaped device where an high-temperature plasma is magnetically confined. External coils are used to generate a toroidal magnetic field that induces the charge particles to follow a closed circular path. An induced current is used to both heat the plasma and stabilized it through a generated poloidal magnetic field. To further increase the plasma temperature, radio waves and microwaves are often used to resonate the charged particles. When the plasma temperature reaches high enough temperatures, light elements can undergo the process of nuclear fusion, releasing energy in the process. The final objective is to collect that energy and convert it into electric power efficiently.

One key factor for the success of the experiment is the determination of the plasma temperature conditions in the different parts of the reactor. This information is vital for the correct control of the plasma. Similarly to celestial bodies in astronomy, the plasma conditions can only be inferred through spectroscopy, meaning that a wide variety of spectrometers are planned to be installed around the device. The divertor is the assembly located on the bottom of the containment vessel (Figure 1.6). It is the point of highest heat load, as it is where the most of the contact between the plasma and the vessel is meant to be. To withstand the extreme conditions, the divertor will be coated with tungsten due to its high melting point, low sputtering, and low tritium retention [103]. The plasma will inevitably be contaminated with tungsten ions, which may hinder the lighter elements fusion process. Nonetheless, a wide range of HCI of tungsten is expected throughout the several plasma regions, with expected emissions in the Extreme Ultraviolet (EUV) and soft X-ray energy ranges. These emissions can be used to assert the charge state balance

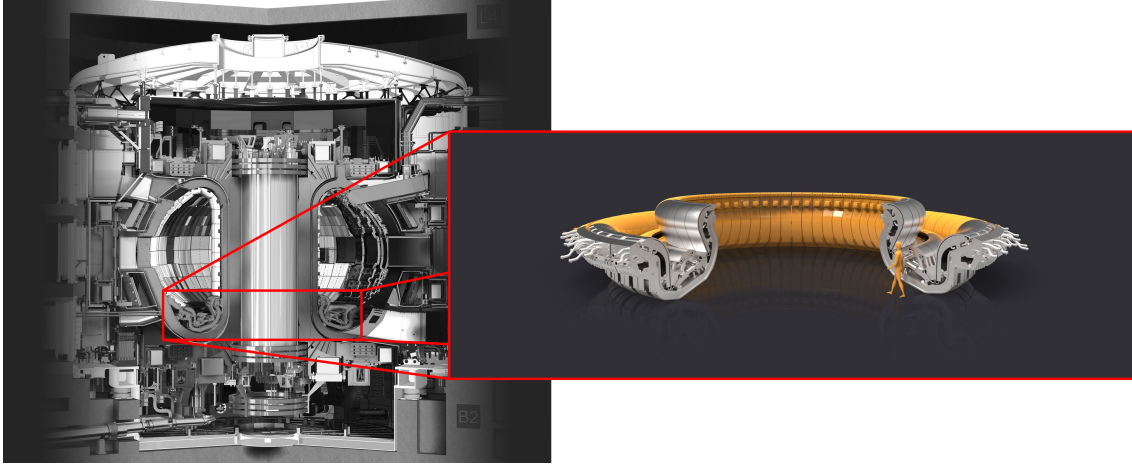


Figure 1.6: (Left) Representation of the ITER tokamak fully assembled. (Right) Focused view of the W coated divertor assembly that will rest on the bottom of the containment vessel of the reactor. The images were adapted from [105].

of the plasma locally, thereby potentially serving as electron temperature and density diagnostics. For this reason, all charge states of tungsten have been the subject of study of many atomic physics research groups over the last few decades [103, 104].

Smaller tokamaks have been extensively used to identify and study tungsten lines in different plasma conditions [11, 106–108]. While they can achieve the similar conditions to what is observed in the ITER, the Maxwellian distribution for the free electron energy ensures a wide distribution of charge states being observed at the same time. Furthermore, no fine control can be had on the electron-ion interactions, the main photon emission process, making it hard to study the atomic processes individually. For these purposes, storage rings and EBITs have been at the forefront of atomic physics research for laboratory cross-section benchmarking. Storage rings are large-scale accelerators that can confine a beam of ions for long periods of time and study them in different ways. The most common way to study electron-ion interactions is through a merged beams technique, where a beam of electrons is merged with the ion beam. The electron beam is usually created by an electron cooler in a small section of the ring. The energy of the electron beam can be matched to the energy of the ion beam, and the relative energy between them can be scanned. Ionization and recombination processes can be monitored by observing the resulting ion beam that deviates into a different path due to the different charge state [109, 110]. These devices can have a very high relative electron energy resolution and study processes with an electron energies of few electronvolt. These are their main advantage, as the EBIT setups cannot probe very low electron energies, and the electron resolution is limited compared to the storage rings electron coolers. Nonetheless, EBIT experiments provide photon emission spectra that are useful for benchmark of atomic physics.

As all charge states of tungsten, and their respective emissions, are important for the correct modeling and diagnose of a real tokamak plasma, a wide range of benchmarks have been made over the years. In the X-ray energy range, EBIT setups have been used,

for example, to study $n = 4$ intrashell transitions of the charge states $21+$ to $46+$ within a wavelength range of $45 - 75 \text{ \AA}$ [111], L-shell emissions of $64+$ [112], $27 - 41 \text{ \AA}$ emissions of partially filled $3p$ and $3d$ subshells charge states [113], as well as $n = 5, 6$ to $n = 4$ transitions of $19+$ to $32+$ [114]. In the EUV wavelength region, there have been EBIT observations of lines from the charge states between $30+$ to $54+$ in a variety of wavelength ranges from 4 to 25 nm [10, 12, 115], and different energy ranges for lower charge states from $5+$ to $9+$ [116, 117].

While there is a wide variety of available observations for highly charge states of tungsten in both the EUV and X-ray energy ranges, there is a notorious lack of experimental data regarding transitions from open $4f$ -shell ions. While less prominent in the tokamak, these charge states are expected to be observed near the divertor, and their transitions could be used to probe the plasma conditions in this region. Emissions from $n = 5$ intrashell transitions have already been theorized [118], yet their observations are usually blended due to the number of charge states present simultaneously with similar lines. One objective of this thesis is to experimentally observe and catalog most of the $n = 5$ intrashell transitions of tungsten for open $4f$ -shell charge states.

Another element of interest for nuclear reactors is krypton. Since tungsten is a very heavy element, its impurities inside the plasma may hinder the fusion process. An alternative to infer the conditions of the plasma would be to inject lighter elements inside the device and study their emission. One good candidate is krypton, since this is an inert element that can easily be injected in controllable amounts. The He-like charge state of this element has already been studied in a tokamak to show its potential for plasma diagnostics [104, 119]. EBIT setups have already been used to study other properties, such as its cooling rates from different processes (bremsstrahlung, radiative recombination, dielectronic recombination, electron-impact excitation) [120], DR cross-sections of several charge states, along with its respective polarization corrections [86] and DR KLL satellite lines for the charge states of He-like, Li-like and Be-like. In this work, the entire DR KLn and excitation structures of Ne-like krypton were analyzed. Although a previous work has already measured and published these structures [120], the resolution was very poor, and was vastly improved in this work.

1.3 Thesis organization

The objective of this thesis is to perform laboratory benchmarks of HCI relevant to astrophysics and nuclear fusion reactors. The experimental measurements were all performed using an EBIT, where the photon emissions were observed with different detectors. As different small experimental works were performed individually to study different elements, these will be categorized according to their most eminent application in another field. The thesis will be organized in the following Chapters:

- **Theory** - The basis of atomic physics theory and atomic collisions will be

introduced. All the different techniques to calculate the relevant atomic data, as well as the definition of all the relevant electron-ion collisional processes are explained. A new approach is introduced to develop a time-dependent model, allowing simulation of dynamical systems like the ones present in the experiments.

- **Experimental methods** - The basic concept of an EBIT is introduced. All the particular hardware of the setup used in this work, as well as the measurement scheme is presented. The different detectors used in the observations are also described. Moreover, a few more types of relevant ions sources are also discussed.
- **Experimental results - Astrophysics** - The specific setups used for the study of the DR and excitation structures of He-like oxygen and calcium are described. The respective results and performed analysis is also presented. The time-dependent CRM is also applied to the He-like oxygen observation to model the metastable state dynamics. Effects related to this dynamics regarding the DR of H-like oxygen are also discussed.
- **Experimental results - Nuclear reactors** - The experimental setups used to observe the DR and excitation structures of Ne-like krypton, and the $n = 5$ intrashell emissions of open $4f$ -shell charge states of tungsten are introduced. The Non-Negative Matrix factorization method is introduced as a tool to decouple blended emission in various scenarios.
- **Conclusions and future prospects** - The main results from this thesis are summarized. Their importance is contextualized and future prospects are discussed.

THEORY

While the main goal is to provide relevant experimental atomic data, its understanding relies on a theoretical formalism. Furthermore, benchmarking existing calculations requires a significant understanding of atomic physics theory and the several methods that were employed in each calculation. In this project, all experimental observations were theoretically modeled, making use of state-of-the-art atomic physics codes. Theoretical data generated by these atomic codes is used to simulate the experimental results in the laboratory conditions. The basis of the theory and simulations employed in this project will be described in this Chapter.

The theoretical basis of single and multiple electron atomic systems will be presented, starting by the calculation of the respective atomic structures, namely the relevant wavefunctions and energy levels. The theory behind atomic transitions and collisions will also be reviewed, as well as the computation of cross-sections from electron-ion collisional processes. With this theoretical data, the CRM method will be introduced as a way to simulate the charge state balance of a plasma and the respective emission spectrum in the experimental conditions.

2.1 Atomic structure

In this Section, the basis of modern atomic theory is presented. The theory presented in this Chapter will follow the Dirac relativistic formulation. This is important, since HCl may have high atomic number, and thus a high Coulomb potential (see Sec. 2.1.1). The electrons in such atomic systems get speeds of fractions of the light speed, making the relativistic effects relevant in the atomic structure. As usual and convenient in atomic systems, the theory here will be presented in atomic units. A description of the atomic units system can be found in Appendix A.

2.1.1 One-electron systems

To investigate the theoretical properties of a quantum system that is the atom, one must find the eigenfunctions and respective eigenvalues of the system. For this description, we

shall refer to the eigenvalues and eigenfunctions as wavefunctions and energy levels. Due to the spherical symmetry of the atom, all the functions will be presented in the polar spherical coordinate system, where the position vector $\mathbf{r}$ is defined in units of $\{\hat{r}, \hat{\theta}, \hat{\phi}\}$. This coordinate system is related to the Cartesian coordinate system through the following set of relations:

$$\begin{aligned} x &= r \sin \theta \cos \phi, & y &= r \sin \theta \sin \phi, & z &= r \cos \theta \\ r &= \sqrt{x^2 + y^2 + z^2}, & \theta &= \arccos z/r, & \phi &= \arctan y/x. \end{aligned} \quad (2.1)$$

The basis of atomic theory starts with the description of H-like ions, systems composed of one nucleus of charge Z and one electron. While this is a two-body problem, the nuclear mass is several orders of magnitude higher than the electron mass and is appropriate to decouple this into one-body problem with center-of-mass coordinates. The electron wavefunction is obtained by solving the Hamiltonian equation

$$H\Psi = E\Psi, \quad (2.2)$$

where H , Ψ and E are the Hamiltonian, wavefunction and energy of a bound state. In order to include the relativistic effects, the previous equation must include the fully-relativistic Dirac-Coulomb Hamiltonian. This Hamiltonian, for a system of N electrons, can be written as

$$H = \sum_i^N h_i + \sum_{i<j}^N V_{ij}^{e-e}, \quad (2.3)$$

where V^{e-e} are all the electron-electron interaction potentials that include both Coulomb and Breit interaction. h_i is the Dirac-Coulomb Hamiltonian for a single electron, given by

$$h_i = c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V_C(r_i), \quad (2.4)$$

where c is the light speed, $\mathbf{p}$ is the linear momentum operator, $V_C(r)$ is the nuclear Coulomb radial potential and $\boldsymbol{\alpha}$ and β are the Dirac 4×4 matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix} \quad \text{and} \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad (2.5)$$

where $\boldsymbol{\sigma}$ are the Pauli spin matrices. If the nucleus is approximated to a point-like charge, the coulomb potential has the form

$$V_C(r) = -\frac{Z}{r}. \quad (2.6)$$

For hydrogen-like systems, the one-electron Hamiltonian is given by

$$[c\boldsymbol{\alpha} \cdot \mathbf{p} + \beta c^2 + V_C(r)] \phi(\vec{r})_{n\kappa m} = E_n \phi(\vec{r})_{n\kappa m}. \quad (2.7)$$

This equation has analytic solutions of

$$\phi(\mathbf{r})_{n\kappa m} = \frac{1}{r} \begin{pmatrix} iP_{n\kappa}(r)\Omega_{\kappa m}(\theta, \phi) \\ Q_{n\kappa}(r)\Omega_{-\kappa m}(\theta, \phi) \end{pmatrix}. \quad (2.8)$$

These solutions are known as the Dirac spinors. Here, n is the principal quantum number, m is the z -component of the total angular momentum j , and κ is the relativistic angular momentum, related to the orbital l and total angular momentum by $\kappa = (l - j)(2j + 1)$. The function $\Omega_{\kappa m}(\theta, \phi)$ is the spherical spinor consisting of angular coupling of spherical harmonics and $1/2$ -spinors. As seen in equation 2.8, the Dirac spinor functions are separated in radial and angular parts, as well as the Hamiltonian equation 2.7, the energy of the corresponding wavefunction is determined by solving the radial part of the Dirac equation. The radial functions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the two components of the relativistic radial wavefunction, usually referred to as the large and small components. By inserting the solution 2.8 in the equation 2.7, one can obtain the radial functions $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ by solving the resulting coupled differential equations [121, 122]

$$(V_C(r) + c^2) P_{n\kappa}(r) + c \left(\frac{d}{dr} - \frac{\kappa}{r} \right) Q_{n\kappa}(r) = E_n P_{n\kappa}(r), \quad (2.9)$$

$$-c \left(\frac{d}{dr} - \frac{\kappa}{r} \right) P_{n\kappa}(r) + (V_C(r) - c^2) Q_{n\kappa}(r) = E_n Q_{n\kappa}(r), \quad (2.10)$$

where E_n is the energy eigenvalue corresponding to the $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ eigenfunctions. This set of equations can be solved analytically. The solutions for the radial functions can be written in terms of the confluent hypergeometric functions $F(a, b, x)$ as [122]

$$\begin{aligned} P_{n\kappa}(r) &= \sqrt{1 + E_{n\kappa}/c^2} N_{n\kappa} e^{-x/2} x^\gamma [(N - \kappa)F(-n + k, 2\gamma + 1, x) \\ &\quad - (n - k)F(-n + k + 1, 2\gamma + 1, x)], \\ Q_{n\kappa}(r) &= \sqrt{1 - E_{n\kappa}/c^2} N_{n\kappa} e^{-x/2} x^\gamma [(N - \kappa)F(-n + k, 2\gamma + 1, x) \\ &\quad + (n - k)F(-n + k + 1, 2\gamma + 1, x)], \end{aligned} \quad (2.11)$$

where $N_{n\kappa}$ is a normalization factor given by

$$N_{n\kappa} = \frac{1}{N\Gamma(2\gamma + 1)} \sqrt{\frac{Z\Gamma(2\gamma + 1 + n - k)}{2(n - k)!(N - \kappa)}}, \quad (2.12)$$

and $N = \sqrt{n^2 2(2 - k)(k - \gamma)}$. In these equations, $\gamma^2 = \kappa^2 - \alpha^2 Z^2$ and α is the fine-structure constant. The respective energy is finally given by

$$E_{n\kappa} = \frac{c^2}{\sqrt{1 + \frac{\alpha^2 Z^2}{(\gamma + n - k)^2}}}. \quad (2.13)$$

This equation can also be expanded in terms of powers of αZ , attaining the form

$$E_{n\kappa} = c^2 - \frac{Z^2}{2n^2} - \frac{\alpha^2 Z^4}{2n^3} \left(\frac{1}{k} - \frac{3}{4n} \right) + \dots \quad (2.14)$$

The first term is the electron rest energy $m_e c^2$, while the second term corresponds to the non-relativistic Coulomb binding energy. The non-relativistic approach to the hydrogen atom predicts that the energy only depends on the value of n . This value defines the shell

of the electron and is the parameter that has the biggest effect in the binding energy of multi-electron systems. The third term corresponds to the leading fine-structure correction, given mainly by relativistic corrections and the spin-orbital interaction. The different interactions a spin can have with the angular momentum lifts the degeneracy of energy for wavefunctions with the same value of n and different values of angular momentum. This expansion also relates with the scaling laws presented in the Chapter 1, as it suggests that intershell transitions scale with Z^2 , while intrashell transitions scale with Z^4 .

While the one-electron system has analytic solutions, the same cannot be said about multi-electron systems. Problems above two bodies are known in physics for not having general analytic solution in both classical and quantum mechanics. While the spherical part of the calculation can be solved analytically, due to the spherical symmetry of the atom still be present in multi-electron systems, the radial the radial part must be calculated with numerical methods and approximations. Several methods can be employed to approximate the electron-electron interactions accurately. Some of them will be explored in the next subsection.

2.1.2 Multi-electron systems

For an atomic system with multiple electrons, the electronic correlation (interaction between electrons) has to be taken into account. For the one-electron case, the total potential was only given by the nuclear Coulomb potential, which given the point-like nucleus approximation is defined as a central-field potential (it is isotropic, meaning it only depends on the value of r). The inclusion of multiple electron adds to the total Hamiltonian the electron-electron Coulomb potential

$$\sum_{i<j}^N V_{ij}^{e-e} = \sum_{i<j}^N \frac{1}{r_{ij}} = \sum_{i<j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}. \quad (2.15)$$

This potential is not isotropic, and the Hamiltonian equation cannot be solved analytically. In this subsection, the Dirac-Fock method will be introduced as a way to approximate multi-electron relativistic wavefunction, as well as multiple methods to improve the wavefunctions and respective energy levels.

Another correction can also be made by taking into account the magnetic interaction and retardation between every pair of electrons. This can be done by summing another potential to the Hamiltonian in the form of [123]

$$V^B = \sum_{i<j}^N \left[-(\alpha_i \cdot \alpha_j) \frac{\cos(\omega r_{ij})}{r_{ij}} + (\alpha_i \cdot \nabla_i)(\alpha_j \cdot \nabla_j) \frac{\cos(\omega r_{ij}) - 1}{\omega^2 r_{ij}} \right], \quad (2.16)$$

where ω is the frequency of the exchange virtual photon and α_i is the vector of the Dirac matrices associated with the i^{th} . The effects of the inclusion of the term in the overall potential is known as the Breit interaction [124].

2.1.3 Angular momentum coupling

Due to the Pauli principle, electrons in an atom must be organized in such way that no two electrons have the exact same set of quantum numbers (n, l, m, s) . The quantum number s is related to spin and can only take the values $m_s = \pm 1/2$. An electron total angular momentum j is defined by the combination of the orbital angular momentum (defined by l) and the spin angular momentum. The spherical spinors are defined as a combination of the spherical harmonics $Y_{l,m}(\theta, \phi)$ with spinors χ_μ

$$\Omega_{l,j,m}(\theta, \phi) = \sum_{m_s} \langle l, m - m_s; \frac{1}{2}, m_s | j, m \rangle Y_{l,m-m_s}(\theta, \phi) \chi_{m_s}, \quad (2.17)$$

where $\langle j_1, m_1; j_2, m_2 | j, m \rangle$ are the Clebsch-Gordan coefficients. More generally, these coefficients assure that when combining two angular momentum eigenvectors with quantum numbers (j_1, m_1) and (j_2, m_2) gives a eigenvectors of angular momentum (j, m) .

The Clebsch-Gordan coefficients coefficients vanish if certain combination rules between the quantum numbers are not followed. When combining two angular momenta, it follows that $|j_1 - j_2| \leq j \leq j_1 + j_2$, where the value of j can only vary by unitary amounts. Furthermore, the value of m is limited by the possible values of l . In this case, they take values of $-l \leq m \leq l$. Moreover, the values of l are also limited by the value of n by the condition $l = 0, \dots, n - 1$. With these rules, each shell can have a total of $2(2l + 1)$ electrons with a unique set of quantum numbers. A shell refers to a specific principal quantum number n and, while it is usually represented with its number, it may be represented by the letters $K, L, M, N, \dots$, corresponding to the values $n = 1, 2, 3, 4, \dots$. The available values of $l = 0, 1, 2, 3, \dots$ are usually represented by the letters $s, p, d, f, \dots$. The set nl defines a subshell. For example, the subshell $2p$ refers to the electrons with $n = 2$ and $l = 1$. Combining with the value of s , the subshell $2p$ may be written as $2p_{1/2}$ and $2p_{3/2}$. Ions with fully filled subshells are known as closed-shell ions. Organizing multiple electrons according to the previous rules is a configuration. The configurations of the first few closed-shell electron have the form $1s^2, 1s^22s^2, 1s^22s^22p^2, \dots$. As electrons are added together in a specific configuration, their angular momenta can be coupled in a variety of combinations. As the number of electrons increases, the number of possible energy levels defined by a single configuration increases exponentially.

2.1.3.1 Dirac-Hartree-Fock method

The Hartree-Fock approximation is obtained by applying the variational principle to the non-relativistic Hamiltonian equation. The relativistic counterpart is known as the Dirac-Hartree-Fock method. This method starts by noting that the total energy of the atomic wavefunction is given by

$$E = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (2.18)$$

Using the variational method to this energy, a trial wavefunction that better describes the system is such that the energy of the system is stationary in regard to small variations of the

radial wavefunctions. This minimization of this quantity determines a set of differential equations for atomic wavefunction that better approximates the system, which are given by [55]

$$\frac{\partial \left(E[H] - \sum_{ij} \varepsilon_{ij} \langle \phi_i | \phi_j \rangle \right)}{\partial P_{n\kappa}(r)}, \quad (2.19)$$

$$\frac{\partial \left(E[H] - \sum_{ij} \varepsilon_{ij} \langle \phi_i | \phi_j \rangle \right)}{\partial Q_{n\kappa}(r)}, \quad (2.20)$$

where ε_{ij} are the Lagrange multipliers, introduced to insure the orthonormality of the wavefunction. The minimization leads to a set of $2N$ (N is the number of electrons) coupled integro-differential Hamiltonian equations where the effective potential self-references the radial part of the wavefunction itself. Hence, these equations are solved iteratively and self-consistently. Electrons are fermions, thus many-electron wavefunctions must be anti-symmetric to ensure the Pauli exclusion principle. For this, it is suitable to combine single-electron Dirac spinors in an anti-symmetric manner with the Slater determinant

$$\Psi^s(r_1, \dots, r_N) = (N!)^{-1/2} \begin{vmatrix} \phi_{(n\kappa m)1}(r_1) & \dots & \phi_{(n\kappa m)1}(r_N) \\ \vdots & \ddots & \vdots \\ \phi_{(n\kappa m)N}(r_1) & \dots & \phi_{(n\kappa m)N}(r_N) \end{vmatrix}, \quad (2.21)$$

where r_i represents the electron space coordinates. The function is totally anti-symmetric and independent of the ordering of the labels i , therefore ensuring that the Pauli exclusion principle is obeyed (if two lines or two columns are the same, the determinant vanishes).

By applying the variational method, one obtains a set of $2N$ equations in the form of

$$\begin{aligned} \left(V_{\text{HF}} - \frac{Z}{r} + c^2 \right) P_a + c \left(\frac{d}{dr} - \frac{\kappa}{r} \right) Q_a &= \epsilon_a P_a, \\ -c \left(\frac{d}{dr} + \frac{\kappa}{r} \right) P_a + \left(V_{\text{HF}} - \frac{Z}{r} - c^2 \right) Q_a &= \epsilon_a Q_a. \end{aligned} \quad (2.22)$$

Here, a corresponds to a set of (n, κ, m) values and ϵ_a refers to the energy corresponding to the single electron radial wavefunctions defined by a . The Hartree-Fock potential of the Coulomb part acting on a radial wavefunction $R_a(r)$ (which can be replaced by either P_a or Q_a) can be written as

$$V_{\text{HF}} = \sum_b (2j_b + 1) \left(v_0(b, b, r) R_a(r) - \sum_k \Lambda_{\kappa_a k \kappa_b} v_k(b, a, r) R_b(r) \right), \quad (2.23)$$

with the Slater integrals $v_k(a, b, r)$ being

$$v_k(a, b, r) = \int_0^\infty dr' \frac{r_{<}^k}{r_{>}^{k+1}} [P_a(r') P_b(r') + Q_a(r') Q_b(r')]. \quad (2.24)$$

Here, the quantities $r_{<}$ and $r_{>}$ correspond to $\min(r, r')$ and $\max(r, r')$, respectively. The value of $\Lambda_{\kappa_a k \kappa_b}$ corresponds to the Slater integrals coefficients

$$\Lambda_{\kappa_a k \kappa_b} = \begin{pmatrix} j_a & j_b & k \\ -1/2 & 1/2 & 0 \end{pmatrix}^2 \Pi(l_a + k + l_b), \quad (2.25)$$

where $\Pi(l)$ is 1 or 0 if l is even or odd and the quantity in parentheses is a 3- j symbol. The two components in the Hartree-Fock potential are often referred as direct and exchange potentials, $V_{HF} = V_{HF}^{\text{dir}} + V_{HF}^{\text{ex}}$. When the Slater integrals depend on the same set of quantum numbers, they translate into the analogue of the potential due to the distribution of an electric charge over the radial wavefunction of that particular set of quantum numbers. This term V_{HF}^{dir} , known as the direct potential, represents the spherically averaged charge distribution of all electrons. The second term relates pairs of different radial wavefunctions and evaluates the non-local part of the electronic potential. The total energy of associated with the final total wavefunction is given by

$$E = \sum_a (2j_a + 1) \epsilon_a - \frac{1}{2} \sum_{ab} (2j_a + 1)(2j_b + 1) \langle \Psi^s | V_{HF}^{\text{dir}} + V_{HF}^{\text{ex}} | \Psi^s \rangle. \quad (2.26)$$

After using the Slater determinant as a trial function, the Hartree-Fock potential can be evaluated, and a new set of radial wavefunctions are calculated numerically by solving the Hartree-Dirac-Fock equations. The new set of radial wavefunctions can be used to calculate a new potential. This process is repeated iteratively in a self-consistent manner, converging into a set of wavefunctions where the electronic correlation effects are accounted for.

2.1.3.2 Configuration Interaction

While a single Slater determinant, or one configuration, can give a reasonable approximation to the many-electron wavefunction, a better approximation is considering a combination of Slater determinants or configurations. This is the basis to the Configuration-Interaction methods and Multi-Configuration Hartree-Dirac-Fock methods. The Configuration State Function (CSF) for an N electron atomic system is defined as a mixture of Slater determinants,

$$\Phi(r_1, \dots, r_N) = \sum_i d_i \begin{vmatrix} \phi_{(n\kappa m)1}(r_1) & \dots & \phi_{(n\kappa m)1}(r_N) \\ \vdots & \ddots & \vdots \\ \phi_{(n\kappa m)N}(r_1) & \dots & \phi_{(n\kappa m)N}(r_N) \end{vmatrix}, \quad (2.27)$$

where d_i are coefficients determined by imposing that the Φ remains an eigenfunction of the operators $\hat{J}_z$ and $\hat{J}^2$. To include correlation effects between the configurations, a final atomic state can be obtained by a linear combination of configuration state functions,

$$\Psi = \sum_k c_k \Phi_k(r_1, \dots, r_N), \quad (2.28)$$

where c_k are the configuration mixing coefficients. In this case, the atomic wavefunction is given by a superposition of CSFs. The trial wavefunctions for the CSFs can be obtained by the previous Hartree-Dirac-Fock method. Afterwards, the variational method can once again be applied to the new total wave function to determine the coefficient values. The energy is then given by

$$E = \sum_{ij} c_i c_j \langle \Phi_i | H | \Phi_j \rangle \quad (2.29)$$

The inclusion of multiple configurations in the same atomic wavefunction, extending the total wavefunction to reflect electron correlation between configuration, leads to the method known as Configuration Interaction (CI). A complete basis of CSFs cannot be used, as the total number of possible configuration states grows to infinity. Assuming a combination of a finite number of configurations, an arbitrary level of accuracy can be achieved by adding more configuration state functions into the mixture [55]. As the dimension of the wavefunction increases exponentially with the number of CSFs, there is usually a compromise between accuracy and calculation time.

The use of a linear combination of CSFs can also be directly used in the Hartree methods. This also includes the full configuration correlation and constitutes the widely used Multiconfiguration Hartree-Fock (MCHF) and Multiconfiguration Dirac-Fock (MCDF) methods. These methods are generally more computationally expensive than the simpler CI method, but can achieve more accurate results.

2.1.3.3 Many Body Perturbation Theory

An alternative approach to the variational principle is the use of perturbation theory. The Many Body Perturbation Theory (MBPT) [55] treats the single electron Hamiltonian as the unperturbed state and the electron-electron interactions as a perturbation. To make this approximation, the Hamiltonian in the equation (2.2) is expanded in the form

$$H = H_0 + H_{\text{pert}}, \quad (2.30)$$

where H_0 is defined by

$$H_0 = \sum_i^N h_i + V_i^C(r) \quad (2.31)$$

and

$$H_{\text{pert}} = \sum_{i < j}^N V_{ij}^{e-e} - \sum_i^N V_i^C(r). \quad (2.32)$$

Here, the unperturbed states can be calculated beforehand with several methods, like the ones presented in 2.1.2 and 2.1.3. Let Ψ be the eigenstate of the Hamiltonian H with a corresponding eigenvalue E . The eigenstate can be decomposed into an unperturbed wavefunction $\Psi^{(0)}$ that satisfies

$$H_0 \Psi^{(0)} = E^0 \Psi^{(0)} \quad (2.33)$$

and a perturbation $\Delta\Psi$. The resulting wavefunction is normalized by the intermediate normalization condition $\langle \Psi^{(0)} | \Psi \rangle = 1$. If $\Psi = \Psi^{(0)} + \Delta\Psi$ and $E = E^0 + \Delta E$, the eigenvalue equation of the problem may be rewritten as

$$(H^0 - E^0) \Delta\Psi = (\Delta E - H_{\text{pert}}) \Psi. \quad (2.34)$$

From these equations follows that

$$\Delta E = \langle \Psi^{(0)} | H_{\text{pert}} | \Psi \rangle. \quad (2.35)$$

By expanding the wavefunction and the respective energy in the forms

$$\begin{aligned}\Psi &= \Psi^{(0)} + \Delta\Psi = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots, \\ E &= E^{(0)} + \Delta E = E^{(0)} + E^{(1)} + E^{(2)} + \dots,\end{aligned}\tag{2.36}$$

where $\Delta\Psi$ and ΔE are the wavefunction and energy corrections to the unperturbed system, the equation 2.34 can be expended in a set of inhomogeneous equations with the form of [122]

$$\begin{aligned}(H^{(0)} - E^{(0)})\Psi^{(1)} &= (E^{(1)} - H_{\text{pert}})\Psi^{(0)}, \\ (H^{(0)} - E^{(0)})\Psi^{(2)} &= (E^{(1)} - H_{\text{pert}})\Psi^{(1)} - E^{(1)}\Psi^{(0)}, \\ (H^{(0)} - E^{(0)})\Psi^{(3)} &= (E^{(1)} - H_{\text{pert}})\Psi^{(2)} - E^{(2)}\Psi^{(2)} - E^{(3)}\Psi^{(0)}, \\ &\vdots\end{aligned}\tag{2.37}$$

The indices of the correction terms indicate the correction order of the wavefunction and energy. These equations can be solved progressively to achieve a perturbation correction to any arbitrary order. Each order of the correction has a smaller impact on the overall correction value. The complexity of the solutions grows with the order of the equation, so the corrections to the wavefunctions and energies are usually made to the first or second order, depending on the application and accuracy requirements. As an example for a non degenerate system, the first order correction of the energy is given by

$$E^{(1)} = \langle \Psi_0 | H_{\text{pert}} | \Psi_0 \rangle,\tag{2.38}$$

while the first order of the wavefunction correction is given by

$$|\Psi^{(1)}\rangle = - \sum_{k \neq n} \frac{\langle \Psi_k^{(0)} | H_{\text{pert}} | \Psi_n^{(0)} \rangle}{E_k^{(0)} - E_n^{(0)}} |\Psi_k^{(0)}\rangle.\tag{2.39}$$

Here, the indices k and n indicate distinct atomic states. The first correction of the wavefunction is defined as a linear combination of the rest of the wavefunctions of the system. Although this is an infinite series, the energy difference between states in the denominator ensures that it converges, and a finite, sufficiently high, number of atomic states can be used to make a good approximation.

2.2 Atomic Transitions

Besides the atomic structure, another fundamental aspect of atomic physics are the transitions between energy levels. These transitions can happen radiatively and non-radiatively. In the first case, an electron in an excited bound state relaxes into a lower energy state by releasing a photon with the corresponding energy given by the difference between the binding energies of the excited and the lower energy state. This is called a radiative transition. The excited ion can also relax non-radiatively by transferring the energy difference into another bound electron. If the energy is sufficient, the other electron may be

ejected from the ion, leading to an ionization. This process is called autoionization, and the transition itself may be called an Auger decay. A brief review of both processes is going to be made in this Section.

2.2.1 Radiative transition

An atomic system can absorb or emit radiation, causing transitions of electrons between atomic states in such a way that the total energy of the system is conserved. These situations can be studied by analyzing the interaction between an atom and the radiation and the time evolution of the combined system. Let the electromagnetic field be composed of electromagnetic plane waves. Radiation propagating in the direction $\hat{k}$ is described by the transverse-gauge vector potential [122]

$$\mathbf{A}_{\pm}(\mathbf{r}, \omega) = \hat{\epsilon}_{\lambda} e^{\pm i\mathbf{k} \cdot \mathbf{r}}, \quad (2.40)$$

where ω , $\hat{\epsilon}_{\lambda}$ and $\mathbf{k}$ are the radiation frequency, the polarization vector and the propagation vector, respectively. The vector potential and the polarization vector are always orthogonal. $\hat{\epsilon}_{\lambda}$ represent the two unit vectors orthogonal between each other and with the propagation vector ($\lambda = \pm 1$). The general solution to the time-dependent wave equation in the transverse gauge is a superposition of plane wavefunctions in the form

$$\mathbf{A}(\mathbf{r}, t) = \sum_i \left(c_i \hat{\epsilon}_{\lambda} e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} + c_i^* \hat{\epsilon}_{\lambda}^* e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \right), \quad (2.41)$$

where i is the set of parameters $(\omega, \hat{k}, \hat{\epsilon}_{\lambda})$ and c_i are the Fourier expansion coefficients.

If one considers a closed box of volume V , the number of possible vectors $\mathbf{k}$ that allow the electromagnetic field to respect certain boundary conditions on the surface of the box is finite. If the coefficients c_i and c_i^* are interpreted as quantum mechanical operators, the electromagnetic field becomes quantized. This way a photon is described by the operator

$$\mathbf{A}_i(\mathbf{r}, t) = \sqrt{\frac{\hbar}{2\epsilon_0\omega V}} \left(c_i \hat{\epsilon}_{\lambda} e^{i\mathbf{k} \cdot \mathbf{r} - i\omega t} + c_i^{\dagger} \hat{\epsilon}_{\lambda}^* e^{-i\mathbf{k} \cdot \mathbf{r} + i\omega t} \right). \quad (2.42)$$

The coefficients c_i and $c_i^{\dagger}$ are the photon annihilation and creation operators. The coefficients of the equation permits the energy of the radiation to be expressed in terms of the number of photons. Similarly to equation 2.41, the general expression for the vector potential is a superposition of the photon potentials 2.42,

$$\mathbf{A}(\mathbf{r}, t) = \sum_i \mathbf{A}_i(\mathbf{r}, t). \quad (2.43)$$

The Hamiltonian of the electromagnetic field is given by [122]

$$\begin{aligned} H_{EM} &= \frac{\epsilon_0}{2} \int d^3r \mathbf{E}(\mathbf{r}, t) \cdot \mathbf{E}(\mathbf{r}, t) + \frac{1}{2\mu_0} \int d^3r \mathbf{B}(\mathbf{r}, t) \cdot \mathbf{B}(\mathbf{r}, t) \\ &= \sum_i \hbar\omega_i \left(\mathcal{N}_i + \frac{1}{2} \right), \end{aligned} \quad (2.44)$$

where $\mathcal{N}_i = c_i^\dagger c_i$ is the photon number operator. With this relation, one can show that the vacuum state is an eigenstate of H_{EM} with energy

$$E_0 = \frac{1}{2} \sum_i \hbar \omega_i. \quad (2.45)$$

This energy is referred to as the *zero-point energy* of the electromagnetic field. Since it is not measurable, the electromagnetic field Hamiltonian is modified to be expressed as

$$H_{EM} = \sum_i \hbar \omega \mathcal{N}_i. \quad (2.46)$$

The interaction between an electron and an external electromagnetic field is given by [122]

$$\begin{aligned} h_I(\mathbf{r}, t) &= -ec \boldsymbol{\alpha} \cdot \mathbf{A}(\mathbf{r}, t) \\ &= \sum_i \left[h_I(\mathbf{r}, \omega) c_i e^{-i\omega t} + h_I^\dagger(\mathbf{r}, \omega) c_i^\dagger e^{i\omega t} \right], \end{aligned} \quad (2.47)$$

with

$$h_I(\mathbf{r}, \omega) = -ec \sqrt{\frac{\hbar}{2\epsilon_0 \omega V}} \boldsymbol{\alpha} \cdot \hat{\epsilon}_\lambda e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (2.48)$$

where e is the fundamental charge constant and c is the speed of light. The many-electron interaction Hamiltonian in the Heisenberg representation becomes

$$H_I(t) = \sum_k \left[H_I(\omega) c_k e^{-i\omega t} + H_I^\dagger(\omega) c_k^\dagger e^{i\omega t} \right], \quad (2.49)$$

where $H_I(\omega)$ is the N sum of one-electron terms,

$$H_I(\omega) = \sum_{i=1}^N h_I(\mathbf{r}, \omega). \quad (2.50)$$

To study the time evolution of a system composed of an atom and an external electromagnetic field, one must consider the effect of adding the interaction Hamiltonian to the sum of the many-electron Hamiltonian $H_0 + V_I$. The eigenvalue equations of this Hamiltonian and H_{EM} are

$$(H_0 + V_I) \Psi_k = E_k \Psi_k \quad (2.51)$$

and

$$H_{EM} |n_k\rangle = n_k \hbar \omega |n_k\rangle. \quad (2.52)$$

Ψ_k and E_k are the eigenfunctions and eigenvalues of $H_0 + V_I$, while $|n_k\rangle$ and n_k are the eigenfunctions and eigenvalues of H_{EM} . If the total Hamiltonian is represented by $H = H_0 + V_I + H_{EM}$, the eigenfunctions of H are given by

$$\Phi_k = \Psi_k |n_k\rangle, \quad (2.53)$$

with eigenvalues $E_k + n_k \hbar \omega$. Let S be the unitary operator that transforms states prepared at $t = -\infty$, when there is no interaction of the form $H_I(t)$, into states in the time $t = \infty$,

where the interaction is once again assumed to vanish. This operator is expressed as $S = U(-\infty, \infty)$. It becomes

$$S = I + \sum_{n=1}^{\infty} S^{(n)}, \quad (2.54)$$

where

$$S^{(n)} = \frac{(-i)^n}{\hbar^n} \int_{-\infty}^{\infty} dt_1 \hat{H}_I(t_1) \int_{-\infty}^{t_1} dt_2 \hat{H}_I(t_2) \dots \int_{-\infty}^{t_{n-1}} dt_n \hat{H}_I(t_n). \quad (2.55)$$

and I is the identity matrix.

By retaining only the first order in H_I ($n = 1$), the transition amplitude for a state Φ_i in the past to evolve into the state Φ_f in the future is given by

$$\begin{aligned} S_{fi}^{(1)} &= \langle \Phi_f | S^{(1)} | \Phi_i \rangle \\ &= -\frac{i}{\hbar} \int_{-\infty}^{\infty} dt \langle \Phi_f | \hat{H}_I(t) | \Phi_i \rangle. \end{aligned} \quad (2.56)$$

The probability of transition from the initial to the final stationary state is given by the square of $S_{fi}^{(1)}$. The operator c_i in the interaction Hamiltonian applied to a state $|n_i\rangle$ leads to a state with $n_i - 1$ photons, while the operator $c_i^\dagger$ results in a state with $n_i + 1$ photons. These states also follow the relation $\langle n_i - 1 | c_i | n_i \rangle = \sqrt{n_i}$. With this, and considering the cases for photon absorption and photon emission, where the final states are given by $\Phi_f = \Psi_f |n_i - 1\rangle$ and $\Phi_f = \Psi_f |n_i + 1\rangle$, respectively, the probability of transition for these processes can be written as

$$\begin{aligned} S_{fi}^{(1)} &= -\frac{i}{\hbar} \sqrt{n_i} \int_{-\infty}^{\infty} dt e^{i(E_f - E_i - \hbar\omega)t/\hbar} \langle \Psi_f | H_I | \Psi_i \rangle \\ &= -2\pi i \delta(E_f - E_i - \hbar\omega) \sqrt{n_i} \langle \Psi_f | H_I | \Psi_i \rangle \end{aligned} \quad (2.57)$$

and

$$\begin{aligned} S_{fi}^{(1)} &= -\frac{i}{\hbar} \sqrt{n_i + 1} \int_{-\infty}^{\infty} dt e^{i(E_f - E_i + \hbar\omega)t/\hbar} \langle \Psi_f | H_I^\dagger | \Psi_i \rangle \\ &= -2\pi i \delta(E_f - E_i + \hbar\omega) \sqrt{n_i + 1} \langle \Psi_f | H_I^\dagger | \Psi_i \rangle. \end{aligned} \quad (2.58)$$

By defining the transition amplitude as

$$T_{fi} = \begin{cases} \langle \Psi_f | H_I | \Psi_i \rangle, & \text{for absorption of a photon} \\ \langle \Psi_f | H_I^\dagger | \Psi_i \rangle, & \text{for emission of a photon} \end{cases}, \quad (2.59)$$

the transition probability can be compactly written as

$$S_{fi} = -2\pi \delta(E_f - E_i \mp \hbar\omega) T_{fi} \begin{pmatrix} \sqrt{n_i} \\ \sqrt{n_i + 1} \end{pmatrix} \delta(E_f - E_i \mp \hbar\omega). \quad (2.60)$$

The transition probability per unit time can be evaluated for both emission and absorption of a photon by evaluating the square of the last couple of expressions and replacing a factor of $2\pi \delta(E_f - E_i \mp \hbar\omega)$ by the total interaction time $T/\hbar$,

$$W_{fi} = \frac{2\pi}{\hbar} |T_{fi}|^2 \begin{pmatrix} n_i \\ n_i + 1 \end{pmatrix} \delta(E_f - E_i \mp \hbar\omega). \quad (2.61)$$

The interaction Hamiltonian depends on $e^{i\mathbf{k}\cdot\mathbf{r}}$. The wavelength of a photon emitted by an atomic transition ranges typically from hundreds of nanometers (visible light) to the order of a few angstrom (X-ray), while the typical atomic distances are in the order of the Bohr radius ($\approx 0.5 \text{ \AA}$), reaching lower values for HCl due to the stronger Coulomb attraction. Since the wavelength is typically much higher than the atomic distances, leading to $\mathbf{k} \cdot \mathbf{r} \ll 1$, this quantity can be approximated as $e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i(\mathbf{k} \cdot \mathbf{r}) + \dots$, where each term refers to a different multipole approximation of the electromagnetic field. For example, taking the first order approximation $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1$ leads to the electric dipole transition, while taking the next approximation $e^{i\mathbf{k}\cdot\mathbf{r}} \approx 1 + i(\mathbf{k} \cdot \mathbf{r})$ leads to the magnetic dipole transition. These are special cases of multipoles, which are the components of expansion of $e^{i\mathbf{k}\cdot\mathbf{r}}$ in vector spherical harmonics with order L and are of electric or magnetic types (two transverse directions to $\mathbf{k}$). Electric dipole transitions can also be represented by the term $E1$, while magnetic dipole transitions can be represented by $M1$. Other higher-order multipoles like electric and magnetic quadrupole, are represented by $E2$ and $M2$. As the transition wavelength and atomic distances scale with Z^{-2} and Z^{-1} along the isoelectronic distance, the wavelength of the emitted radiation for low charge states is much higher than the size of the atom, making the $E1$ the predominant multipole. These wavelengths get much closer to the size of the atoms for the case of HCl, making the remaining multipoles relevant in such atomic systems.

These transitions are only possible if they follow a set of selection rules. Due to the conservation of angular momentum, they must follow the triangular inequality

$$|J_i - J_f| \leq L \leq J_i + J_f, \quad (2.62)$$

with the z components satisfying the relation

$$M_i = M_f + M_L. \quad (2.63)$$

Parity must also be conserved. This is defined by $\pi = (-1)^\ell$, where ℓ is the orbital angular momentum. For a multipole transition to be allowed, the following relation must be verified:

$$\pi_i = \pi_f (-1)^{L+\lambda+1}. \quad (2.64)$$

The selection rules for $E1$, $M1$, $E2$ and $M2$ transitions are summarized in Table 2.1.

In a given interval of wave numbers d^3k , the number of photons of a particular polarization is

$$d^3n_i = \frac{V}{(2\pi)^3} d^3k = \frac{V}{(2\pi c)^3} \omega^2 d\omega d\Omega_k \quad (2.65)$$

where Ω_k represents a solid angle in the wave number space. The number of transitions per second for this interval of wave number can be evaluated by the relation $d^3w_{fi} = W_{fi} d^3n_i$. By integrating over ω , and considering that the spectral density can be defined as $\rho(\omega) = \hbar\omega^3/\pi^2c^3$, the photon emission probability per second of an excited state Ψ_i

Table 2.1: Angular momentum selection rules for E1, M1, E2 and M2 radiative transitions.

E1	M1	E2	M2
$\Delta J = 0, \pm 1$	$\Delta J = 0, \pm 1$	$\Delta J = 0, \pm 1$	$\Delta J = 0, \pm 1$
if not	if not	if not	if not
$J = 0 \leftrightarrow 0$	$J = 0 \leftrightarrow 0$	$J = 0 \leftrightarrow 0, 1; \frac{1}{2} \leftrightarrow \frac{1}{2}$	$J = 0 \leftrightarrow 0, 1; \frac{1}{2} \leftrightarrow \frac{1}{2}$
$\Delta M_J = 0, \pm 1$	$\Delta M_J = 0, \pm 1$		
if not $M_J = 0 \leftrightarrow 0$	if not $M_J = 0 \leftrightarrow 0$	$\Delta M_J = 0, \pm 1, \pm 2$	$\Delta M_J = 0, \pm 1, \pm 2$
when $\Delta J = 0$	when $\Delta J = 0$		
$\pi_f = -\pi_i$	$\pi_f = \pi_i$	$\pi_f = \pi_i$	$\pi_f = -\pi_i$

into a lower energy state Ψ_f can be defined as [122]

$$A_{if}^{r_{\text{total}}} = \left(1 + \frac{\pi^2 c^3}{\hbar \omega^3} \rho(\omega)\right) \frac{\alpha}{2\pi} \omega \sum_{\lambda} \int d\Omega_k |T_{fi}|^2. \quad (2.66)$$

From this equation, it is apparent that that only one of the two terms depends on the spectral density (stimulated emission). As such, the spontaneous emission (emission without the need for a prior spectral density) rate is

$$A_{if}^r = \frac{\alpha}{2\pi} \omega \sum_{\lambda} \int d\Omega_k |T_{fi}|^2. \quad (2.67)$$

In the electric dipole approximation, where $e^{\mathbf{k} \cdot \mathbf{r}} \approx 1$, the transition amplitude is given by

$$T_{fi} = \langle \Psi_f(\mathbf{r}) | \boldsymbol{\alpha} \cdot \hat{\mathbf{e}} | \Psi_i(\mathbf{r}) \rangle. \quad (2.68)$$

This quantity can also be expressed as

$$T_{fi} = i \frac{\omega_{fi}}{c} \langle \Psi_f(\mathbf{r}) | \mathbf{r} | \Psi_i(\mathbf{r}) \rangle \cdot \hat{\mathbf{e}}, \quad (2.69)$$

with

$$\omega_{fi} = \frac{E_f - E_i}{\hbar}. \quad (2.70)$$

The radiative transition rates are a fundamental propriety of atomic physics and are of paramount importance to the dynamics of atomic systems populations in excited states.

2.2.2 Autoionization

If the transition energy of an excited electron surpasses the binding energy of another bound electron, the excited electron can decay with the excess energy of the transition being transferred to an ejected electron. This electron carries a kinetic energy given by its binding energy minus the other transition energy. This process is know as Auger decay,

and the ejected electron is an Auger electron. Analogously to the radiate decay, the Auger (or autoionization) decay rate can be expressed as [121]

$$A_{if}^a = \frac{2\pi}{\hbar} \sum_{\kappa} \left| \langle \Psi_f, \kappa; J_T M_T | \sum_{l < m} \frac{1}{r_{lm}} | \Psi_i \rangle \right|^2, \quad (2.71)$$

where Ψ_i and Ψ_f are the excited state and the final state with one less electron. The final wavefunction $|\Psi_f, \kappa; J_T M_T\rangle$ is composed of the final bound state Ψ and the free wave of the ejected electron with relativistic angular momentum defined in the last Section. Since the energy is transferred by an electron-electron interaction, the matrix element is the Coulomb potential. The time-inverse process is the Dielectronic Capture (DC), where a free electron recombines with an ion with simultaneous excitation of another bound electron. The resonant strength (integral of the cross-section) of this process, given in atomic units, is defined as

$$S^{DC} = \frac{g_i}{2g_f} \frac{\pi^2}{E_{if}} A_{if}^a, \quad (2.72)$$

where g_i and g_f are the statistical weights of the initial and final states, given by $g = 2J + 1$, and E_{if} is the resonant energy (excitation energy minus the binding energy of the recombined electron). The importance of this type of recombination will be cleared later when discussing multi-step resonant processes.

When an electron is in an excited level, it can only decay via a radiative decay or an Auger decay. The probability of an electron in an excited level i transition into another level f depends of the rate of the respective transition and the rate of any other possible transitions parting from i . This probability is called the branching ratio, and is defined as

$$B_{if} = \frac{A_{if}^x}{\sum_k A_{ik}^r + \sum_{k'} A_{ik'}^a}, \quad (2.73)$$

where A^x is the radiative or non-radiative transition rate and k and k' are all the possible energy levels to which the excited electron can transition into radiatively and non-radiatively, respectively.

2.3 Collisional processes

Besides interacting with photons, ions can also interact with free electrons by collisional processes, namely in plasmas. When a free electron collides with an ion, it can either be scatter elastically, inelastically or be captured. In the second case, the free electron can only transfer an amount of energy to the ion corresponding to processes allowed by its atomic structure. During a collision, a bound electron can be excited resonantly or non-resonantly, it can ionize the ion by ejecting a bound electron, or recombine with the ion, leading to a loss of charge. The most relevant electron-ion collisional processes in a coronal plasma are represented in Figure 2.1. Since this is the kind of plasmas studied in this project, only this collisional processes will be presented.

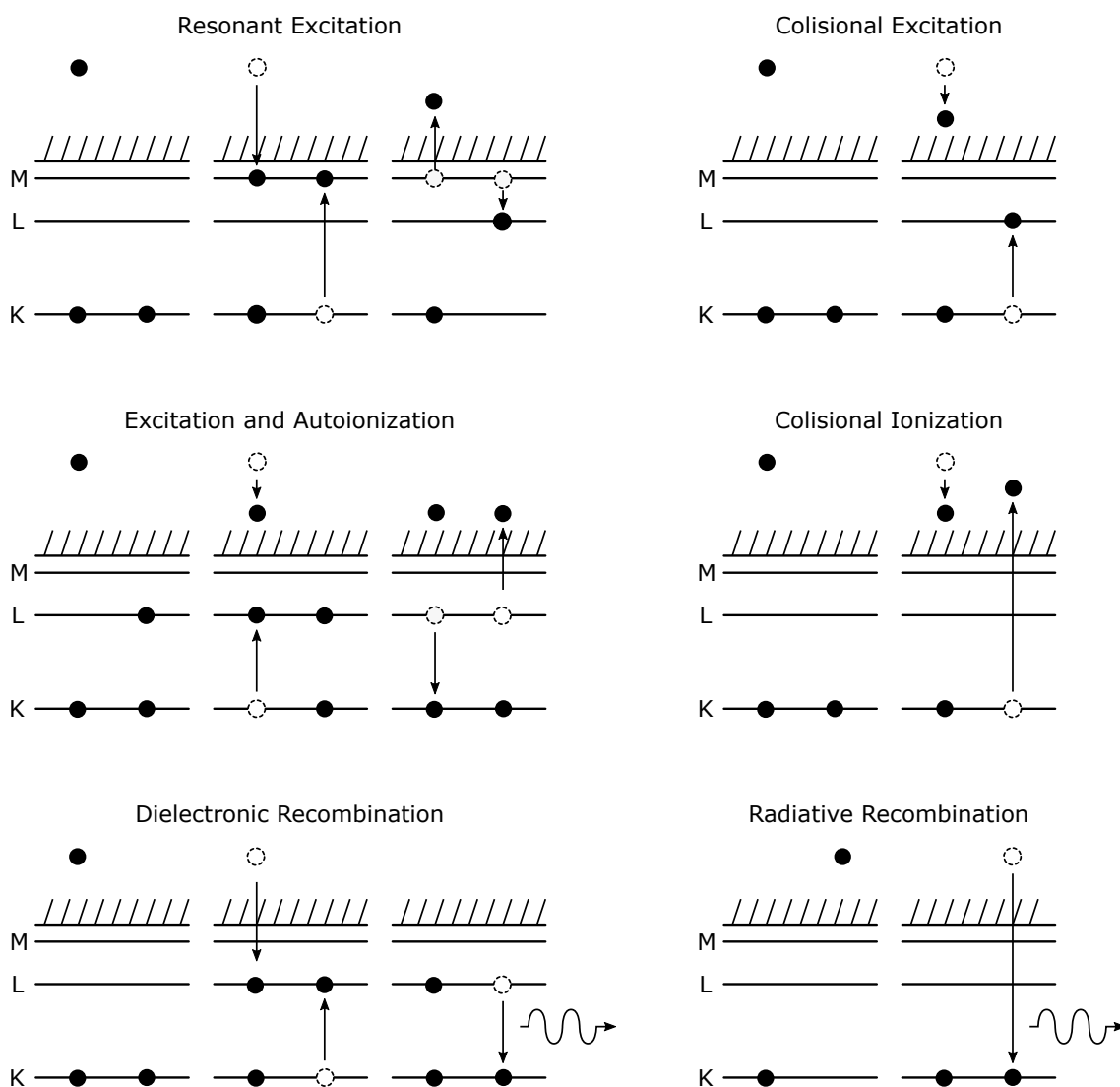


Figure 2.1: Schematic of several atomic processes: collisional and resonant excitation, excitation and autoionization, collisional ionization, dielectronic recombination and radiative recombination. In every individual scheme, each horizontal line represents an atomic shell (K, L and M) below the continuum. The black dots represent an electron (free if above the continuum threshold) and the curvy lines represent photons. Every scheme is represented in either 2 or 3 moments in time and the circles with a dotted outline represent the previous position of an electron.

2.3.1 Collisional excitation and ionization

Some of the most common processes in collisions of HCl with electrons are the collisional excitation and collisional ionization processes (see Figure 2.1). The process of excitation takes place when the kinetic energy of an incident electron is above the required threshold energy to excite the ion, i.e. the difference between the lower and higher energy levels. If the kinetic energy is transferred to the ion, it becomes excited and can decay by either emitting a photon, a cascade of photons, or an Auger electron. Schematically, the first case

is described as

$$\text{CE: } A^{q+} + e^- \rightarrow [A^{q+}]^* + e^- \rightarrow A^{q+} + e^- + h\nu, \quad (2.74)$$

where A^{q+} denotes an ion of charge $q+$, e^- represents a free electron, $h\nu$ a photon and the superscript $*$ denotes an excited state. Analogous to the Auger rate, the collisional strength is give by

$$\Omega_{01} = 2 \sum_{\kappa_0 \kappa_1} \sum_{J_T} (2J_T + 1) \left| \langle \Psi_0^c(\varepsilon_0) \kappa_0, J_T M_T | \sum_{i < j} \frac{1}{r_{ij}} | \Psi_1^c(\varepsilon_1) \kappa_1, J_T M_T \rangle \right|^2. \quad (2.75)$$

The collisional strength is, by definition, dimensionless. Similarly to the Auger, both initial and final states have a free electron with relativistic angular momentum κ_0 and κ_1 . Also, classically, the collision occurs mediated by the coulomb potential that the incident electron and scattered electron interacts. Here, J_T is the total angular momentum of both final and initial states coupled with the free electron, since total angular momenta of the composed system is conserved. The cross-section of CE, σ_{CE} , with the collisional excitation from an initial state Ψ_0 to a final state Ψ_1 is related to the quantity collisional strength Ω_{01} by [121, 125]

$$\sigma_{CE} = \frac{\pi}{k_0^2 g_0} \Omega_{01}, \quad (2.76)$$

where g_0 is the statistical weight of the initial state, k_0 is the (relativistic) wavenumber of the incident electron, related to its kinetic energy ε_0 by

$$k_0^2 = 2\varepsilon_0 \left(1 + \frac{\alpha^2}{2} \varepsilon_0 \right), \quad (2.77)$$

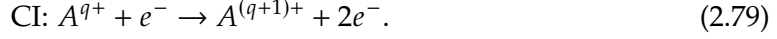
with α corresponding to the fine structure constant. The collisional excitation can only occur when the incident electron has a kinetic energy higher than the energy difference between the two bound atomic states involved in the excitation, with the outgoing free electron carrying the energy excess in the form of kinetic energy. For this reason, the energy difference between the two bound states is known as the excitation threshold, below which the excitation cross-section is zero.

Since the excited state has both the possibility to decay to a lower energy state or autoionize, the cross-section associated to the process described in (2.67) must take into account the probability of radiative decay rather than Auger transition (branching ratio). A partial cross-section of CE from a state i into an intermediate state d , leading to a radiative transition from state i to state f is

$$\sigma_{CE'}^{i \rightarrow f} = \sigma_{CE}^{i \rightarrow d} \frac{A_{df}^r}{\sum_f A_{df'}^r + \sum_{f''} A_{df''}^a}, \quad (2.78)$$

where f' and f'' represent all the possible states to where the electron in the intermediate state d can decay into.

If the kinetic energy of the incident electron surpasses the binding energy of a bound electron, the ion might be ionized in the collision, leading to the collisional ionization process



This process can be calculated by an expression analogous to the equation (2.70), where the final state wavefunction is substituted with the continuum atomic wavefunction corresponding to the ejected electron. The inclusion of an electron wavefunction in the continuum interacting with an ion is not trivial. Several methods to solve this problem will be discussed in Sections 2.3.5 and 2.3.6. The cross-section of this process for few-electron ion systems can be estimated with the well known semi-empirical Lotz formula [126], which has proven to be sufficiently accurate when compared to experimental results. For electron energies E_e much larger than the binding energy P_i of an electron within the suborbital i , the Lotz formula is given by

$$\sigma_i = a q_i \frac{\ln(E_e/P_i)}{E_e/P_i}, \quad (2.80)$$

where $a = 4.5 \times 10^{-14} \text{ cm}^2 \text{ eV}^2$ is an empirical constant and q_i is the number of equivalent electrons in the subshell i .

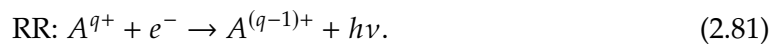
Ionization processes have been studied extensively for HCI in ion storage rings, such as the Test Storage Ring (TSR), in Heidelberg [99, 127, 128].

2.3.2 Electron-ion recombination

Besides emission originated from CE, X-ray spectra of these systems are also dominated by structures originated by electron-ion recombination processes. Like the ionization processes, they also play a fundamental role in charge state population balance and are key processes for plasma modeling. These processes are divided in non-resonant, namely radiative recombination, and resonant, like dielectronic recombination.

2.3.2.1 Radiative Recombination

The radiative recombination process is a non-resonant process and can happen with any initial free electron with kinetic energy ε . A free electron can approach an ion and recombine in a state with binding energy E_b . As a result of the recombination, there is an emission of a photon with energy $\omega = E_b + \varepsilon$ (conservation of energy principle),



Since this is a non-resonant process, the resulting radiation can contribute to the background of the experimental spectra where the free electron energy is scanned. The associated cross-section σ_{RR} is related to the photoionization (PI) cross-section by the Milne relation [129],

$$\sigma_{RR} = \frac{\alpha^2}{2} \frac{g_i}{g_f} \frac{\omega^2}{\varepsilon(1 + \frac{1}{2}\alpha^2\varepsilon)} \sigma_{PI} \quad \text{and} \quad \sigma_{PI} = 2\pi\alpha \frac{df}{dE}. \quad (2.82)$$

Here, g_i and g_f are statistical weights of the respective states, ω is the photon energy in atomic units and ε is the energy of the free electron. The quantity df/dE is the differential oscillator strength and can be computed by

$$\frac{df}{dE} = \frac{\omega (\alpha\omega)^{2L-2}}{g_i (2L+1)} \sum_{\kappa_{JT}} |\langle \Psi_f, \kappa; J_T | O^L | \Psi_i \rangle|^2. \quad (2.83)$$

The operator O^L is the multiple operator of rank L which induces the transition and Ψ_i and Ψ_f are the wavefunctions before and after the photoionization. The PI process is the time-inverse process of RR, where an ion is ionized by an incident photon of sufficient energy. The RR process is known well enough for its calculation to be fairly accurate. For this reason, theoretical calculations of RR are often used as cross-section calibrations.

2.3.2.2 Dielectronic Recombination and Resonant Excitation

The DR is a two-step process in which, similarly to the RR process, an incident electron recombines with an ion. A free electron is captured by an ion via a dielectronic capture (see Sections 2.2.2), leaving the ion in a doubly excited state. This can only happen when the kinetic energy of the incident electron equals the excitation energy of the bound electron, thus being a resonant process. Afterwards, the excited electrons can either decay radiatively or autoionize, the former corresponding to the DR process and the latter to the resonant excitation process (RE):

$$\begin{aligned} \text{DR: } A^{q+} + e^- &\rightarrow [A^{(q-1)+}]^* \rightarrow A^{(q-1)+} + h\nu \text{ (cascade),} \\ \text{RE: } A^{q+} + e^- &\rightarrow [A^{(q-1)+}]^* \rightarrow A^{q+*} \rightarrow A^{q+} + h\nu \text{ (cascade),} \end{aligned} \quad (2.84)$$

This process has a relatively high cross-section and can dominate the spectra of these ion systems. It has an important role in the charge state balance and, with a good understanding of its underlying theory, can become an important diagnostic tool for astrophysical and fusion plasmas. It is usual to apply a nomenclature similar to the one found in the auger electron emission process to identify the DR process. It consists of three letters indicating the atomic shells where the bound electron belongs before and after the excitation and the shell where the free electron is captured, respectively. As an example, the KLL DR process corresponds to the capture of a free electron to the L-shell with an excitation of a bound electron from the K to the L-shell. This example is represented in Figure 2.1.

The DR cross-section can be expressed as [130]

$$\sigma_{idf}^{DR}(E_e) = \frac{\pi^2 \hbar^3}{m_e E_e} \frac{g_d}{2g_i} A_{di}^a B_{df} L_d(E_e), \quad (2.85)$$

where E_e is the free electron energy, A_{di}^a is the autoionization rate from an intermediate state d to an initial state i , B_{df} is the branching ratio (equation 2.73) of the intermediate excited state d to a final state f and $L_d(E_e)$ is the Lorentzian profile of the resonance. The

quantities g_d and g_i are the statistical weights of the states after and before recombination. Here, J is the total angular momentum of a given state.

The normalized Lorentzian profile is defined by

$$L_d(E_e) = \frac{\Gamma_d/2\pi}{(E_e - E_{id})^2 + \Gamma_d^2/4}, \quad (2.86)$$

where $E_{id} = E_d - E_i$. Γ_d is the width of the resonance, defined by the sum of all the possible autoionizing and radiative decays starting with the state d , i.e. $\Gamma_d = \hbar \left(\sum_n A_{dn}^a + \sum_m A_{dm}^r \right)$.

The resonant strength is the integral of the cross-section, given by the relation

$$\begin{aligned} S_{idf}^{DR} &= \int_0^\infty \sigma_{idf}^{DR}(E_e) dE_e \\ &= \frac{\pi^2 \hbar^3}{m_e E_e} \frac{g_d}{2g_i} \frac{A_{di}^a A_{df}^r}{\sum_n A_{dn}^a + \sum_m A_{dm}^r}. \end{aligned} \quad (2.87)$$

This quantity is often used to make comparisons between different atomic theories and experimental result, since it does not depend on the experimental resolution and translates the intensity of a single resonance into a single numerical value that can be more easily compared with an experimental DR peak integral.

In thermal plasmas, such as those studied in astrophysics and nuclear reactors, the free electron energy often follows a Maxwellian distribution characterized by an electron temperature T . The modeling of this kind of plasmas is indirectly linked to the DR cross-section, by the convolution of the former with a Maxwellian distribution. The integral of this quantity constitutes the DR rate coefficient, and it is used in several plasma modeling codes, such as CLOUDY [131], XSTAR [132] and CHIANTI [35], to simulate charge state dynamics and also determine ion populations in steady-state conditions. The DR rate coefficient becomes [133]

$$\alpha_{if}^{DR}(T) = \int_0^\infty \sigma_{idf}^{DR}(E_e) \sqrt{\left(\frac{2E_e}{m_e}\right)} f(T, E_e) dE_e, \quad (2.88)$$

where $f(T, E_e)$ is the Maxwell-Boltzmann distribution, given by

$$f(E_e, T) = \frac{2}{\sqrt{\pi} (K_B T)^{3/2}} \sqrt{E_e} \exp\left(-\frac{E_e}{K_B T}\right). \quad (2.89)$$

Here, K_B is the Boltzmann constant and T is the electron temperature. By computing the integral, the dielectronic rate coefficients become

$$\alpha_{if}^{DR}(T) = \frac{1}{2g_i} \left(\frac{4\pi E_H}{K_B T}\right)^{3/2} a_0^3 \sum_d \exp\left(-\frac{E_{id}}{K_B T}\right) g_d A_{di}^a B_{df}, \quad (2.90)$$

where a_0 is the Bohr radius and E_H is the Rydberg constant.

The RE process is calculated in a similar manner. In this case, if the final state has the same number of bound electrons as the initial state, the branching ration is modified to give

$$B_{df} = \frac{A_{df}^a}{\sum_n A_{dn}^a + \sum_m A_{dm}^r}. \quad (2.91)$$

With this, the final cross-section becomes

$$\sigma_{idf}^{DR}(E_e) = \frac{\pi^2 \hbar^3}{m_e E_e} \frac{g_d}{2g_i} \frac{A_{di}^a A_{df}^a}{\sum_n A_{dn}^a + \sum_m A_{dm}^r} \frac{\Gamma_d/2\pi}{(E_e - E_{id})^2 + \Gamma_d^2/4}. \quad (2.92)$$

As is the case for the DR process, the RE is a resonant process. While the DR happens when the electron energy is below the CE threshold, the RE is only possible above this threshold.

2.3.3 Other multi-step processes

Besides DR and RE, there are other multi-step processes that can have an impact in a plasma charge state balance. While these two have a resonant process as a first step, some can also begin with a non-resonant process. For example, if there is an Auger decay after a CE, the process is called an Excitation-Autoionization (EA). The process is represented by

$$\text{EA: } A^{q+} + e^- \rightarrow [A^{q+}]^* + e^- \rightarrow A^{(q+1)+} + 2e^-. \quad (2.93)$$

This process leads to a variation of charge state and can have a greater cross-section than direct CI near the excitation threshold, and thus must be taken into account when modeling a plasma. Similarly to the previous case, the EA cross-section can be defined as

$$\sigma_{EA}^{i \rightarrow f} = \sigma_{CE}^{i \rightarrow d} \frac{A_{df}^a}{\sum_f A_{df'}^r + \sum_{f''} A_{df''}^a}. \quad (2.94)$$

Another example of a multi-step process in the Resonant-Excitation Double-Autoionization (REDA), where, after an RE (a multi-step process itself), the excited ion may double-autoionize, losing two electrons. This is a resonant ionization process that can happen superimposed to the EA and the CI processes.

2.3.4 Charge exchange

A final not-less important charge-changing collisional process in the charge exchange. Ion-atom and ion-ion collisions can lead to charge transfer between projectile and target. This is effective with slow atoms or molecules approaching HCl. Therefore, if one goal is to achieve a dominant population of a certain ion species, the chamber of an experimental apparatus must be maintained at an Ultra-High Vacuum (UHV), typically below 10^{-10} mbar. At these pressures, the residual gas is mainly hydrogen due to the degassing of the chamber walls. Therefore, a charge exchange process of interest is

$$A^{q+} + \text{H} \rightarrow A^{(Z-1)+} + \text{H}^+. \quad (2.95)$$

It was theoretically shown that the cross-section of this process depends mainly on the atomic number Z and the collision velocity v for ions with $Z \geq 16$ and $0.04 \leq v \leq 1.8$

(values in $\times 10^8 \text{ cm/s}$) [134]. A reasonable fit from the experimental results for this cross-section (in cm^2) gives the semi-empirical formula

$$\sigma_{CX} = 2.25 \times 10^{-16} Z \ln \left(\frac{15}{v} \right). \quad (2.96)$$

Since the cross-section varies with v (10^8 cm/s), different pressures yield different cross-sections. Higher residual pressure values increase the CX cross-section, thereby increasing the ionization rate and decreasing the average charge state of the population balance.

2.3.5 Distorted-Wave

Computing cross-sections of collisional processes involving a free electron (e.g. CE, from sec. 2.3.1) requires the knowledge of the wavefunction describing the free electron approaching the ion. There are several Born approximations that can describe the continuum wave function. The Plane-wave (PW) Born approximation describes the free electron as an unperturbed plane wave. A more realistic approach is the Coulomb-Wave (CW) Born approximation, which takes into account the distortion of the continuum by a pure Coulomb potential. An higher level of refinement can be held by calculating the orbitals in a potential that takes into account the electronic structure of the target ion. This is known as the Distorted-wave (DW) Born approximation, which provides more accurate results than the other two approximations.

The DW method can be applied by solving the Hamiltonian equation for the free electron wavefunction with a central potential $U(r)$, similar to what is used to calculate the atomic structure either with Hartree methods or the CI method [121]. This potential can be modified to include an high-lying subshell to account for the free electron feeling the screening of one extra electron at large distances. The large component of the continuum wavefunction, $F(r)$, requires an asymptotic amplitude of $\sqrt{k\epsilon}$, where k and ϵ are the incident electron momentum and energy. While the internal part of the radial wavefunction can be integrated from the Hamiltonian equation, the external part has a period too small for direct integration, and can be approximated by

$$F(r) = A \frac{1}{\eta^{1/2}(r)} \sin \phi(r), \quad (2.97)$$

where A is a normalization constant and the $\eta(r)$ and $\phi(r)$ functions must satisfy the following equations

$$\phi(r) = \int_0^r \eta(s) ds, \quad (2.98)$$

$$\eta^2(r) = \eta^{1/2}(r) \frac{d^2}{dr^2} \eta^{-1/2}(r) + \omega^2(r), \quad (2.99)$$

where

$$\omega^2(r) = 2[\epsilon - U(r)] - \frac{\kappa(\kappa + 1)}{r^2}. \quad (2.100)$$

With the radial part of the continuum wavefunction calculated, the respective matrix elements corresponding to the amplitude of the collisional processes can be computed. The DW has proven to be sufficiently accurate for most applications, and is widely used to generate atomic data for plasma diagnostics.

2.3.6 R-Matrix

In all the Born approximation methods, the interaction between multiple excitation channels is neglected. Resonant processes, like DR and RE, must be included separately, and each resonance is calculated individually with the methods described before. This is known as the isolated resonance approximation. Furthermore, no interference between different excitation or recombination channels is present, and can only be taken into account by perturbation methods.

A better alternative to the DW approach is the use of Close-Coupling (CC) methods. These methods take into account the coupling between different excitation or recombination channels. By including closed channels (like dielectronic capture induced double excitations), resonances arise naturally corresponding to the structures of DR and RE. Moreover, the coupling of channels leads to quantum interference, which reshapes resonances into Fano profiles (which have been observed experimentally).

In Close-Coupling methods, the incident electron is treated as one of the bound electrons of the ion, feeling the electron exchange and correlation with all the electron in the included electronic configurations. Usually this is solved with a CI expansion, so a similar approach to the CI method is appropriate for this problem. The R-Matrix method is a particular close-coupling method where the configuration space is partitioned in two regions separated by a radius $r = a$, where r is the distance between the incident electron and the nucleus [135]. The CI method is used to calculate the incident electron wavefunction inside of the radius a . The radius a is chosen so that, when outside, most of the charge distribution of the ion is contained within the sphere of radius a , making the exchange between electrons negligible. In this region, the electron moves in the long-range multipole potential of the ion, and the wavefunction can be obtain by either an asymptotic expansion or perturbation methods. The R-Matrix (RM) acts as the link between the two regions in the boundary $r = a$.

In this method, the basis of the total wavefunction takes the CI expansion form

$$\Psi_k(r_1, \dots, R_{N+1}) = \mathcal{A} \sum_{ijk} c_{ijk} \Phi_i(r_1, \dots, R_N) \frac{1}{r_{N+1}} u_{ij}(r_{N+1}), \quad (2.101)$$

where $u_{ij}(r_{N+1})$ are the continuum orbitals and $\mathcal{A}$ is the antisymmetrisation operator. Inserting this basis into the Hamiltonian equation, and using the variational principle with the appropriate boundary conditions at $r = a$, one can write the total wavefunction inside the radius a in the form

$$\Psi = \sum_k A_{Ek} \Psi_k, \quad (2.102)$$

where E is the total energy corresponding to the $N + 1$ electrons wavefunction. These coefficients can be determined as

$$A_{Ek} = \frac{1}{2a(E_k - E)} \sum_{i,j} c_{ijk} u_{ij}(a) \left(a \frac{dF_i}{dr} - b F_i \right)_{r=a}, \quad (2.103)$$

where $F_i(r)$ are the radial wavefunctions of the incident electron. Their value at $r = a$ is given by

$$F_i(a) = \sum_j R_{ij}(E) \left(a \frac{dF_j}{dr} - b F_j \right)_{r=a}. \quad (2.104)$$

From this, we get the definition of the R-Matrix

$$R_{ij}(E) = \frac{1}{2a} \sum_{i,j,k} \frac{c_{ijk} u_{ik}(a) c_{ijk} u_{jk}(a)}{E_k - E}. \quad (2.105)$$

The external radial wavefunctions are calculated with an asymptotic method similar to DW and the R-Matrix is adjusted to ensure the boundary conditions are met at $r = a$.

While this method includes more physical phenomena than the DW method, it is significantly more computationally expensive. Since the DW is sufficiently accurate for most cases, it is usually preferred.

2.4 Atomic codes

Since the techniques presented to calculate the atomic structure, decay rates and collisional cross-section have become standardized over the last few decades, modern atomic calculations are usually made with widely available atomic codes. When computing technology started to become fast enough for complex atoms to be modeled theoretically, many groups around the world started to develop codes based on the presented theories. The initial codes (and a significant portion of the modern codes) used to be closed projects, only available to members of the respective laboratories and collaborators. During the last few decades, many of these projects have become open-source, meaning that the source-code is widely available to the general public and users can contribute to their further development of the codes. Some of these codes are being used to calculate the relevant atomic data for this project. They will be presented in this section.

2.4.1 Flexible Atomic Code

The Flexible Atomic Code (FAC) is currently one of the most popular atomic codes among atomic and plasma physicists, thanks to its efficiency, ease of use and its open-source nature. It is extensively used in astrophysics, atomic physics and nuclear physics, particularly for plasma modeling and spectral simulation. This code uses the fully relativistic CI method to calculate the atomic structure and radiate transitions. By default, it takes into account higher order effects that were not covered in this theoretical review, such as the nuclear finite size, the Breit correction and first-order (Quantum Electrodynamics (QED)) effects.

The efficiency of this code comes from the fact that it calculates the wavefunction basis using a modified central potential which approximates the electron correlation effects. This step effectively avoids the need of performing an Hartree-Dirac-Fock calculation for building the wavefunction basis. While not the most accurate atomic structure calculation code, for the X-ray energy range it is usually accurate to a few eV. A significant advantages of this code is that it can be used to calculate atomic systems with millions of different energy levels, something that is too big of a task for most of the other codes. For more complex systems, the code also includes the Unresolved Transition Array (UTA) mode, based on the Spin-Orbit Split Array (SOSA) approximation, where it skips part of the angular momentum coupling as if it was a non-relativistic calculation, while still maintaining the relativistic corrections. While this mode results in some loss of structure details, it can reduce the number of energy levels by more than an order of magnitude, allowing the computation of complex systems that would otherwise be difficult to calculate.

Besides the atomic structure, it also calculates the cross-sections for several electron-ion collisional processes, such as excitation, recombination and ionization processes. It uses the DW approximation to calculate the cross-sections of all processes involving a free electron. This method is the default one, delivering accurate enough results for most applications while being very efficient. FAC also supports the use of the R-Matrix approach. It can calculate the collisional processes in a closed-coupling manner, thereby including all the quantum interference (and resulting Fano profiles) between channels, something that is not possible in the DW approach due to its isolated resonance nature. This comes at the expense of computational time, as it can be orders of magnitude more expensive to compute than the DW counterpart.

This code can also be used as a plasma modeling software. It includes a CRM package which allows the computation of the energy level populations of an ion in a plasma in different electron distributions, as well as the plasma charge state balance. This package is designed to only calculate the population for equilibrium conditions. With the populations, it calculates the emissivity of each transitions, and this information is often used to reproduce the emission spectra observed in plasma experiments.

2.4.2 MCDF codes

Codes based on the MCDF theory are often used when high accuracy in the atomic structure is required. While the accuracy of FAC is usually in the order of few eV, MCDF calculations can achieve levels of accuracy in the meV range depending on the size and complexity of the calculation. A disadvantage of this method over the CI method is the computational resources needed for the calculations. While FAC is capable of calculating millions of energy levels with low computational resources, the same calculations would not be feasible in the same type of computing unit. It is therefore more suited to the study of specific transitions accurately, rather than simulating the complexities of collisional plasma with multiple unresolved transition arrays.

One of the most popular codes using this method in the General Relativistic Atomic Structure Package (GRASP), which is an MCDF code originally developed by Parpia *et al* [136]. Updated and open-source versions of the code are now widely available [137, 138]. Another atomic code is the Multiconfiguration Dirac-Fock General Matrix Elements (MCDFGME), developed by Desclaux and Indelicato [139, 140]. The GRASP code is solely dedicated to atomic structure and radiative transition calculations, lacking any methods for estimating autoionization rates or calculating collisional cross-sections. On the other hand, the MCDFGME is capable of calculating both autoionization rates and collisional cross-sections. Since it uses the form factor approach, it gives good results for high energies, but our work showed inconsistencies near the excitation thresholds for excitation cross-sections given by this code.

2.5 Collisional Radiative Model

The simplest non-Maxwellian electron distribution is the almost mono-energetic electron beam present at an EBIT. This device produces a well-controlled coronal plasma, where the charge state balance of the ions can be controlled with the electron-beam properties. This makes EBIT a popular ion source for laboratory atomic physics studies [78, 79, 82, 91, 141, 142]. A CRM is a common choice for modeling EBIT observations, and many works have presented the use of this tool to reproduce the EBIT plasma emissions with an high degree of success [115, 143]. These works evaluate the atomic levels populations, and their respective emissions, as well as charge state distributions, electron temperature and density conditions, all in steady-state conditions. However, EBIT setups often rely on fast electron beam energy scans to probe the trapped ions without disturbing the charge state balance of the plasma. While a steady-state CRM is enough to predict the main features of emission spectra, the commonly used tools fail to reproduce emissions from metastable levels in non-equilibrium EBIT plasmas, as shown by our previous work [144], particularly when metastable states have lifetimes of the order of the plasma dynamics. EBIT experiments with dynamical electron beam energy distributions and metastable population dynamics motivate the need for a method of combining the dynamics of metastable states, slow collisional processes, and fast radiative transitions in the same CRM consistently.

In this Thesis, a new time-dependent full-detailed fine-structure CRM is presented, capable of simulating spectra of plasma under non-equilibrium conditions. Developed upon our previous code focused on charge-state balance evolution [145], the new CRM combines the features of electron beam plasma dynamics with the framework of collisional radiative modeling to simulate EBIT spectra produced by dynamical electron beam energy schemes. In our method, the local equilibrium principle [29] is included as a two-step process, instead of constructing a complex set of equations after including the (quasi-) steady-state solutions of non-metastable levels. First, in each integrating step, all level-rate equations are solved with allowed radiative rates being set to zero according to a threshold.

Second, the population gain of fast (non-metastable) levels in each step is redistributed according to its branching ratios since their population are in equilibrium. This allows the calculation of population dynamics in a slower timescale, while maintaining the inherent mechanisms of the fast cascades. After laying the groundwork, this simulation framework will simulate the metastable dynamics and emission spectrum of EBIT measurements of He-like oxygen with a fast electron beam energy scan. As the energy scan crosses the triplet $1s2s\ ^3S_1$ metastable state, there is a periodical growth and decay pattern of its population. The framework is shown to be capable of describing the metastable dynamics, as well as the emission spectrum.

2.5.1 Population balance rates

In order to simulate the dynamics of the emissions of a plasma, one has to describe the population evolution of each individual atomic state. The time variation of the population of an energy state depends on the collisional processes that populate or depopulate the level, such as collisional excitation, collision ionization, radiative recombination, dielectronic capture and charge exchange, as well as the radiative and non radiative transitions. The dynamics of the states N_j is obtained by numerically solving a set of coupled differential equations given by

$$\begin{aligned} \frac{dN_j}{dt} = & \sum_i^{\text{states}} n_e v_e \left[N_i \left(\sigma_{ij}^{CE} + \sigma_{ij}^{CI} + \sigma_{ij}^{RR} + \sigma_{ij}^{DC} \right) \right. \\ & \left. - N_j \left(\sigma_{ji}^{CE} + \sigma_{ji}^{CI} + \sigma_{ji}^{RR} + \sigma_{ji}^{DC} \right) \right] \\ & + N_i \left(A_{ij}^r + A_{ij}^a \right) - N_j \left(A_{ji}^r + A_{ji}^a \right) \\ & + N_i \sigma_{ij}^{CX} n_0 \bar{v}_i - N_j \sigma_{ji}^{CX} n_0 \bar{v}_j, \end{aligned} \quad (2.106)$$

where A_{ij}^x represents the rate of radiative ($x \equiv r$) and auger ($x \equiv a$) decays, σ_{ij}^x is the cross-section of a collisional process ($x \equiv CE, CI, RR, DC$), all between the i and j levels. n_e and v_e are the electron density and velocity, respectively. The quantities $\bar{v}_j$ and $\bar{v}_i$, for the charge exchange rates, represent the mean velocity of the charge state between levels j and i . All these atomic quantities were calculated with Flexible Atomic Code [121]. An immediate issue with directly solving these equations is that electric dipole allowed transitions typically have rates of 10^{-12} s. Solving this equation accurately would require a time step much shorter than this, which would make the study of the dynamics of metastable states, often in time scales higher than milliseconds, not feasible. This is solved with the local-equilibrium principle. In this work, we present a new implementation of this principle in a two-step manner without loss of accuracy or spectral details.

To simplify the notation, let the relaxation rates be expressed as $A_{ij} = A_{ij}^a + A_{ij}^r$, and the collisional rates be expressed as $\Omega_{ij} = n_e v_e \sum_x \sigma_{ij}^x + \sigma_{ij}^{CX} n_0 \bar{v}_i$, where x stands for the collisional processes CE, CI, RR and DC. The previous rate equations (2.106) can be

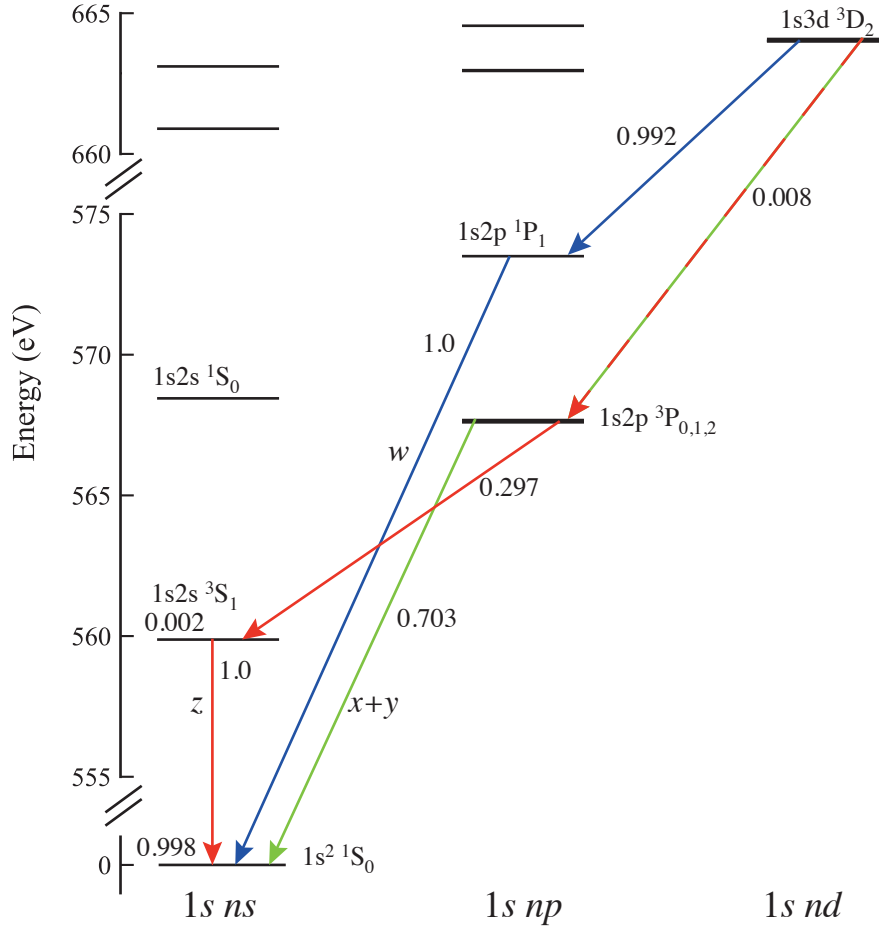


Figure 2.2: Energy level diagram of the K, L and M shells of He-like oxygen. Only the ground and singly excited states $1s n \ell$ are represented. Each columns represent the orbital angular momentum of the excited electron. As an example, the cascades of the excited level $1s_{1/2} 3d_{5/2} J = 2$ are represented by the arrows. The three different colors represent the three main cascade paths that start from the aforementioned excited state.

compactly rewritten in the matrix form as

$$\frac{d}{dt} \mathbf{N} = (\mathbf{\Omega} + \mathbf{A}) \cdot \mathbf{N} - \mathbf{N} \cdot (\mathbf{\Omega} + \mathbf{A})^T, \quad (2.107)$$

where $\mathbf{N}$, $\mathbf{\Omega}$ and $\mathbf{A}$ represent the matrices for the atomic level populations, collisional rates and transitions rates.

2.5.2 Numerical solutions

The integration of these differential equations is done in time-steps sufficiently accurate for the metastable and EBIT parameters timescales. Let the decays be categorized according to a threshold, denominating fast and slow transitions by $\mathbf{A}^f$ and $\mathbf{A}^s$. Correspondingly, populations are sorted as fast $\mathbf{N}^f$ if a given level decays at least with one fast transition, or slow ones $\mathbf{N}^s$, otherwise.

As a first step of the method, a temporary population evolution is obtained by numerically solving (2.107) a single time-step with only slow rates, i.e., solving

$$\mathbf{N}'(t_n) = \mathbf{N}(t_{n-1}) + \int_{t_{n-1}}^{t_n} (\mathbf{\Omega} + \mathbf{A}^s) \cdot \mathbf{N}(t_{n-1}) - \mathbf{N}(t_{n-1}) \cdot (\mathbf{\Omega} + \mathbf{A}^s)^\top dt. \quad (2.108)$$

where $\mathbf{N}'$ is a set of temporary populations calculated with only slow transitions $\mathbf{A} \rightarrow \mathbf{A}^s$. Then, since the short-lived $\mathbf{N}^f$ populations are in equilibrium at the integration time-step, their growth due to collisional processes must be equal to the decrease due to fast radiative decay. Therefore, the "artificial" gain of $\mathbf{N}^f$ population, while integrating Eq. (2.108) without $\mathbf{A}^f$, has to be redistributed according to the respective branching ratios (see equation 2.73). These are calculated beforehand for all excited states. With this, the branching ratio for an excited state i to decay into a final ground or metastable state j taking a specific path through a set of intermediate states $\{n_1, n_2, \dots, n\}$ is given by

$$B_{ij} = b_{in_1} b_{n_1 n_2} \cdots b_{nj}. \quad (2.109)$$

Then, a matrix $\mathbf{C}$ is constructed containing all the possible cascade paths connecting an excited state into the final long-lived states. As an example, the portion of the $\mathbf{C}$ matrix related to the $1s^2$ and $1s2\ell$ atomic states, as well as the ground states of H-like and Li-like, is shown in Eq. (2.110).

Each term C_{ij} is the total branching ratio from level i to j , having all paths connecting these levels. The decays paths of the level $1s3d_{5/2} J = 2$ of He-like oxygen are illustrated in Figure 2.2, leading to the total branching ratios shown there and in Eq. 2.110. For this example, an high threshold for slow rates was considered, so that only the $1s2s \ ^3S_1$ is considered metastable, thus only this level and ground levels have non-zero values of the respective lines in $\mathbf{C}$. This is sufficient for the timescale of the simulations that will be used to benchmark the experimental observations in the next Chapters.

In the second step, the excited populations are redistributed according to the calculated cascades with the $\mathbf{C}$ matrix. The short-lived states are corrected to zero, with their temporary population being transferred to the ground and metastable states. The populations in the end of the time step are given by

$$\mathbf{N}(t_n) = \mathbf{C} \cdot \mathbf{N}'(t_n). \quad (2.111)$$

During the construction of the matrix $\mathbf{C}$, a matrix $\mathbf{P}$ is also built to reconstruct the emissions during the subsequent cascades of an initial excited state. This matrix stores the complete branching ratios for every possible path, allowing for the evaluation of every photon emitted during a specific cascade path. The components of this matrix, storing a cascade path from an initial excited state i into a final stable or metastable state j , are

$$\mathbf{C} = \begin{pmatrix} 1s\ 1s_{1/2} & \dots & 1s^2\ 1s_0 & 1s2s\ 3s_1 & 1s2s\ 1s_0 & 1s2p\ 3p_0 & 1s2p\ 3p_1 & 1s2p\ 3p_2 & 1s2s\ 1s_0 & 1s2p\ 1p_1 & \dots & 1s3d\ 3d_2 & \dots & 1s2s\ 1s_{1/2} & \dots & \dots \\ 1 & \dots & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \dots & 0 & \dots & \dots \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \dots & 1 & 1 & 1 & \dots & \dots & \dots & \dots & 1 & \dots & 0.998 & \dots & \dots & 0 & \dots & \dots \\ 0 & \dots & 0 & 0 & 0 & 0 & 0.86 & 0.01 & 0 & 0 & \dots & 0.002 & \dots & \dots & 0 & \dots & \dots \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & \dots & 0 & 0 & 0 & 0 & 0.14 & 0.99 & 0 & 0 & \dots & \dots & \dots & \dots & 1 & \dots & \dots \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix} \quad \begin{matrix} 1s\ 1s_{1/2} \\ \vdots \\ 1s^2\ 1s_0 \\ 1s2s\ 3s_1 \\ \vdots \\ 1s^22s\ 1s_{1/2} \\ \vdots \end{matrix} \quad \begin{matrix} (2.110) \end{matrix}$$

defined as the following:

$$\begin{aligned} P_{i1}^i &= b_{in_1}, \\ P_{12}^i &= b_{in_1} b_{n_1 n_2}, \\ &\vdots \\ P_{nj}^i &= b_{in_1} b_{n_1 n_2} \cdots b_{nj}. \end{aligned} \tag{2.112}$$

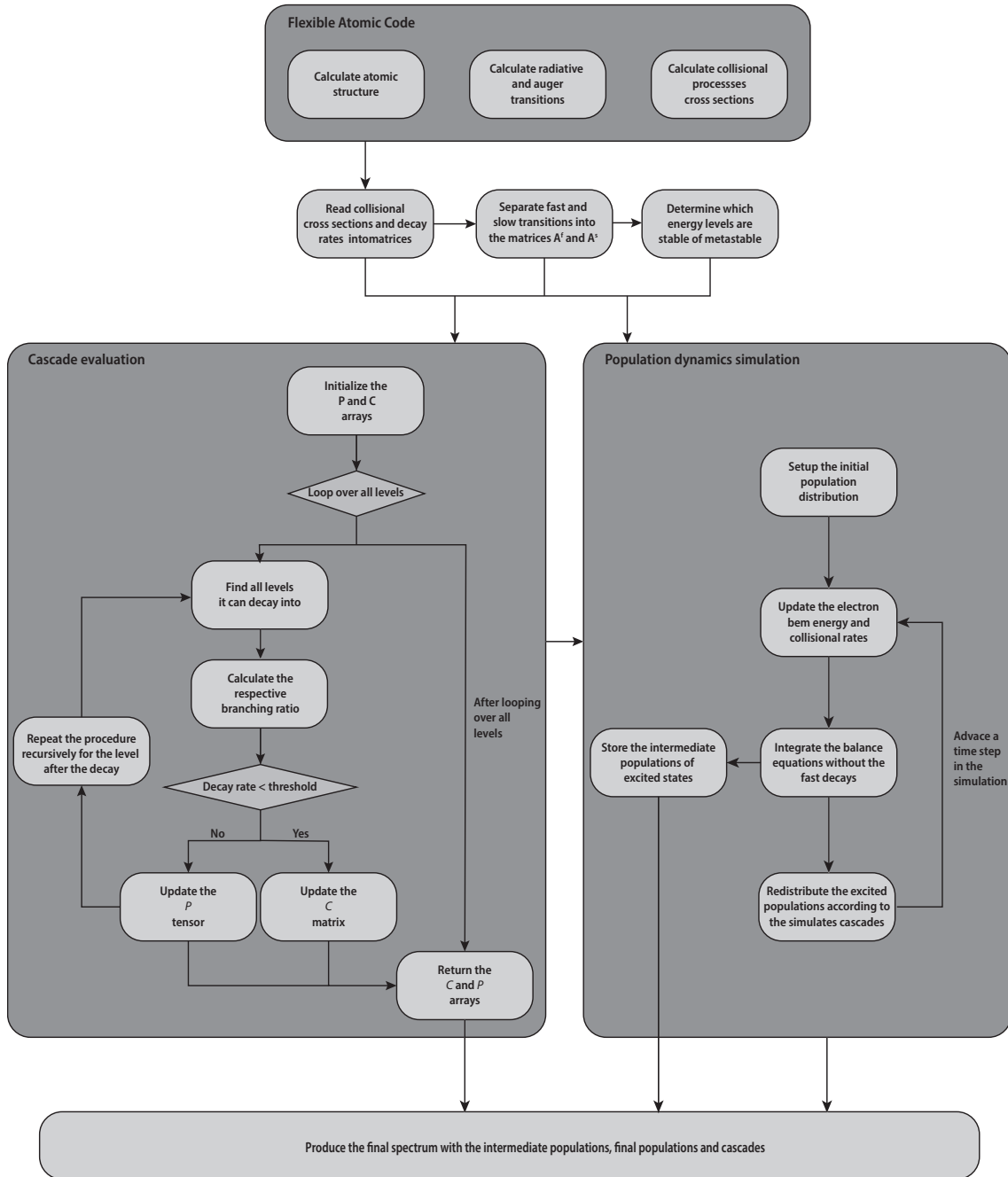


Figure 2.3: General diagram of the simulation framework, divided into three phases: Calculation of the atomic data, simulation of the fast cascades of excited states, numerical integration of the balance equations and productions of the emission spectrum.

The index on top of the matrix represents the original excited state from which the calculated cascades are being propagated, while the second and third indexes represent a specific transition. The matrix expresses how an initial excited state population contributes to emissions of every transition during a fast cascade. If another cascade parting from the same initial state goes through a transitions that is already non-zero due to a previous cascade, the respective branching ratios are summed. Due to their purpose, the $\mathbf{C}$ matrix is used during the simulation, while the $\mathbf{P}$ is only used to reconstruct the emission spectrum in the end of the simulation. As an example, using the colored transitions represented in Figure 2.2, the components of the matrix $\mathbf{P}$ corresponding to the cascades from the excited state $1s3d_{5/2} J = 2$ are given by

$$\begin{aligned}
 P_{3D_2 \ 1P_1}^{3D_2} &= b_{3D_2 \ 1P_1}, \\
 P_{1P_1 \ 1S_0}^{3D_2} &= b_{3D_2 \ 1P_1} b_{1P_1 \ 1S_0}, \\
 P_{3D_2 \ 3P_{0,1,2}}^{3D_2} &= b_{3D_2 \ 3P_{0,1,2}}, \\
 P_{3P_{0,1,2} \ 1S_0}^{3D_2} &= b_{3D_2 \ 3P_{0,1,2}} b_{3P_{0,1,2} \ 1S_0}, \\
 P_{3P_{0,1,2} \ 3S_1}^{3D_2} &= b_{3D_2 \ 3P_{0,1,2}} b_{3P_{0,1,2} \ 3S_1}, \\
 P_{3S_1 \ 1S_0}^{3D_2} &= b_{3D_2 \ 3P_{0,1,2}} b_{3P_{0,1,2} \ 3S_1} b_{3S_1 \ 1S_0}.
 \end{aligned} \tag{2.113}$$

2.5.3 Matrix approach

An alternative approach for the mathematical framework already presented is the calculation of the matrices corresponding to the cascade processes using matrix operations. In matrix form, the balance equations can also be written as

$$\frac{d\mathbf{N}}{dt} = [\mathbf{\Omega} + \mathbf{A} - \mathbf{diag}(\mathbf{1} \cdot (\mathbf{\Omega} + \mathbf{A}))] \cdot \mathbf{N}, \tag{2.114}$$

where $\mathbf{\Omega}$ and $\mathbf{A}$ represent the matrices for the collisional and transition rates, and $\mathbf{N}$ is the level-population vector. $\mathbf{diag}$ is the diagonal matrix with elements of a vector and $\mathbf{1}$ is a vector of ones. The matrix on the right of 2.114 is constructed to ensure it has zero column-sum as required for conservation of the total population. In this form, the temporary populations are calculated by integrating the equations

$$\begin{aligned}
 \mathbf{N}'(t_n) &= \mathbf{N}(t_{n-1}) + \\
 &\int_{t_{n-1}}^{t_n} [\mathbf{\Omega} + \mathbf{A}^s - \mathbf{diag}(\mathbf{1} \cdot (\mathbf{\Omega} + \mathbf{A}^s))] \cdot \mathbf{N}(t_{n-1}) dt,
 \end{aligned} \tag{2.115}$$

where $\mathbf{N}'$ is a set of temporary populations calculated with *only* slow relaxation transitions $\mathbf{A} \rightarrow \mathbf{A}^s$ and collisional processes.

Once again, the rapidly decaying populations N^f must be distributed according to their respective branching ratios. These branching ratios are calculated beforehand for all excited states and stored in a matrix with its non-diagonal elements given by,

$$B_{ij} = \frac{A_{ij}}{\sum_k A_{ik}} = \frac{A_{ij}^a}{\sum_k A_{ik}} + \frac{A_{ij}^r}{\sum_k A_{ik}} = B_{ij}^a + B_{ij}^r, \tag{2.116}$$

with i and j ($i \neq j$) being the initial and final levels. Additionally, the diagonal terms of this matrix for stable (slow and ground) and fast levels are one and zero, respectively, addressing either the stability or a fast decay of these levels. With this, a cascade matrix $\mathbf{C}$ is also constructed before integrating equation 2.114, which contains the population transferred from all levels into the stable levels through all possible cascades. This quantity is given by a l -time-matrix multiplication of $\mathbf{B}$,

$$\mathbf{C} = \mathbf{B} \cdot \mathbf{B} \cdot \mathbf{B} \dots = \mathbf{B}^l, \quad (2.117)$$

where l is a number of cascade layers sufficient high for all the population being at the ground and metastable levels. Each term C_{ij} is the total branching ratio from level i to j , having all paths connecting these levels. Note that if cascade layers are enough for the populations to be in stable levels, additional multiplications of $\mathbf{B}$ are redundant, as return same matrix $\mathbf{C}$, due the sub-matrix of $\mathbf{B}$ being the identity matrix ($\mathbf{I}$) for stable levels. An example of some of the propagation of populations of a few energy levels through two layers is presented in Figure 2.4, along with the respective portion of the matrix $\mathbf{B}$. This example corresponds to the same situation described above, where it was only considered a few energy levels with $n = 2, 3$ of he-like oxygen.

In the second step, the temporary populations are redistributed according to the calculated cascades with the $\mathbf{C}$ matrix.

2.5.4 Emissivity

The emissions spectrum within a specific time step of duration $\Delta t = t_n - t_{n-1}$ is made taking into account the intermediate populations, and the possible transitions parting from them, as well as the long-lived state populations and the respective radiative decay rates, using the relation,

$$\mathbf{I}(t_n) = (\mathbf{N}(t_n)) \cdot \mathbf{A}_r^s + \frac{1}{\Delta t} \sum_k^{n_{\text{states}}} (N'_k(t_n) \mathbf{P}^k), \quad (2.118)$$

where $\mathbf{A}_r^s$ represents the radiative decay rate matrix for slow transitions. While the emissions from the metastable populations are given by their respective populations and radiative transitions, the emissivity from the excited states is calculated based on the excited intermediate populations and their respective cascades with the $\mathbf{P}$ matrix. As the matrix $\mathbf{P}$ stores the emissions from the sum of all the possible cascade paths of every single excited state, weighting by the intermediate populations produces the emission spectrum of the respective intermediate states within a time step. By taking the inner product, one gets the sum of the spectrum produced by each excited state weighted by the respective excited state populations, thereby producing a two-dimensional array in the shape of the transitions rate matrix representing the total emission spectrum of fast transitions.

In Figure 2.3 we present a detailed flow chart describing the basic steps of this model. We start by calculating all the necessary atomic data in FAC, namely the atomic structure,

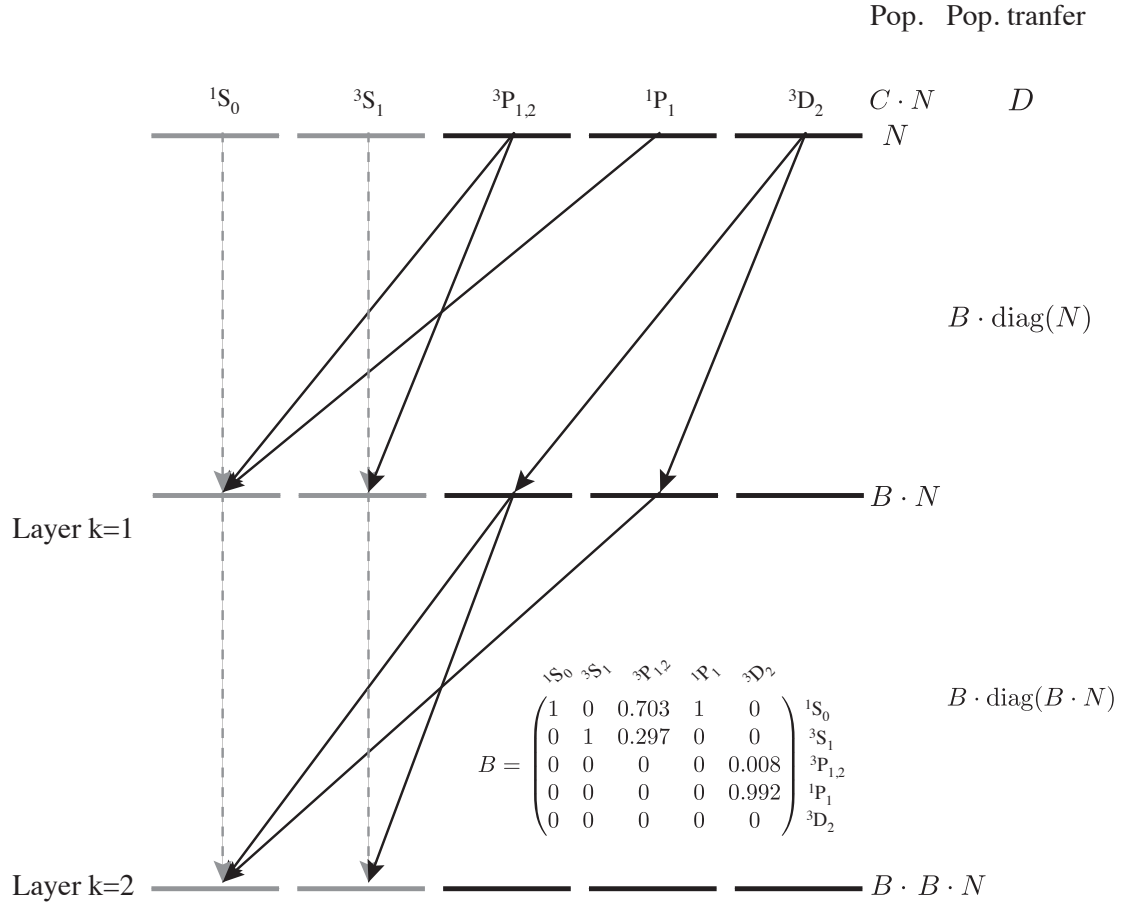


Figure 2.4: Representation of the propagation of the populations between energy levels layers upon the application of the branching ratio matrix $\mathbf{B}$. Two layers are represented, along with the respective population and transfer of population calculations on the right. The portion of the branching ratio matrix involving these transitions is also represented. Two layers are enough to complete the cascades of every excited level represented in this example.

radiative and non radiative decay rates and the cross-sections of each collisional process between every energy level. We then parse all the atomic data and relevant information from the FAC output files and build a set of square matrices, one for each of the processes. The transitions matrices are then separated into fast and slow transitions, and the cascades for the fast transitions are evaluated, building the $\mathbf{C}$ and $\mathbf{P}$ in the process. The population dynamics simulation is then performed with an initial population within the two-step procedure presented. In the beginning of each time step, the collisional processes rates are calculated for the current electron energy and density conditions to take into account the possible dynamics of these parameters. This can, for instance, be used to simulate the energy ramp of an EBIT electron beam energy, making this simulation scheme suitable for EBIT emission dynamics simulations. The balance equations are solved using the Fourth order Runge-Kutta (RK4) method [146]. Our code was developed in *Python* taking full advantage of the *Numpy* framework to automatically parallelize the workload while doing

matrix multiplications for the integration and population distribution procedures. Finally, the final and intermediate populations, as well as the matrix $\mathbf{P}$, are used to produce the emission spectrum for the entire time or beam energy range.

Note that this method automatically incorporates complex multi-step processes: the DR process is completed by considering the radiative cascade from the DC, while EA is given by the Auger cascade after a CE. Other atomic processes, such as REDA, follow a similar procedure. Furthermore, this method considers all atomic processes as independent steps within the isolated resonance approximations, neglecting quantum interference effects between processes that would be present in a complete coupled-cluster calculation.

The free electron energy profile is included in the simulation by making a convolution of the collisional cross-sections with the electron energy dispersion profile. Although only collisional excitation and ionization, radiative recombination and dielectronic capture cross-sections are included by default, different direct processes, such as photoexcitation and photoionization, can be included by modifying the balance equations by adding the corresponding transition rates.

For the matrix framework, the calculation of the emissivity matrix is calculated with the matrix $\mathbf{B}$ instead of the matrix $\mathbf{P}$. To avoid confusion, the new emissivity matrix will be represented by $\mathbf{E}$. While the matrix $\mathbf{C}$ is constructed beforehand, a matrix $\mathbf{D}(t_n)$ is built at the end of the second-step to reconstruct the emissions due to fast radiative cascades. For this purpose, $\mathbf{D}(t_n)$ contains all intermediate population radiative decays between all levels during all cascade processes at each time step. Similarly to $\mathbf{C}$, $\mathbf{D}$ is also defined with the branching matrix $\mathbf{B}$ according to,

$$\begin{aligned}\mathbf{D}(t_n) &= \sum_{k=1} \mathbf{D}^{(k)}(t_n) \\ &= \sum_{k=1}^l \mathbf{B}^r \cdot \text{diag}(\mathbf{B}^{k-1} \cdot \mathbf{N}'(t_n)) ,\end{aligned}\tag{2.119}$$

where the summation here is over the cascade layers. At each layer of cascades, the population vector is transformed from the previous layer with $\mathbf{N}'(t_n) \rightarrow \mathbf{B}^{k-1} \mathbf{N}'(t_n)$ ($\mathbf{B}^0 = \mathbf{I}$), having the next population change, due to only radiative decays, being stored in $\mathbf{B}^r \cdot \text{diag}(\mathbf{B}^{k-1} \cdot \mathbf{N}'(t_n))$.

The emission spectrum within a time step ($\Delta t = t_n - t_{n-1}$) is made taking into account the long-lived level populations and their slow radiative decays, as well as the fast intermediate populations, and the possible radiative decays from them. We define a matrix emissivity that is given with the previous matrices by the relation,

$$\mathbf{E}(t_n) = \mathbf{A}_r^s \cdot \text{diag}(\mathbf{N}^s(t_n)) + \frac{\mathbf{D}(t_n)}{\Delta t},\tag{2.120}$$

where $\mathbf{D}(t_n)$ contains only non-diagonal elements of $\mathbf{D}(t_n)$, i.e. $\hat{D}(t_n)_{ij} = D(t_n)_{ij}$ if $i \neq j$, and 0 otherwise, addressing only fast radiative transitions and not the continuity of stable levels (diagonal terms). While the emissions from the slow levels are given by their

respective populations and radiative transitions, the emissivity from the excited states is calculated based on the population changes due to fast radiative decays with the $\mathbf{D}$ matrix per unit of time. The sum of the two components produces the two-dimensional $\mathbf{E}(t_n)$ matrix, which reflects the emissivity of every single transition from a level i to a level j at a given time t_n in units of s^{-1} . Finally, each transition wavelength is stored in a matrix $\mathbf{W}$ enabling further filtering of emissivities in a wavelength region according to its matrix position.

The use of the matrix form can potentially be beneficial for large CRMs, since modern computing architectures are designed to be efficient at parallel computing of matrix operations.

2.5.5 Code implementation

The simulation framework presented in this Chapter has been implemented in *Python* to allow the simulation of the charge state distribution and emissivity dynamics of EBIT plasmas to compare with and aid in the interpretation of experimental observations. The code was written from the ground up with most functions depending on operations based on *Numpy* arrays. The *Numpy* operations are written in the C language, making use of the advantageous speed of a compiled programming language. Furthermore, depending on the *Numpy* installation in the local machine, math operations can be optimized for the specific computing unit architecture and take advantage of multiple-core setups, taking full advantage of the local machine computing resources.

While compiled languages, such as *C* and *Fortran*, are significantly faster than *Python*, the latter provides flexibility and portability when the objective is mainly experimentation with dynamical conditions or the integration of the simulation framework in other projects. The speed improvements from the use of *Numpy* for matrix operations do not improve the time the simulation spends with pure python operations, namely the main simulation loop. Another technique to further accelerate the simulation runtime is the use of the *Numba* package. This package automatically rewrites the *Python* code in C. This can either be applied to the entire code or to portions that need a performance improvement. This optimization has been applied to all python loops and can be optionally used if supported by the system.

The file-system structure of the simulation framework is presented in Figure 2.5. All the necessary scripts are located in the root folder of the project, with the input atomic data in the *Data* folder and the results from the simulation located in the *Out* folder. The *CRM.py* script is the main script where all the simulation parameters are defined.

This script starts with the definition of the time-scale and time-step size to use in the simulation. It then calls several function from the *DataReader.py* script to read all the necessary atomic data into *Numpy* arrays. This data is stored in square two-dimensional arrays $\mathbf{A}$ and $\mathbf{\Omega}$ with the size given by the number of energy levels present in the input atomic data. The reading script is written to parse data generated by FAC, but other

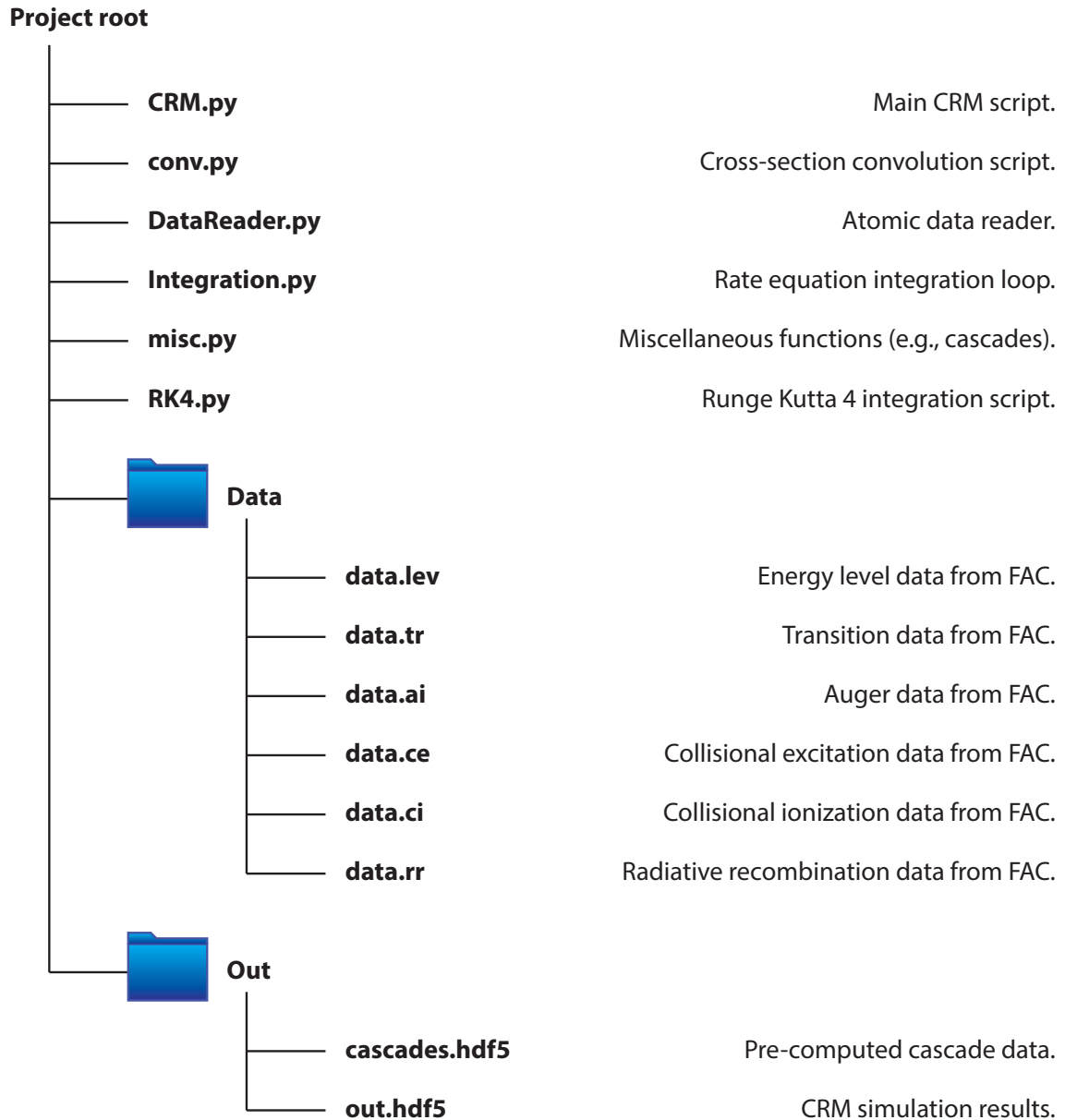


Figure 2.5: Representation of the file and folder structures of the developed CRM package. A simple description of each file is displayed on the right.

functions could, in principle, be added to support data given by other atomic codes. Specific transition rates can easily be added individually to the respective matrix, allowing the possibility of including specific processes, such as two-photon transitions. The collisional processes cross-sections are read into a three-dimensional arrays, with the third index representing the electron energy. At this point, the cross-sections are convoluted with the free electron energy profile with the *conv.py* script. For the EBIT simulations, the free electron energy profile is a simple Gaussian distribution with a width given by the experimental parameters. A thermal plasma could also be simulated by convolving the collisional cross-sections with a Maxwellian distribution.

With all the radiative and auger transition rates stored, the *misc.py* file is used to compute the fast transition cascades. A loop is made simulate the cascades starting from all the energy levels. Within each initial excited state, a recursive function is used to calculate the branching ratio of every possible cascade step with the given radiative and auger transitions. In each step, the branching ratio is used to fill the **P** matrix. Within each step, the total transition rate is checked. If it is lower than a certain threshold, the current state is considered metastable and the specific cascade path is considered completed. The total branching ratio of the path is stored in the **C** matrix. As this process can become expensive, the iterative process is only considered if the total branching ratio of a step is higher than a minimum value (10^{-6} is the default value). Both the **P** and the **C** matrices are exported into the *cascades.hdf5* file inside the *Out* folder. This file can be read to make several simulations without the need of recalculating the cascade matrices. The use of a Hierarchical Data Format (HDF) file allows the storage of multiple large datasets in an organized manner into a single file. As this type of file is not proprietary, the stored arrays can be read by different programs for other purposes besides the CRM.

The electron beam energy function is also defined in the *CRM.py*. As the main objective of this CRM is the simulation of the plasma of an EBIT, the default electron beam energy scheme is a periodic triangular wave, simulating energy sweeps downwards and upwards. After defining the initial population values, the *Integration.py* file is used to perform the dynamical simulation. Before starting the simulation itself, the collisional processes rates are calculated for all the beam energy values to be used in the simulation. This avoids the need to recalculate the rates for every single time-step. A loop is then started over all the time-steps. In each time-step, the Runge-Kutta method of the fourth order is used to integrate the balance equations with the correct collisional rates for the specific electron beam energy, summed with the slow transition rates. These results in a set of intermediate excited populations, which are stored for further use. The **C** matrix is then used to redistribute the intermediate populations into the stable and metastable states. The final populations are also stored, and the loop proceeds to the next time-step. At the end of the loop, the **P** matrix and the intermediate populations are used to calculate the emissivities of each transition as a function of time. The emissivity matrix, intermediate matrix and final population matrix are exported into the *out.hdf5* file. This file can be read to plot the evolution of the charge state balance, track metastable dynamics and plot

emissivity spectra as a function of the photon energy and the electron beam energy.

2.5.6 Verification in static conditions

In this subsection, a practical example of an application of this method to predict He-like oxygen spectra is presented. This was chosen as an example, as experimental observations regarding this ion were made for this thesis, which will be compared with CRM results in later Chapters. The He-like system is relatively simple, with its emission being dominated by transitions connecting the L shell excited states with the $1s^2\ ^1S_0$ ground state. The four main lines are the w line, coming from the singlet level $1s2p\ ^1P_1$, the x and y intercombination lines, coming from the triplet states $1s2p\ ^3P_{1,2}$, and the z line, coming from the metastable level $1s2s\ ^3S_1$.

The electron beam energy and density dictate the relative population of each excited state. The simplest case is when the plasma parameters are constant in time, and the populations are assumed to be in equilibrium, i.e. the population derivatives in equation (2.106) are zero and the populations are retrieved from the set of linear equations. As mentioned above, this is the case that most CRM codes solve, including the CRM package of FAC. The current method is able to calculate the excited state populations in equilibrium by leaving the plasma parameters constant and letting the populations evolve until equilibrium is reached. Opposed to the case of FAC, the populations themselves at equilibrium are only calculated for stable and metastable states, since the emissivities are derived by the excitation and subsequent cascade procedure described before, thus the populations of the excited states cannot be compared directly with results from FAC. To benchmark our method, we chose to compare the FAC-CRM results with our calculated emissivities directly, as the two different methods should provide comparable numerical values. In Figure 2.6, the relative differences between the emissivities of the main four lines for different electron energies and densities (600, 800 and 100 eV; 10^9 , 10^{10} and 10^{11} cm^{-3}) given by each code is presented. Given the profile of the electron beam energy spread, both methods made use of a Gaussian energy distribution for the electron beam energy with the same width. An excellent agreement was found between the FAC-CRM results and our method, agreeing for all conditions within less than 0.4%. The FAC-CRM solves the balance equations without any approximations. The proximity of results proves the reliability of our two-step model and validates the emissivity equation 2.118, where the CEQ approximation was employed. For this example, the electronic structures calculations for He-like oxygen singly excited state configurations with a excited electron with a principal quantum number $n = 2, 3, \dots, 10$. Using the matrix approach to calculate the cascades, as their respective emissions, propagating the populations through only 10 layers is enough to complete the cascade for every single initial excited state. A representation of the propagation of the populations throughout every layer is represented in Figure 2.7. In this Figure, one can see that the lines connecting the layers 9 and 10 are vertical, meaning no transitions occur between different states. Furthermore, there are only two lines. These

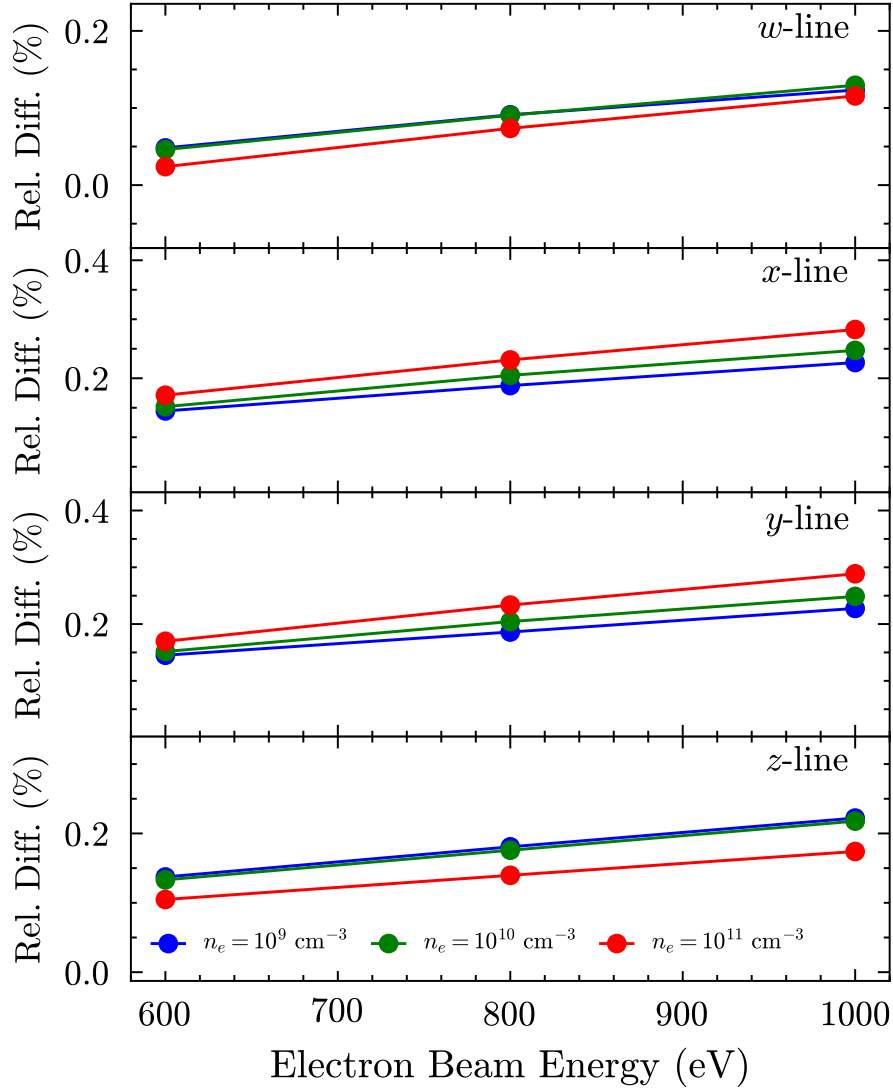


Figure 2.6: Relative difference between the emissivities calculated with the CRM from FAC and the newly developed time-dependent CRM in steady-state conditions. Each subplots represents the relative differences for the lines *w*, *x*, *y* and *z*, respectively. The colors red, green and blue were used to represent the relative differences under different electron density (n_e) conditions: 10^9 , 10^{10} and 10^{11} cm^{-3} .

correspond to the two only available metastable states: the ground state, which is stable, and the $1s2s \ ^3S_1$ state.

Another feature of a CRM is the possibility of calculating the charge state dynamics of a plasma. While the ionization and recombination processes cross-sections can be calculated with FAC with the distorted wave approach, a simpler approximation was used in this work for demonstration purposes. For ionization, the semi-empirical formula by Lotz [126] was used. The charge exchange cross-sections were estimated with the semi-empirical formula by Janev [134]. For the radiative recombination cross-sections, the formula by Kim [147]. In Figure 2.8, the evolution of the ground state of every charge state

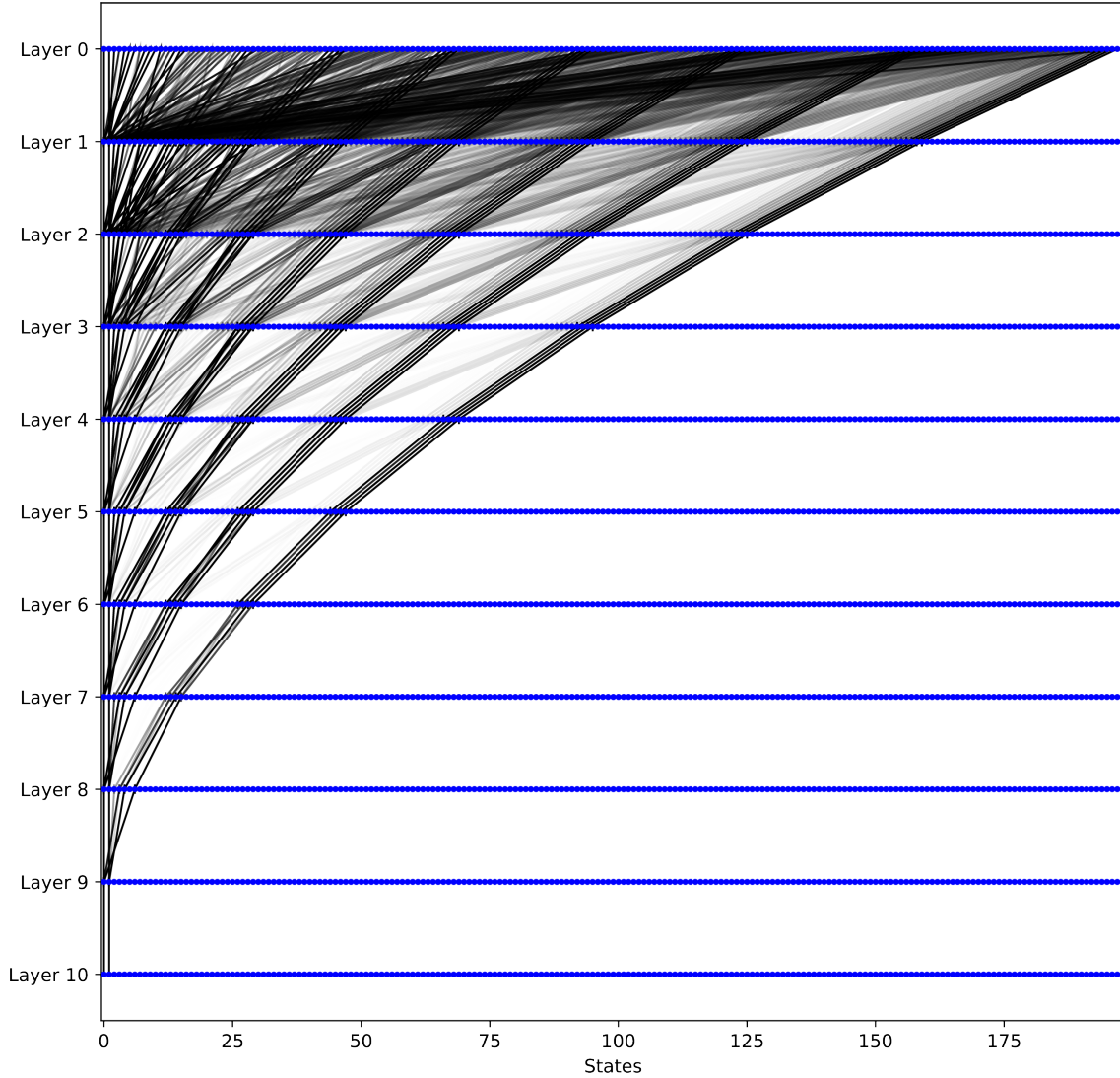


Figure 2.7: Representation of the cascades of He-like oxygen. The population propagation is represented through 10 layers, where, within each layer, the energy levels are represented by the blue dots. The transitions are represented by the arrows. The arrows opacity is given by the branching ratio of each transition (darker is higher).

starting from an initial population of neutral atoms is presented. Here we employed an electron density of $n_e = 10^{10} \text{ cm}^{-3}$ and electron energy of $E_e = 800 \text{ eV}$. An equilibrium is reached with a population of around 80 % of He-like ions and 20 % of H-like ions, very similar to what was found in our experimental results. Note that, in this Section, only the result for a static electron beam energy, representing-steady state conditions, is being represented.

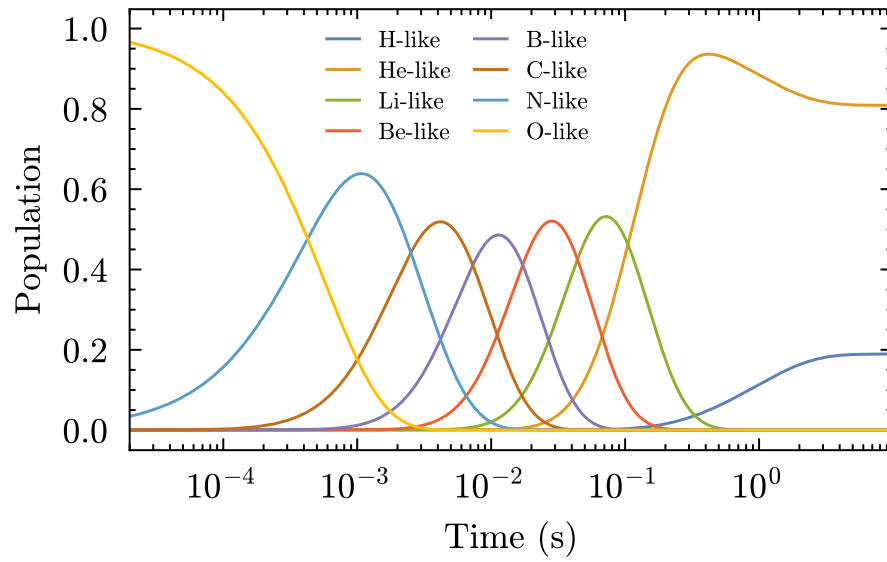


Figure 2.8: Simulation of the charge state population balance of oxygen for a constant free electron energy of $E_e = 800$ eV and an electron density of $n_e = 10^{10} \text{ cm}^{-3}$.

EXPERIMENTAL METHODS

The production, trapping and study of HCI is done by different experimental techniques. These techniques are divided in two main categories: ion sources and acceleration devices. In the first category, the ions are produced by ionization with energetic electrons and confined locally with electromagnetic traps. These include mainly the Electron Cyclotron Resonance Ion Source (ECRIS) , the Electron Beam Ion Source (EBIS) and the EBIT. In the second category, ions are accelerated and ionized by colliding with beamfoils. These ions are sorted by charge state and stored in storage rings. The works performed in this thesis are mainly focused in the production and study of HCI in an EBIT.

While the EBIT is one of the most used ion sources, there are a number of other experimental setups that have advantages and disadvantages over the EBIT. While all of the work for this project is being carried out in an EBIT, it is useful to understand other techniques that may prove useful in solving problems that cannot be undertaken in the current setup. As such, a brief description of some of these setups will be made in this Section. Storage Rings and Electron Cyclotron Resonance Ion sources are presently some of the most popular ion sources.

3.1 Storage Ring

The storage ring is a charged particle accelerator. It consists of a close-looped vacuum chamber where charged particles are accelerated and maintained in a stable orbit for long periods of time. The charged particles are accelerated by Radio Frequency (RF) cavities. To maintain a closed orbit, their path is bend by dipole magnets, refocused by quadrupole magnets and corrected for chromatic aberration by hexapole magnets. The ions must be injected into the ring by an external ion source. Simple ovens can be used to inject ions into the ring, and their charge state can be manipulated by making the ion beam go trough a target to strip electrons. A better choice is to use an ECRIS to produce the target ions and inject them into the ring. This option usually yields a higher and more stable ion current. Details about the ECRIS setup will be presented in the next subsection. A scheme of the CRYRING, a low energy storage ring currently stationed at the GSI Helmholtzzentrum

für Schwerionenforschung, in Darmstadt, is presented in Figure 3.1.

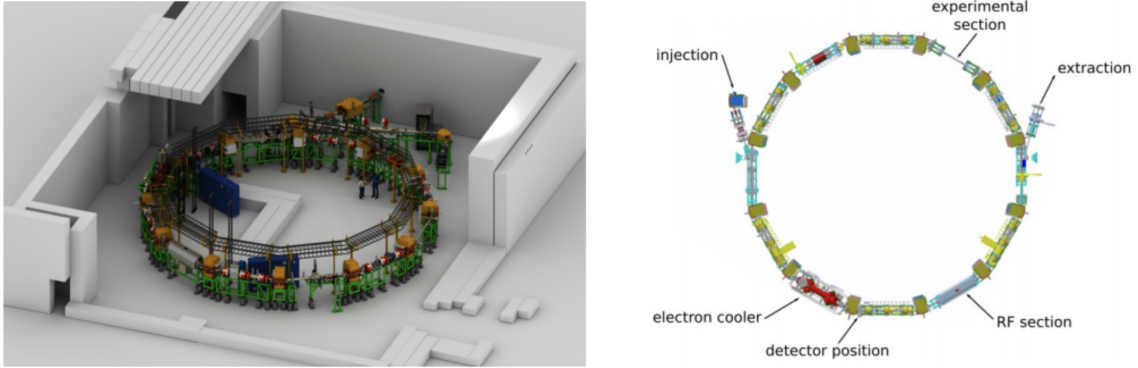


Figure 3.1: Representation of the Cryring. On the left is a rendering of the Cryring setup inside the experimental cave. On the right is a schematic representation, with the identification of the storage ring main components, such as the injection, RF acceleration sections, diagnostic detectors and electron cooler. Figures adapted from [148].

A storage ring can have a multitude of destructive and non-destructive instrumentation to diagnose and probe the ion beam in different experimental conditions. Among them are the Beam Position Monitors (BMP) or the 0-degree camera. The BMP consists of a pair of cylindrical electrodes with an oblique separation between each other. When a charged beam passes through the electrodes, a mirror charge of the beam is induced in the electrodes, resulting in a measurable voltage. By observing the difference between the electrode voltages, one can estimate the rough position of the beam in one axis with an accuracy of 1 mm (the axis is defined by the electrode orientations). The 0-degree cameras are usually mounted after the RF acceleration portion of the rings. It relies on the detection of neutral atoms formed by the interaction of the ion beam with the residual gas. After a portion of the beam recombines with the residual gas via charge exchange, neutral atoms are created. These ions do not change trajectory after going through the magnetic dipole bender. As such, there is a detector after the bending (tangential to the ring) composed of two Microchannel Plate (MCP), followed by a phosphor screen and a CCD camera. The neutral ions hit the MCP, producing a current of electrons that gets amplified in the second MCP. The secondary electrons collide with the phosphor screen, producing photons that are collected by a CCD camera, which in turn forms an image representative of the original ion beam shape.

The electron-ion interactions are usually studied by merging the ion beam with an electron beam. This can be done with an electron cooler, a device that generates an electron beam parallel to the ion beam and merges the two. The electron cooler works in the opposite way of an EBIT, using a magnetic field to expand the electron beam instead of compressing it. Although the electron density current is lower, the electrons are effectively cooled in their longitudinal direction of motion, allowing the electron energy spread to be much lower than the ones usually found in EBIT setups. As some ions recombine with the electrons at certain relative electron energies, these have different trajectories after

the next dipole magnet. As such, these ions are collected, and their current is measured and compared to the ion beam current and the electron beam current. This allows the precise calculation of the recombination rate, which can be converted into recombination cross-sections.

This type of setup allows the observation of recombination cross-sections with much higher precision than the EBIT setups. However, it does not provide any information about the photon emissions by default, and, due to its complexity, needs a constant team of specialized operators and dedicated beamtimes to perform experiments.

3.2 Electron Cyclotron Resonance Ion Source

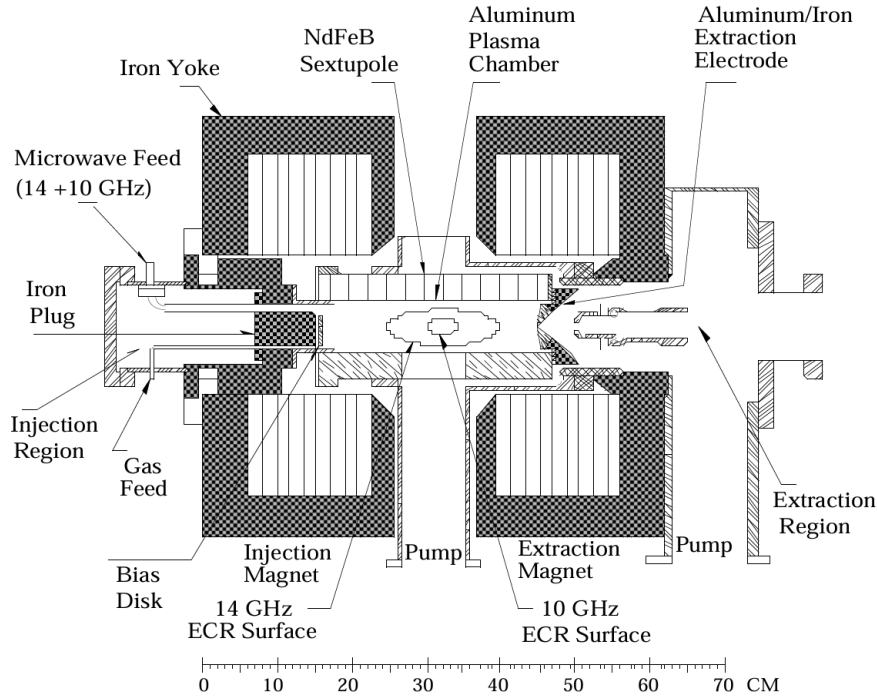


Figure 3.2: Schematic representation of an electron cyclotron resonance ion source. Adapted from [149].

The ECRIS is an ion source that produces and traps a plasma of highly charge ions using microwave radiation super imposed by a strong magnetic field. Due to the magnetic field, free electrons spiral around the field lines with a cyclotron frequency that depends on the magnetic field strength. The injected microwave radiation is tuned to match this frequency and, when this happens, the electron absorbs the microwave radiation resonantly, consequently heating the plasma and, thus, sustaining high degree of ionization. A representation of an ECRIS can be found in Figure 3.2.

The production of higher charge states is dependent on the time an ion is confined inside the machine, as longer trapping times yield more interactions with the free electrons, yielding higher ionization probabilities. The confinement is done by a combination of

magnetic field generating components. A pair of solenoid coils provide the field that traps the ions along the axis, while an hexapole magnet provides the field to trap them radially. Together, these components generate a magnetic field geometry that works as a magnetic bottle, trapping the ions long enough to achieve multiple ionization. The injected pressure of the neutral gas of the element to ionize can be controlled to increase or decrease the ionization and recombination balance, thus controlling the general charge state balance of the plasma.

As the ECRIS environment is less controlled when compared to an EBIT setup, it usually is not used to study electron-ion collisional cross-sections within itself. Instead, its main advantage is the high HCI production rate. As it works in a continuous manner, with a constant injection of neutral gas and continuous plasma heating and ionization, the resulting ions can be extracted by applying an electric field, accelerating them out of the device. It is therefore mostly used as an ion source, being routinely used as the source for storage rings and tokamaks.

3.3 Electron Beam Ion Trap

The EBIS was first invented and developed by Donets and collaborators [150, 151]. Its initial goal was to produce the required ions for experiments elsewhere, but it was realized that the device itself is capable of storing the ions for probing purposes. After improvements in the electrostatic trap potentials, the device started to be used in the configuration of an Electron Beam Ion Trap, where all the ion production and study is done at the same place. The first EBIT was developed at the Lawrence Livermore National Laboratory, in California [152], with a second, high energy capable device, known as Super EBIT, developed a few years later [153]. The second device was shown to be capable of producing HCI up to bare uranium [154]. All the experiments in this project were carried out at the FLASH-EBIT, in Heidelberg, which was originally design for free-electron laser experiments [155]. While most general details are common across all EBIT setups, some specific details will be provided regarding the FLASH-EBIT.

3.3.1 Overview

The basic principle of the machine is the production of ions by crossing a beam of atoms with an electron beam. This beam ionizes the atoms, which in turn feel attracted by the electron beam due to its space charge. As the ions get closer to the beam, they get ionized further, and their electric charge increase, increasing the electrostatic force between the ions and the electron beam. This process leads to a consecutive ionization of the ions until reaching HCI. To make this process efficient, the electron beam is compressed by an intense magnetic field in the trap central region. The rate of ionization is proportional to the current density, and, in these devices, is typical to achieve currents in the order of the mA within radius of tens of μm .

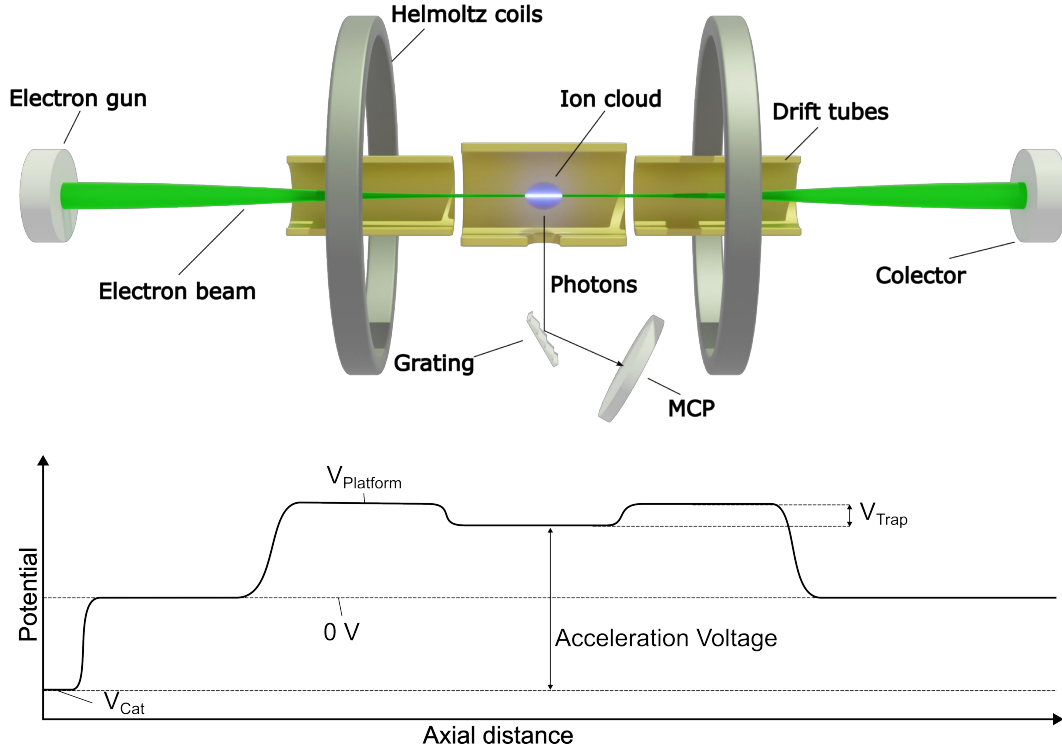


Figure 3.3: Pictorial representation of an electron beam ion trap. The electron gun, drift tube assembly and collector are represented, as well as the electron beam generating an ion cloud in the center of the picture. The magnets used to produce the magnetic field are also represented. On the bottom, the different potentials that affect the electron beam energy throughout the EBIT are represented. Here a port with a EUV detector to observe the ion cloud emissions is shown as an example of possible experimental setup.

The beam itself can also be used to probe the trapped ions. This is achieved by scanning the electron beam energy in a variety of schemes that will be explored later. The integration of the beam with the ions leads to several collisional processes, some of which emit photons that can be detected in different detectors, depending on the energy or wavelengths range that is to be observed.

A schematic representation of an EBIT is shown in Figure 3.3. In this Figure, one can see the electron beam being produced by the electron gun and retrieved by the collector. The electron beam passes through the drift tube assembly, where its voltages are used to build a potential well to trap an ion cloud. The electron beam interacts with this cloud, and the emitted photons are being observed in a side port. A general representation of the voltages can also be found in the bottom of the scheme. The difference between the electron gun cathode voltage and the drift tube assembly voltage dictates the acceleration voltage of the electron beam. The individual drift tubes of this assembly (here only three are represented) can be controlled individually. In this case, the middle one as a slightly lower voltage than the neighboring ones to create a potential well. In the following subsections, the details about each of the parts necessary to inject the gas, produce the beam, trap the ions and observe the photon emissions will be described.

3.3.2 Electron beam

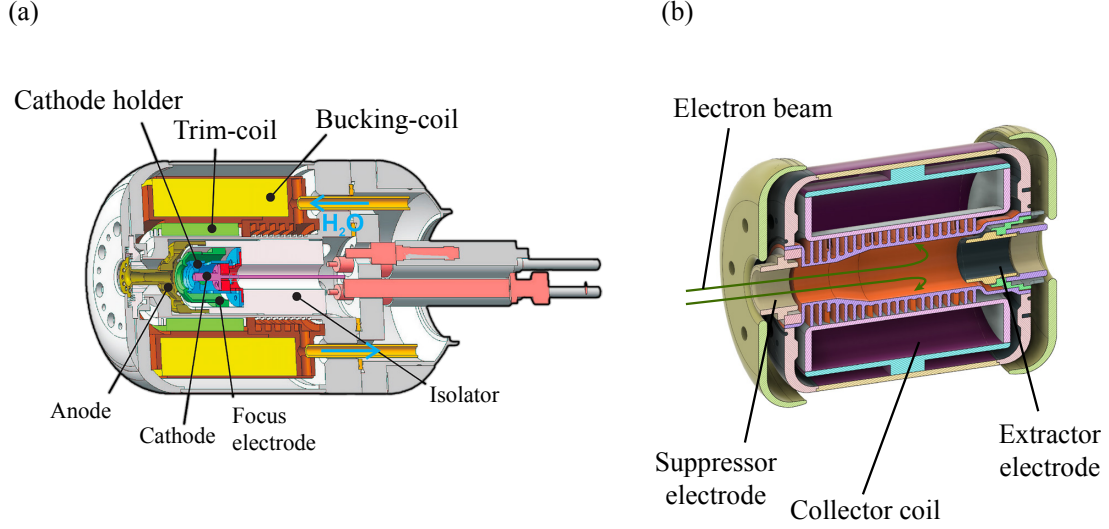


Figure 3.4: Render of the electron gun and collector assemblies. (a) Representation of the electron gun with the respective magnetic coils. Figure adapted from [156]. (b) Representation of the collector, with the extractor and suppressor electrode, collector coil and a visualization of the electron beam trajectory.

The electron beam is essential for the formation and trapping of the ions inside the device. It is produced by an electron gun, where a cathode with a negative electric potential is heated by a surrounding coil to temperatures typically between $T_{\text{cat}} = 1300$ K and $T_{\text{cat}} = 1500$ K. Free electrons are emitted from the cathode via thermionic emission. Additional electrodes redirect and focus the beam, while an anode accelerates them out of the gun, forming a steady stream of electron. The cathode is made of a tungsten filament, coated with a layer of barium oxide. The surface of these elements has a work function of around 2 eV, making the electronic emission feasible at a relatively low temperature, aiding in the longevity of the cathode. The electron gun assembly of the FLASH-EBIT is represented in Figure 3.4. In the Figure, in the (a) subplot, one can see the electron gun assembly, with a schematic representation of the Pierce type electron gun. Additionally, there are two magnetic coils (trimming and bucking coils) designed to suppress the magnetic field of the Helmholtz coils at the cathode, which gives a higher compression of the beam at the trap.

The voltage difference between the anode and the cathode determines the beam current through the relation

$$I_e = pV_{\text{cat}}^{3/2}, \quad (3.1)$$

where I_e is the electron current of the beam, p is the voltage difference and V_{cat} is the cathode voltage. As it is important to achieve high current densities in the middle of the trapping region, a somewhat accurate model of the electrons distribution in the beam is necessary to further optimize the beam parameters. Higher densities are achieved with a

high current passing through a small cross-section area. Herrmann's theory tries to describe the shape of an electron beam taking into account the non-laminar flow of the electrons and the finite temperature of the cathode [157]. In this theory, the beam cross-section has a two dimensional Gaussian profile, and the radius that includes 80% of the electrons is given by

$$r_H = r_B \sqrt{\frac{1}{2} + \frac{1}{2} \sqrt{1 + 4 \left(\frac{8m_e K_B T_c r_c^2}{e^2 B^2 r_B^4} + \frac{B_c^2 r_c^4}{B^2 r_B^4} \right)}}, \quad (3.2)$$

where T_c , B_c and r_c are the electron temperature, magnetic field near the cathode and the cathode radius. B represents the magnetic field in the trap. As expected, the beam radius decreases with the increase of the magnetic field. On the other hand, the relationship between the magnetic field in the trap and near the cathode also plays a role in the beam shape. To minimize the radius, the magnetic field near the cathode should be near zero. As such, the bucking coils in the electron gun assembly can be used to generate a magnetic field counteracting the one generated by the superconducting magnets in the drift tube assembly. This ensures that the magnetic field near the electron gun is minimized and, thereby, maximizing the beam compression in the trap region. The Herrmann radius r_H is actually just a correction to a simpler model, where, assuming a laminar flow of electron with no temperature or magnetic field at the cathode, the radius of the beam is given by

$$r_B [\mu\text{m}] = \frac{150}{B[\text{T}]} \sqrt{\frac{I_e [\text{A}]}{E_e [\text{keV}]}} \quad (3.3)$$

where E_e is the mean electron kinetic energy [158].

For an EBIT, it is typical to achieve current in the order of tens of mA within a radius of $30 \mu\text{m}$. For these kind of values, superconducting coils can be used to achieve magnetic fields up to 6 T in the trap region (the case of FLASH-EBIT). This is not always the case, and different types of EBIT setup can use lower magnetic fields with permanent magnets. Only the superconducting FLASH-EBIT was used in the experiments presented in this work. The mentioned electron beam values correspond to electron densities in the order of 10^{12}cm^{-3} . Due to the nature of the trap, the ions form a cloud around the beam that is wider than the beam itself. For this reason, the effective electron density must take into account the overlap volume between the electron beam and the ion cloud. Electron trajectory simulations and empirical evidences suggest that the actual effective electron densities for the plasmas created in these devices is typically closer to 10^{10}cm^{-3} . This order of magnitude will be verified in this work by comparing theoretical CRM results with experimental observations.

The electron beam itself can also be used to probe the ions by exciting them in different electron beam energies. The beam energy is important to discriminate different atomic processes, and can be controlled by adjusting the voltage bias in the drift tube assembly. As the electrons leave the gun, they are accelerated towards the trap with a potential difference between the cathode and the drift tubes assembly. Furthermore, the electrons

and the ions themselves create a space charge potential Φ that affects the mean kinetic energy of the electron. This overall kinetic energy is given by

$$E_e = e(U_{DT} - U_{cat} + \Phi), \quad (3.4)$$

where U_{DT} is the drift tube assembly bias positive potential. The electron and ion cloud space charge potentials are not trivial to estimate theoretically. Its value can be determined experimentally by observing resonant structures with different electron beam currents and studying the nominal beam energy shift. It is also common to simply calibrate the electron beam energy with theoretical calculation, often by also matching resonance structures, such as dielectronic recombination.

After passing through the drift tube assembly, the electron beam must be dumped to complete the electric circuit. This is done with the collector assembly. The collector of FLASH-EBIT is represented in Figure 3.4 (b). The electron beam reaches the collector with very high kinetic energies and still in focus. The interaction of the beam with the wall of the machine would damage it, ejecting material which would hinder the vacuum of the device. Furthermore, the electron-atom interactions in the devices walls would also produce unintended X-rays that would interact elsewhere. The electrons can be stopped by defocusing the beam. This is done by setting a very high negative voltage in the extractor electrode at the end of the collector. Further defocusing can be made by adjusting the collector-coil, generating a magnetic field that can be use to further deviate the electrons path. The electrons, now a with lower kinectic energy, are absorbed by the collector walls, thus completing the electronic circuit. This absorption generates heat, so the collector assembly is cooled with a water chiller to maintain a stable operation. Likewise, the electron gun assembly is also cooled with another water chiller.

3.3.3 Electromagnetic trap

In order to study the ions, they must be trapped inside the trapping region for long enough periods to be probed. As mentioned before, the compressed electron beam creates a strong enough space charge to trap the ions radially. The higher the electron beam current, the higher the space charge and, thus, the higher the electrostatic force between the ions and the electrons.

The ions must also be confined along the beam axis, direction in which the space charge of the electron beam does not act upon the ion cloud. To this end, a set of drift tubes is setup in succession, allowing the user to prepare a electrostatic well capable of confining the ions. Each drift tube is an electrode ring with a voltage that can be applied individually. The drift tube assembly from FLASH-EBIT is represented in Figure 3.5. This assembly is composed by a central drift tube, where the ion cloud is accumulated, with four other electrodes positioned at each side. The four drift tubes located on the gun-side of the assembly are labeled from G1 to G4, while the collector-side drift tubes are labeled as C1 to C4. The middle drift tube has several openings that allow the photons generated by the

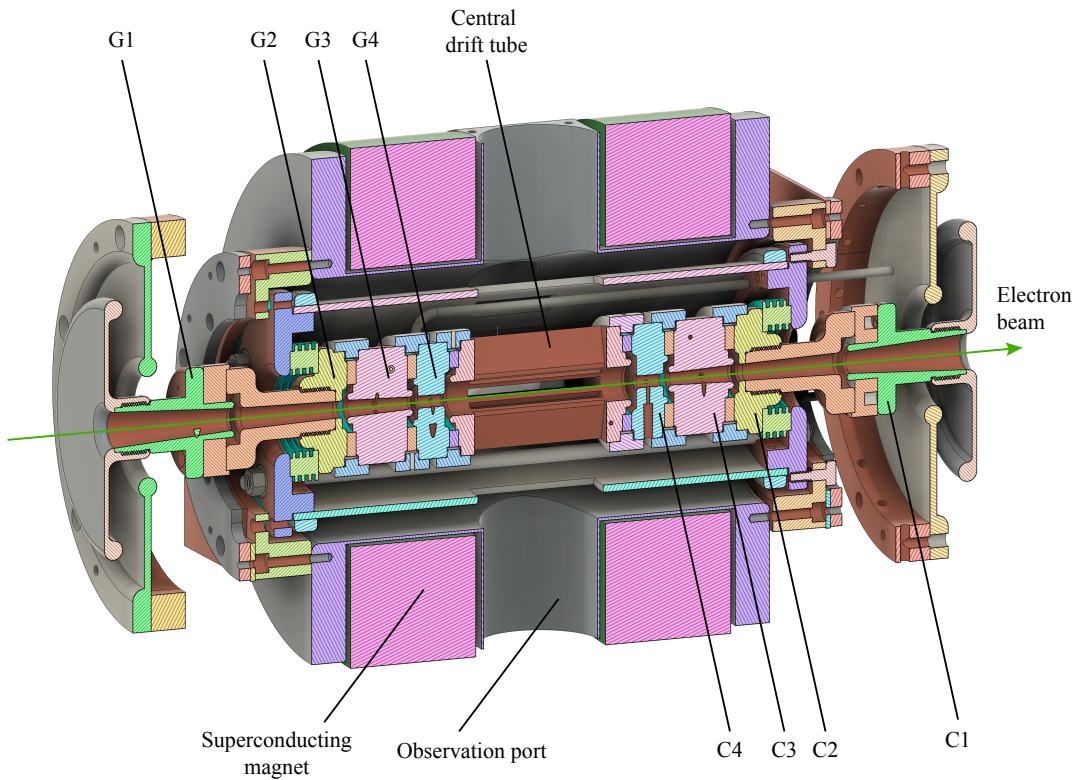


Figure 3.5: Rendering of the drift tube assembly. The guns-side and collector-side electrodes are represented by G1 to G4 and C1 to C4, respectively. The superconducting magnets are also represented. Observation ports can also be observed on the top and bottom of the rendering. These ports can be used to attach other component, such as photon detectors.

plasma to escape. The primary vacuum chamber has several ports aligned with the middle drift tube plane, allowing the setup of different detectors to measure the spectral emission of the photons that escape the drift tube assembly. The shape of the well is customized by adjusting the potential of each drift tube individually. The potentials used for the well are usually in the order of dozens to hundreds of volts. Although these values might seem low at first glance, the electrostatic force that act upon the ion is proportional to its electric charge, meaning that the higher the charge state, more stronger is the confinement. The individual control of each electrode is also important, as sometimes, often due to complicated or unforeseen reasons, asymmetrical potentials can be beneficial to control the trapping and dynamics of the ions and contaminations entering and leaving the trap. One case where this is necessary is when one wants to extract ions from the trap. This can be done by lowering the voltage on the collector side and increasing the voltage on the middle drift tube, *kicking* the ions in the direction of the collector. The extractor electrode in the collector can be used to control the extraction of the ions to do experiments with highly charges ions outside the EBIT. For example, a mass spectrometer could be installed next to the collector to analyze the contents of the trap periodically.

The superconducting magnets used to produce the main magnetic field are also

represented in Figure 3.5. These magnets have an operational current of around 90 A and produce a peak magnetic field of around 6 T in the center of the trap. The magnetic field is necessary to compress the electron beam and increase the current density. With the magnetic field, the charge particles start to describe a cyclotron motion with a radius tighter for higher magnetic field values. As it also affect the ions, the EBIT can actually be used in a magnetic trapping mode, where the electron beam is turned off and the ions are momentarily trapped only by the magnetic field. This technique is useful when one want to, for example, measure atomic lifetimes without the electron-ion interactions. To achieve superconductivity, the magnets are cooled by a cold head and helium compressor, which maintain the magnet temperature at around 4 K. This has another benefit, as the cryogenically cooled assembly also works as a cryopump, improving the overall vacuum conditions inside the machine. This works by adsorbing the residual gas molecules to the cold walls, effectively freezing the contaminating material. The FLASH-EBIT vacuum is maintained by a set of turbomolecular pumps which, with the aid of the cryopump, reach pressures around 5×10^{-10} mbar, ensuring ultra-high vacuum conditions. This is essential for the experiments, as higher pressures would result in charge exchange between the ions and the residual gas, hindering the ionization process. Moreover, if the conditions are poor enough, the electron beam itself would interact with the residual gas, not being able to propagate through the entire EBIT setup.

If the study focus on very high charge states, a lower trap depth barrier can be applied. This ensures that the highly charge states remain trapped, while lower charge states have a grater chance of escaping the trap. Furthermore, lighter elements, like hydrogen or oxygen, commonly present in the residual gas, tend to gain energy when interacting with heavier elements in the trap. As these gain energy, and are generally less confined by the drift tubes potential, they carry the energy lost by the heavy ions out of the trap, effectively cooling the trapped ions. This process is known as evaporative cooling, and allows heavy ions to be trapped with relatively low trap depths, as these have generally low kinetic energy due to the aforementioned cooling, not being able to escape the trap.

It is also common to observe cathode contaminants in the trap, mainly barium and tungsten. To mitigate their presence, it is also common to periodically empty the trap by making the central drift tube voltage temporally positive. This avoids the accumulation of contaminant over time at the expense of having the target ions less time inside the trap. It is important to note that the energy of the electron beam is controlled by the voltage applied to the entire drift tube platform, while the voltages applied to each individual drift tube are relative to the drift tube platform voltage.

Top and side view photographs of the FLASH-EBIT setup can be found in Figure 3.6. In this Figure, the electron gun manipulator is on the right, with the vacuum chambers with the magnet and drift tube assembly, as well as the collector chamber, present on the left. In the subplot (b), the injection system is also observable connected to the main chamber. The gun manipulator allows the adjustment of the electron gun position with linear movement in three degrees of freedom and rotational movement in two degrees

of freedom. This adjustment is vital for the stable operation of the EBIT, as a misaligned beam can hit the drift tubes, resulting in a loss of beam current, while possibly damaging the electrodes and hindering the vacuum conditions in the main chamber.

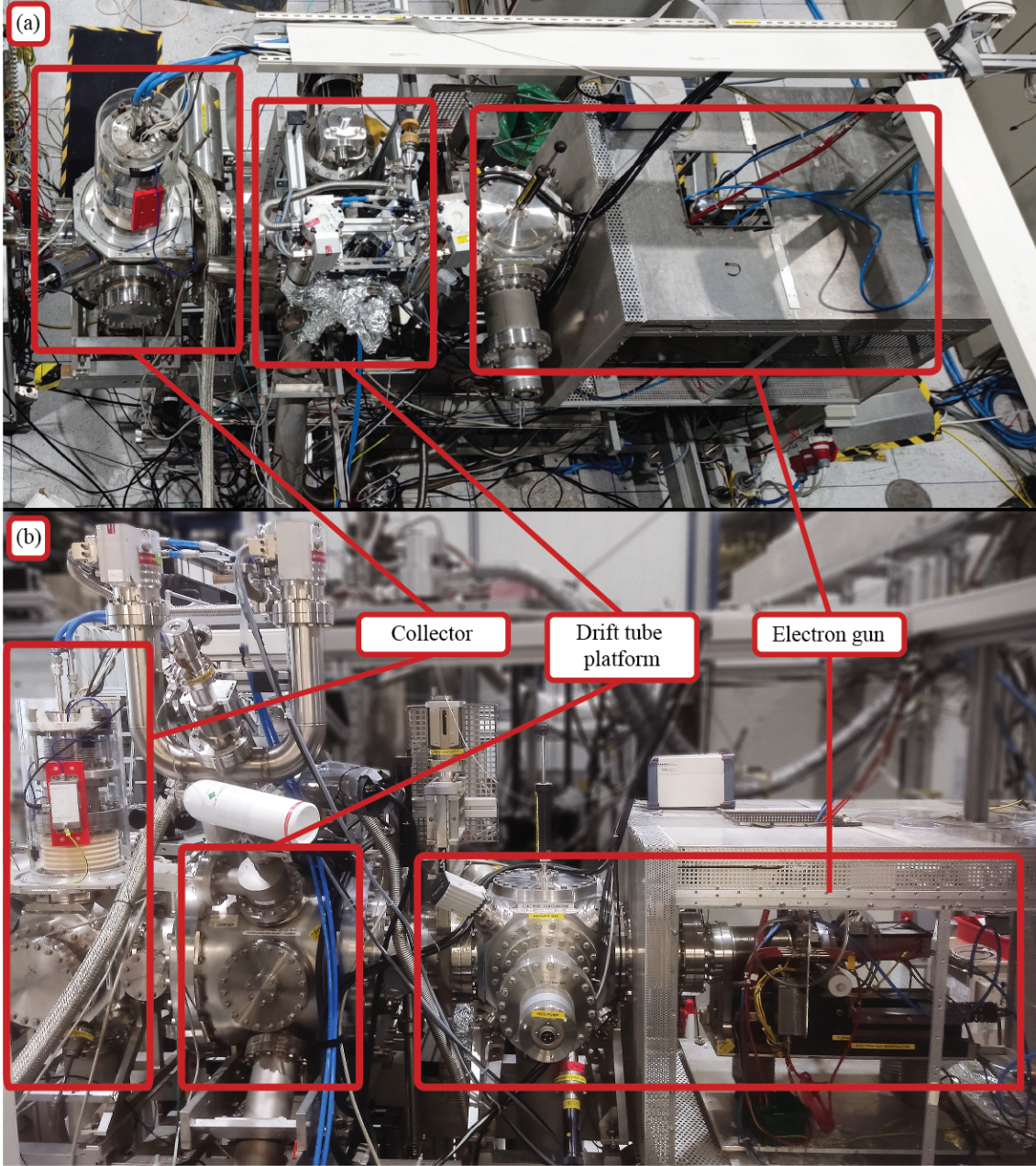


Figure 3.6: Photograph of FLASH-EBIT. (a) Top view. (b) Side view. The electron gun, drift tube assembly in the main chamber and collector are labeled.

3.3.4 Injection system

In order to ionize and trap an element, it first needs to be injected into the system. To this end, there is a differentially pumped injection system mounted to the main vacuum chamber. The injection system has two stages separated by a slit, both pumped by

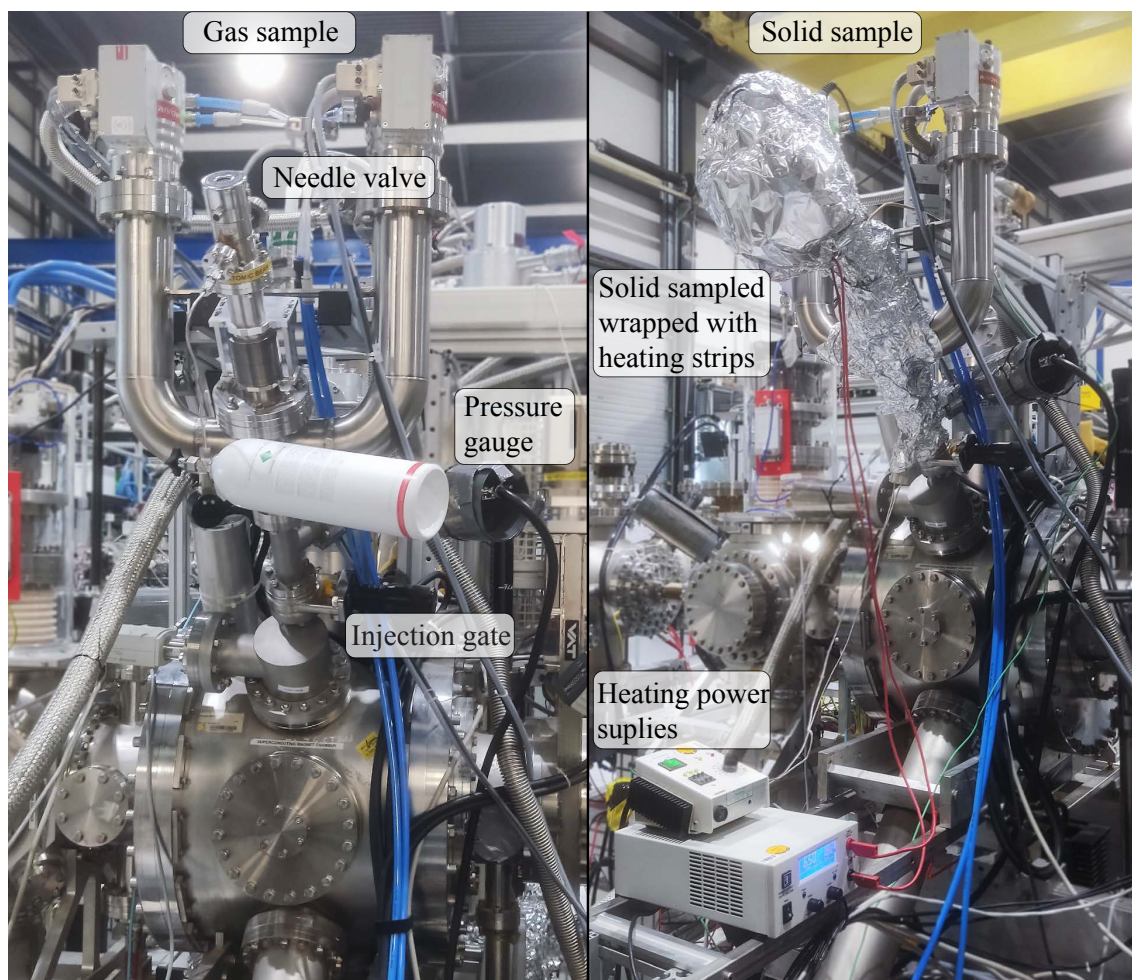


Figure 3.7: Photograph of the injection system. On the left is the injection of a gas sample, directly from a gas bottle. On the right is the injection of a solid sample. The container, as well as the rest of the injection system, have been wrapped with heating strips and thermal insulation to increase the vapor pressure of the sample.

individual turbomolecular pumps. The pressure differential between the two stages creates a stream of neutral atoms and molecules, which is directed to one of the openings of the central drift tube, where the atoms ultimately interact with the electron beam. The injection of the element into the first stage is done by directly attaching a container to a needle valve, which in turn is connected to this stage. The needle valve allows the precise control of the injection pressure, which directly correlates to the amount of atoms that are being supplied to the trap. In order to control this, a pressure gauge is connected to the second stage, before the main vacuum chamber, which probes the pressure at which the residual gas is right before it enters the drift tube assembly chamber.

Photographs of the injections system can be found in Figure 3.7. The injected compound in either solid, liquid or gas phase can be inserted in the system. The simplest case is the use of a gas, as a gas bottle can be attached to the needle valve. Due to the high pressure of the bottle, and the gas nature of its contents, the compound will naturally flow through the

needle valve into the first stage, where it is differentially pumped into the EBIT. Subplot (a) shows an example of a gas phase compound injection setup, with a compressed gas bottle connected to the needle valve. Liquid and solid compounds can also be injected by filling a container and attaching it to the needle valve. In this work, several solid samples were injected into FLASH-EBIT. In this case, the low pressure of the system is enough to slowly evaporate the material in the container, thus proceeding as the case of the gas injection. This process is entirely dependent on the vapor pressure of the inserted compound. Some compounds have an high enough vapor pressure to evaporate easily at room-temperature, at which case attaching the container to the needle valve is enough to inject the material. Other compounds have very low vapor pressure at room-temperature, in which cases a heating strip can be used to raise their temperature and initiate the evaporation process. In this case, the entire injection system needs to be heated, as the evaporated material can condensate in the pathway walls before reaching its destination. This can be done by enveloping the system with electric heating strips and an outside layer of fiber glass material and aluminum foil to thermally isolate the system and avoid energy losses. A power supply, connected to temperature probe near the compound container, is used to power the heating strips and maintain the target temperature. An example of a solid sample injection setup is represented in subplot (b), where most of the injection system is being heated by the power supplies at the bottom of the image.

3.3.5 Photon detection

While the contents of the trap can be inferred by sending the ions into a mass spectrometer, EBIT studies are usually carried out by probing the ions with the electron beam and observing the outgoing photons. Specific electron beam energy schemes can be used to study specific charge states and observe the emissions over a range of electron beam energies. EBIT systems can be used to make high precision spectroscopy in a wide range of photon energies, from the optical to X-ray regime. As all the work in this project was made by observing emission from EUV to X-ray, only detectors for energy ranges will be presented.

3.3.5.1 X-ray photon detection

One of the most common type of X-ray detectors are the solid state detectors, namely the SDD [159]. The SDD is based on semiconductor technology. Its base is a disc-shaped, n-doped, silicon crystal. The back of the detector has an p-doped layer connected to a positive potential. The front of the disk has a series of concentric p-doped rings, with the center connected to a negative potential. These rings use a voltage divider to maintain a voltage gradient from the outer rings to the inner rings. A scheme of a typical SDD setup is represented in Figure 3.8.

When an X-ray photon hits the detector, it create an electron-hole pair in the substrate. Due to the voltages applied to the different electrodes, the electrons tend to drift to the

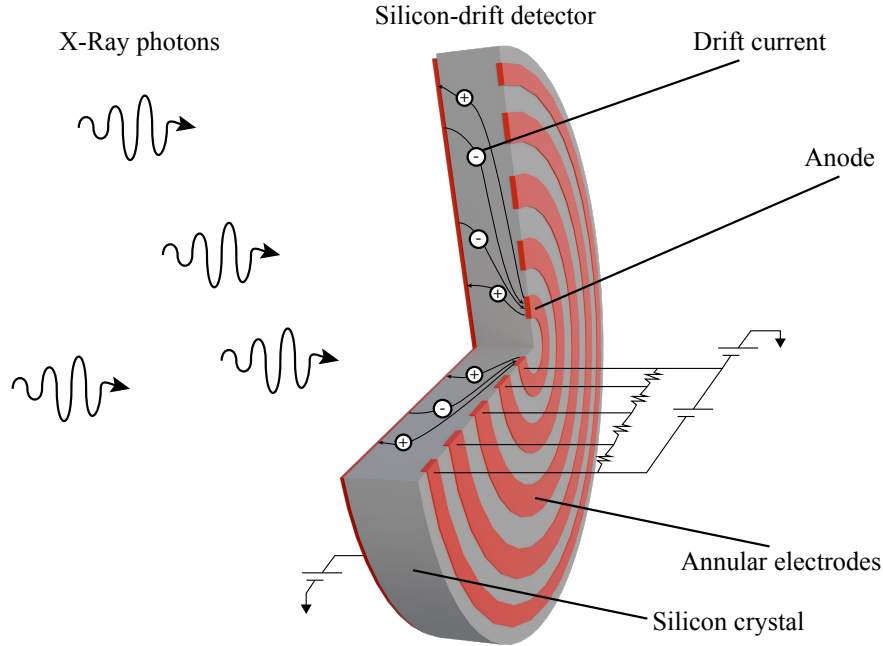


Figure 3.8: Schematic representation of silicon drift detector. The grey and red portions of the detector represent n-doped and p-doped silicon, respectively. In this picture, incident photons create electron-hole pairs that drift apart due to the applied voltages. The electrons drift to the anode, where the signal is collected.

front of the detector. Moreover, due to the rings with different voltages, this electrons drift to the central electrode, being collected in the anode. This voltage setup ensures that most of the generated electron flow into the anode instead of other parts of the detector, concentrating a great amount of charges and, therefore, aiding with the efficiency and resolution of the detector. These electrons produce an electrical pulse, which is amplified and converted into a digital signal with an Analog to Digital Converter (ADC).

This digital signal is registered as a photon event, corresponding to the direct observation of a single photon hitting the detector. Besides working as a photon counter, the number of electrons, of which depends the amplitude of the signal, is proportional to the incoming photon energy. This detector can, therefore, produce a photon energy differential spectrum by probing a wide range of photon energies simultaneously. The SDD can measure a typical energy range of about 200 eV to 20 keV with a resolution of around 100 eV of FWHM.

At the FLASH-EBIT, an SDD is placed in the main vacuum chamber at an angle of 90° in relation to the electron beam axis. It is placed relatively close to the drift tube assembly to maximize the solid angle and, therefore, improve statistics. This detector was the main source of data collection for the majority of the experiments presented in this thesis.

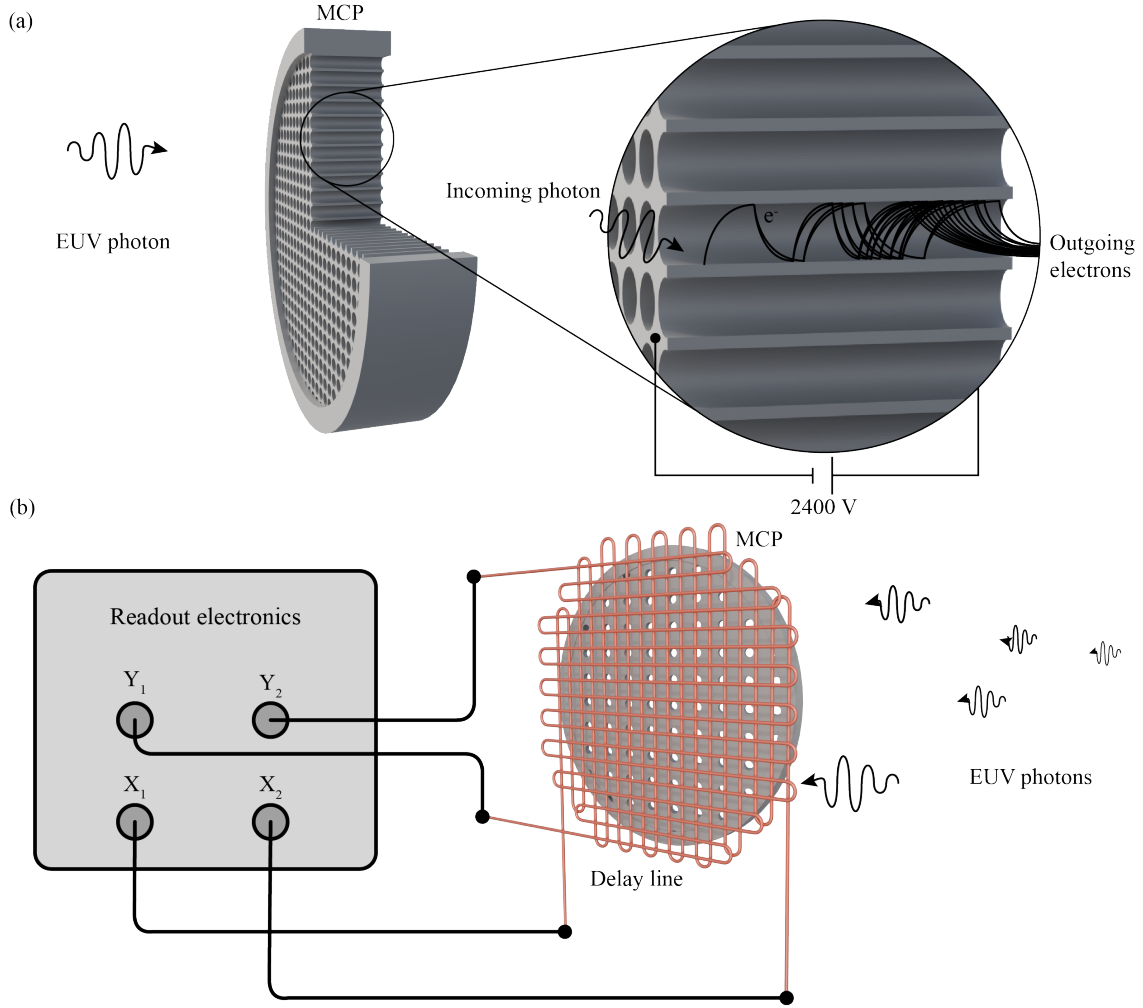


Figure 3.9: Representation of the MCP portion of the EUV detector. (a) representation of a photon hitting a hole of an MCP, creating a cascade of electrons that is propagated to the back of the MCP due to the applied high voltage. (b) Representation of the delay-line anode that collects the electrons from the MCP and provides the time-delayed signal to the readout electronics. The time delay between signals from different terminals of the delay lines are used to map the location of the MCP where the photon was collected.

3.3.5.2 EUV photon detection

A second detector was attached to the main chamber in another observation port to observe emission in the EUV range. These are lower in energy, and are usually described in terms of wavelength due to the wavelength dispersive nature of the detector. This detector uses a grating to disperse the incoming light according to its wavelength, followed by an MCP [160] to act as a position sensitive detector. More details about the EUV detector can be found in [161].

An Hitachi flat-field grating [162] (with a spectral range between 5 nm to 35 nm) is used to reflect incoming photons at grazing incidence, reflecting the light with different

angles, according to its wavelength, to the MCP. Light reflected from a grating follows the general grating equation

$$m\lambda = d(\sin \theta_i + \sin \theta_m), \quad (3.5)$$

where m is the diffraction order, λ is the photon wavelength, d is the groove spacing of the grating and θ_i and θ_m are the incoming and outgoing angles of the photon in relation to the normal vector of the grating surface.

After being dispersed, the photons are collected by an MCP. An MCP is build with a glass slab, encased by two metal plates. The glass has an array of perforation, usually tilted in relation to the normal vector of the surface of the glass. The model used in the present experiments used a tilt angle of 8° . The inner walls of the perforations are coated with a semiconducting material. The metal plates are used to apply a voltage difference between the front and the back of the MCP. In the works presented in this thesis, a voltage difference of 2400 V was applied. The tilt angle of the holes is present to avoid an incoming photon passing through the MCP without hitting the walls. By interacting with a wall coated with semiconducting material, electrons are ejected from the wall. The material is chose so that when one electron interacts again with a wall, a few electrons are also ejected. Due to the electric potential generated by the metal plates, the electrons are accelerated to the back of the MCP, hitting the walls several times and multiplying the amount of electrons in the process, phenomenon know as an electron cascade. Since the holes are tilted, possible radiation generated by the propagation of the cascades through the MCP are collected again in the walls, further increasing the number of electrons accelerated. A single particle hitting the MCP typically generates 10^3 to 10^4 electrons at the back of the MCP. This signal can be collected, further amplified and fed into a data acquisition system. A scheme of the process of electron amplification in an MCP is represented in Figure 3.9 (a). The MCP model used in this work was a DLD 40, by Roentdek [163]. Modern applications of this device usually setup two MCPs on top of each other, rotated by 180° . In this configuration, which was used in this work, there is no incident angle in which a particle can avoid interaction in the inner walls. Moreover, the amplification of the single is multiplied, achieving values in the order of 10^7 .

The method employed in this detector to measure the signal at the back of the MCP was the use of a delay-line anode [164]. This anode consist on two bent wires, covering the back of the MCP in the shape of fine grid. A schematic representation of this anode is shown in Figure 3.9 (b). As the secondary electrons reach the end of the hole, they are collected by the anode, generating a signal in the two wires, which is registered by the signal processing electronics. As there are two individual wires, the signal reaches the end of the wires at different times. The time delay between signals is unique for every possible position of the delay-line grid, which means it can be used to triangulate the position of the MCP surface where the signal was generated. This position is stored as an event, and allows the construction of an image of the photons hitting the MCP. As the angle of the photons reflected by the grating depend on the respective wavelength, photons with

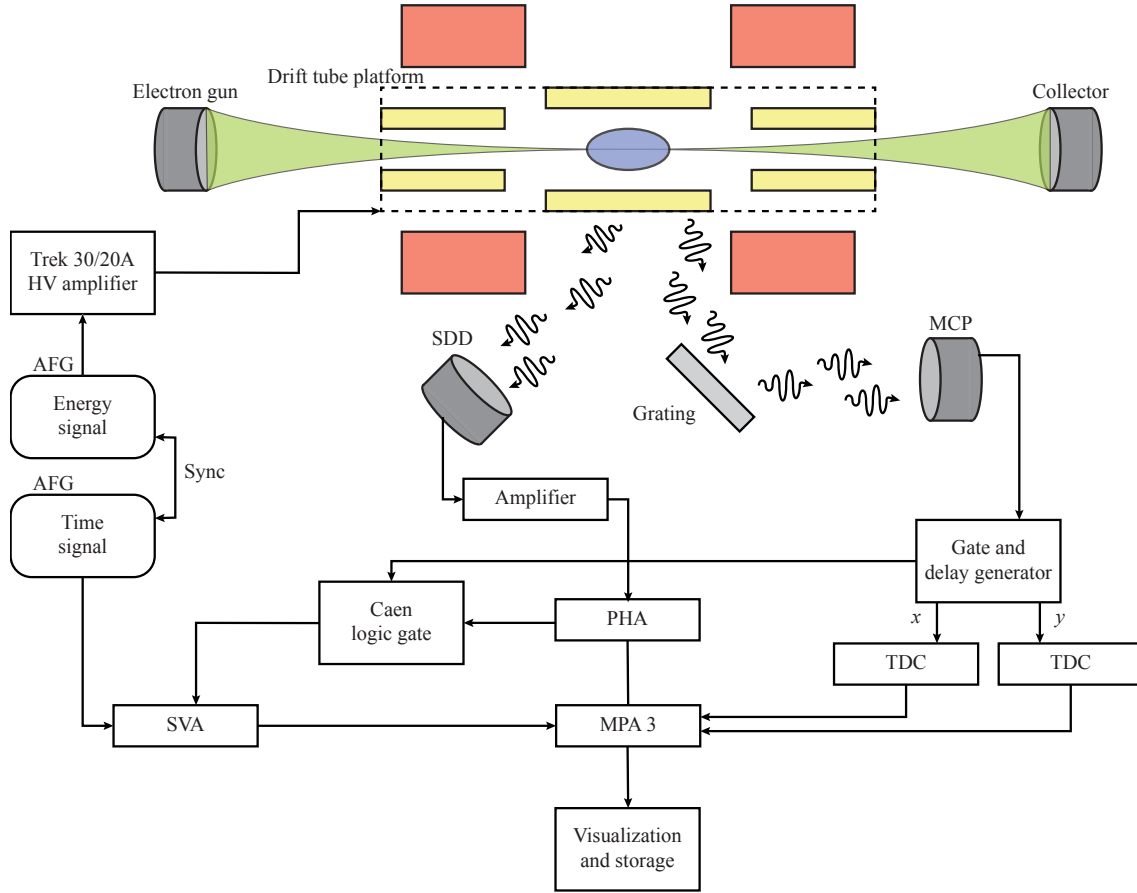


Figure 3.11: Schematic representation of all the electronic components setup together for a complete EBIT experiment. The electronic circuit connecting the AFGs with the drift tube platform and the logic gate used to coincide with the signals from both the SDD and the MCP detectors is represented. All the signals are stored in binary files for further analysis using the MPA 3 system.

While an electron beam at a constant energy can produce, trap and probe the ions, the ability to control the beam energy dynamically allows the possibility of doing energy scans, thereby producing two-dimensional spectra of intensity as a function of electron beam energy and photon energy. While the photon energy axis is enough to study the emission energies, the electron beam energy axis is key to study the collisional cross-sections for the different photon emitting electron-ion processes. A pair of Arbitrary Function Generators (AFG) was used to generate all the signals that controlled the experiments. The first AFG generates a signal designed to control the drift tube platform voltage. This signal is supplied to a TREK 30/20A high voltage amplifier to achieve high voltages, which in turn are used to control the drift tube assembly bias voltage. This AFG, therefore, is responsible for controlling the electron beam energy. The second AFG is synchronized to the internal clock of the first AFG, and is used to generate the time signal, used to time-stamp the detected photons and correlate with the corresponding electron beam energy. The functions set in these AFG are highly dependent on the time of experimental

setup one wants to use. These can vary according to the electron beam energy scan speed, energy range or breeding period. The energy scheme used for each experiment will be described in the respective Chapters.

The data acquisition system uses several ADC to analyze the signals coming from the detectors. The signal from the MCP is fed to an ADC in Pulse-Height-Analysis (PHA) mode. This is important, as the maximum of every pulse is evaluated and converted into the energy of the detected photon. For the case of the MCP, the respective signal passes through a gate and delay generator, which creates a time signal that is independent of the original signal intensity. This is done to increase the accuracy and consistency of the time delay measurements. The time signals are read by two Time-Delay-Converters (TDC), which read the time delays and digitize them into a control software that calculates the event position in the detector surface. The detector signals are gated by the time signal generated by the second AFG to coincide with the time of the energy scan cycle. This is what allows the creation of the two-dimensional spectra. The events from the ADCs are then fed to the acquisition system MPA-3, where the data is stored in binary files for further analysis. The experimental results can also be visualized in real-time during experiments with the *MPANT* software. A general scheme of this setup is represented in Figure 3.11.

EXPERIMENTAL RESULTS - ASTROPHYSICS

As seen in the Chapter 1, lighter elements are ubiquitous in a wide range of astrophysical settings. Accurate knowledge of the atomic properties of these elements in their several charge state configurations is of paramount importance for plasma diagnostics. Among the most important proprieties for astrophysical modeling are the energy level structure and transitions energies, radiative and autoionization rates and cross-sections from the several excitation, ionization and recombination processes (see Section 2.5). In this Chapter, the EBIT experimental setup and data will be presented for the study of oxygen and calcium.

Oxygen is one of the most prominent elements in astrophysical observations, particular with its He-like charge state emissions being used in a myriad of diagnostic purposes (as mentioned in previous Section 1.2.2). The dielectronic recombination and excitation structures near the $K\alpha$ excitation threshold will be explored using the FLASH-EBIT. This setup was also used to study the effects of having a metastable state with a lifetime in the order of the energy scan timescale.

Iron is another element that is very prominent in soft X-ray astronomical observations. This element has been studied a number of times in the FLASH-EBIT in the past, and its always subject of new studies and laboratory benchmarks. Nonetheless, other elements with similar values of Z are routinely observed by X-ray telescopes. Notably, the latest high resolution X-ray observatory (XRISM) has observed several lines of calcium, element for which there is a severe lack of reliable laboratory benchmarks and experimental atomic data available in the literature. The He-like calcium lines could represent an alternative to the diagnostics that rely on the Ne-like iron lines, which at the moment are not yet observable with this telescope, as no lines can be observed under 2 keV [165]. As such, experiments at the FLASH-EBIT were also performed to observe the dielectronic recombination and excitation structure for the $K\alpha$ lines of calcium.

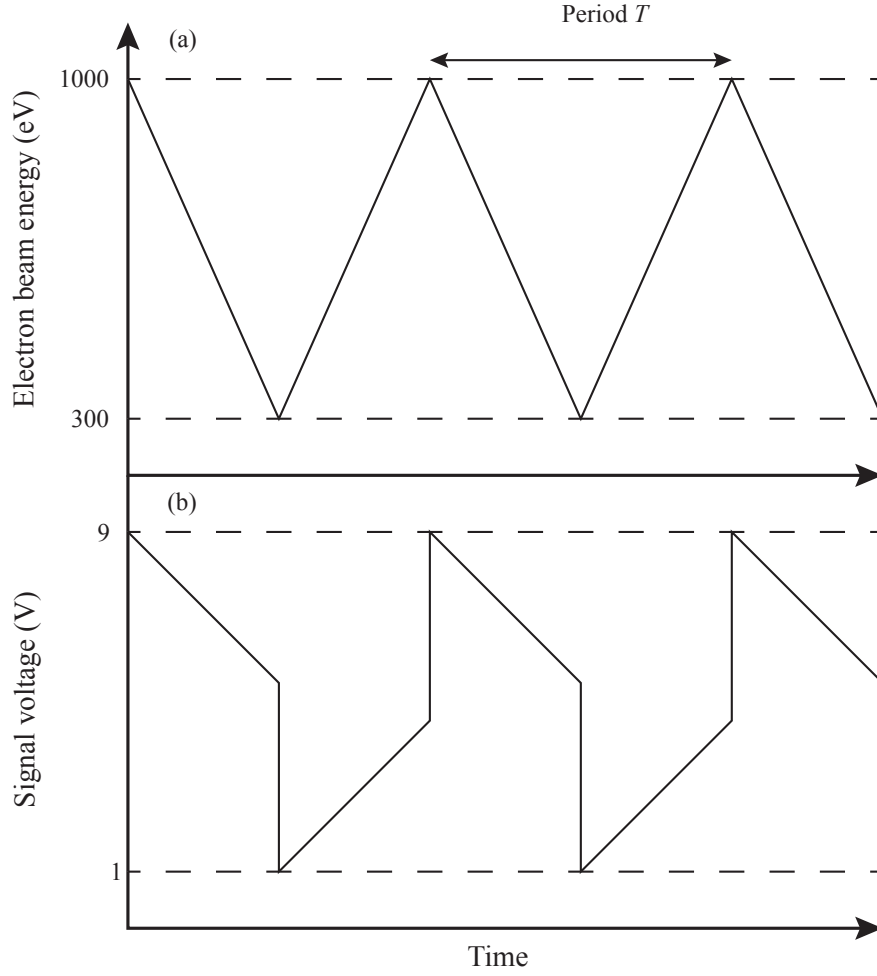


Figure 4.1: Simplified voltage scheme used for the electron beam energy setup use during scans. (a) Nominal electron beam energy given by the difference between the drift tube platform and the electron gun anode voltage. (b) Voltage signal used to discriminate the photon emission detection by the corresponding electron beam energy.

4.1 Oxygen

4.1.1 Experimental setup

The oxygen measurements were carried out with the FLASH-EBIT (see Chapter 3), where the almost mono-energetic electron beam dissociated the molecular oxygen (O_2) injected into the trap region, and sequentially generated, by electron impact ionization, highly charged ions of this element, with He-like ions being the dominant species.

The drift tube platform voltage was set by a triangular wave function generated by the first AFG, see Figure 4.1 (a), while the second AFG was used to generate a second signal presented in Figure 4.1 (b). The signal from the second AFG is given to an ADC, and it is used to time-stamp each event with the corresponding value of the electron beam energy, thus allowing the production of electron beam energy differential spectra. By mapping the electron beam energy with the second signal at different voltage ranges,

the scans performed downwards and upwards scans are stored independently, allowing the comparison between the two types of scans. Moreover, while the signal from the second AFG could be a simple ramp-up, this would result in the production of two scans mirrored in the electron energy axis. The current configuration, by mapping the direction of the signal to the direction of the scan, corrects for this issue automatically without requiring any further operations needed in the data analysis. The electron beam current was controlled by adjusting the current of the electron gun cathode. Since this cathode is made of a tungsten and barium, high currents lead mainly to contaminations of barium in the trap. Given the high atomic mass of barium compared with oxygen, small contaminations are enough to dominate the trap content. For this reason, the electron beam current was adjusted to be as high as possible, to increase the ionization efficiency and the collisional rates, but low enough to minimize the barium contaminations. The current was maintained constant at 15 mA.

The soft X-ray emissions during the beam energy scans were registered with an SDD mounted side-on near the trap region, and perpendicular to the electron beam, with resolution around 200 eV FWHM at 600 eV. This resolution does not allow us to resolve the $K\alpha$ emission lines z , x , y and w , with their energy ranging between 560 and 575 eV. However, as was observed in a previous work made with this EBIT [141], an excellent electron beam energy resolution of 5.5 eV at 520 eV opens the possibility of selectively excite various DR and RE resonances. These often decay by only one transition, which therefore can be effectively separated from others based of selecting a Region Of Interest (ROI). In such cases, the low-resolution signal from the SDD can yield the transition energy with an accuracy limited by the statistical accuracy of the centroid determination. The experimental setup applied in this work followed a scheme based on early studies of DR at the LLNL EBIT [166] and later works at MPIK focused on iron XVII (Ne-like iron) [141, 167, 168]. In all cases, the electron energy scans over a defined region, probing the various atomic processes of excitation and recombination leading to photon line emission. Previously, the electron energy duty cycle of the electron beam energy scheme consisted of a breeding time at a constant energy, followed by a linear ramp-down and a symmetrical ramp-up. The breeding time was necessary for preparing a specific ion population. This time generally takes longer times scales, some times in order of seconds, to ensure the charge state balance reaches an equilibrium, while the probing time must be fast enough to prevent dynamics of the charge state balance, being often in timescales of milliseconds. While dynamical charge states could be suitable for only studying the DR resonance energy positions and photon emission energies, a constant charge state population during energy scan is vital to extract unmodulated emissivities proportional to the collisional cross-sections. Such duty cycle was introduced in Ref. [166, 169] and used routinely in other measurements (e.g., [170–172]). As for He-like oxygen, a significant drop in the count rate relative to previous measurements was observed, which could be due to a smaller efficiency in trapping light ions. A periodical triangular duty cycle of range 0.3–1.0 keV without breeding time was employed to compensate for this rate drop, as shown in Figure

Table 4.1: Ionization energies of each charge state of oxygen, as well as the respective ground electronic configurations. Values taken from the NIST ASD.

Ion species	Charge	Ground configuration	Ionization energy (eV)
O I	0	$1s^2 2s^2 2p^4 \ ^3P_2$	13.62
O II	1+	$1s^2 2s^2 2p^3 \ ^4S_{3/2}$	35.12
O III	2+	$1s^2 2s^2 2p^2 \ ^3P_0$	54.94
O IV	3+	$1s^2 2s^2 2p \ ^2P_{1/2}$	77.41
O V	4+	$1s^2 2s^2 \ ^1S_0$	113.90
O VI	5+	$1s^2 2s \ ^2S_{1/2}$	138.12
O VII	6+	$1s^2 \ ^1S_0$	739.33
O VIII	7+	$1s \ ^2S_{1/2}$	871.41

4.1 (a). Removing the breeding time for investigating oxygen VII is valid since the Li-like ionization threshold (≈ 138 eV) is still below the scanning energies. The ionization energies of all oxygen charge states can be found in Table 4.1. The ionization energy thresholds of both the He-like (≈ 739 eV) and the H-like (≈ 871 eV) ions were also present in the energy scan. With this energy range, it is expected for the charge state balance to include a significant part of H-like ions. While emissions of H-like ions are not a subject of this study, their DR resonances allows calibration of electron beam energy against previous accurate measurements at a storage ring [173], to compensate the electron space charge. The electron beam energy axis was calibrated by fitting the DR resonances of He-like and H-like ions and fitting the centroids against the previously measured TSR experimental data and new calculations made with FAC. Since these are known in the literature, they can contribute to the calibration of the electron beam energy which, although given by the voltages of the drift tube platform and the electron gun anode, there is still a component given by the space charges of the ion cloud and the electron themselves which are not trivial to estimate.

An example of a measurement can be found in Figure 4.2. At the subplot (a), one can see the raw data obtained directly from the experiment. The ADC used to record the SDD and the AFG signals has a resolution of 8000 channels, and only a region of interest around the effective emissions is presented in this subplot. Here one can see the application of the AFG signal shown in Figure 4.1 (b), where we can see in Figure 4.2 (a) the downwards scan followed by the upwards scan without being mirrored. Although all the $K\alpha$ are blended, the photon energy axis was also roughly calibrated. This was made to estimate the location of the main lines, as well as the $K\beta$ lines and emissions from contaminations from other elements in the trap. This calibration was made by taking advantage of the fact that the RR photon energy is given by the energy of the incident electron minus the recombination energy for the specific atomic shell. Thus, the RR emission structure is composed of a diagonal line (see Figure 4.2 (a)) with a unitary slope. By making gaussian fits along the RR line visible in Figure 4.2 (a) and making a linear fit with the respective centroids, one can rescale the axis to transform this slope into a unitary one. Furthermore,

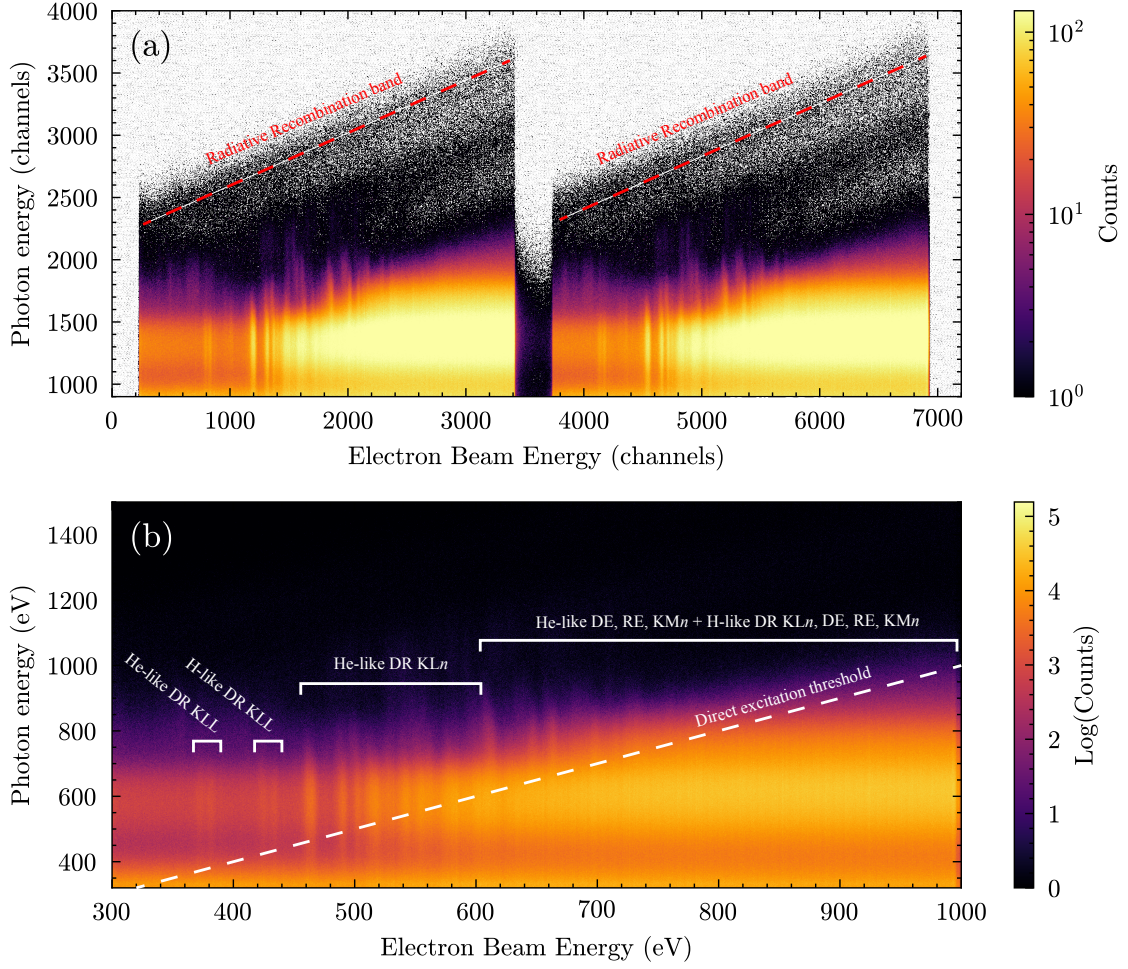


Figure 4.2: Emission intensity as a function of the photon energy and electron beam energy for a He-like oxygen measurement. (a) Raw spectrum, with the up and down emissions represented side-by-side. The axes in this plot are uncalibrated. The radiative recombination emission structure is highlighted in this plot. (b) Sum of the up and down scans with calibrated axes. The DR and resonant and non-resonant excitation structures are labeled.

the offset of the axis was estimated by fitting the main $K\alpha$ line and correcting its value to the one present in the NIST Atomic Structure Database (ASD) [174]. Figure 4.2 (b) presents the data from the top subfigure calibrated with this procedure. In this subplot, can can also see (labeled in the Figure) the positions of the DR resonances, as well as the RE resonances and the direct excitation structure. As expected, both DR structures from the charge states of He-like and H-like are present, although the latter being much fainter.

Measurements were done with four different duty cycles for the electron beam energy scheme: 400, 200, 20 and 1 ms. The raw experimental data for these four measurements is presented in Figure 4.3, where the individual spectrum from each of the scan directions are superimposed in the same subplot. All these plots were calibrated with the methods mentioned before, with the presented data being a projection into the electron beam energy axis using a region of interest from 400 to 700 eV of photon energy. This includes

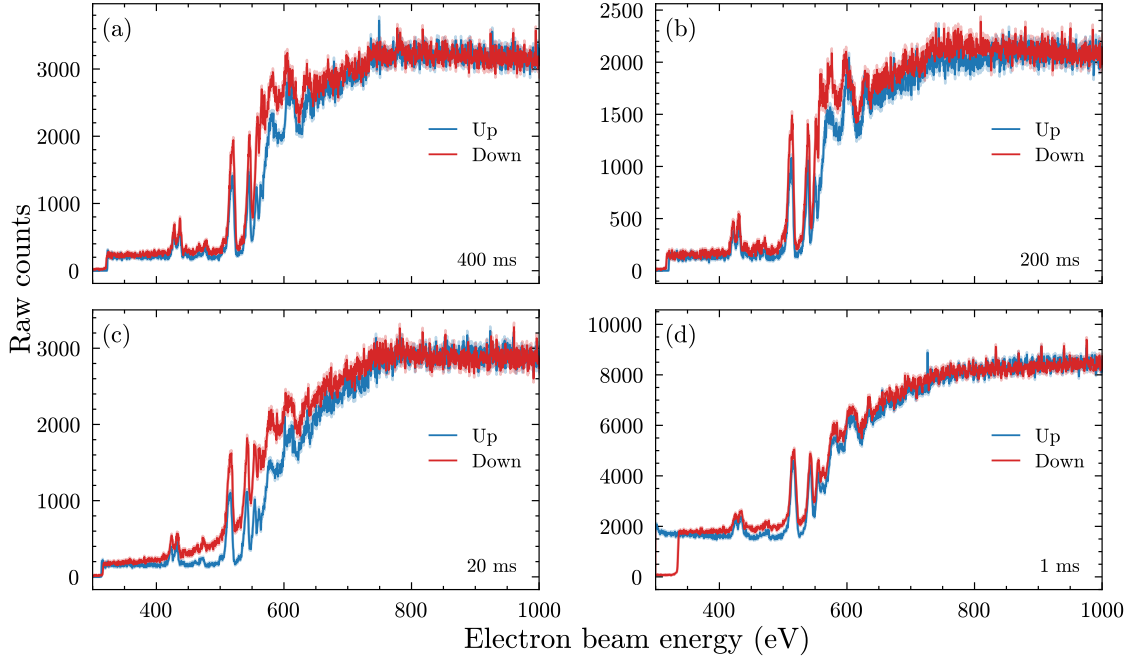


Figure 4.3: Experimental emission from the downwards (red) and upwards (blue) scans as a function of the electron beam energy for (a) 400 ms scan, (b) 200 ms scan, (c) 20 ms, (d) 1 ms. The plots were made by projecting the two-dimensional data over the electron beam energy axis around a photon energy region of interest between 300 and 700 eV.

both the $K\alpha$ lines, the respective DR satellites and higher n transitions which cannot be decoupled from the main lines. In the 400 and 200 ms, it is evident that the DR resonances intensity of the He-like ion change in intensity depending on the direction of the scan. This points towards a variation of the He-like population during the scan, being generally lower in the DR portion of the scan in the upwards scan. This is an expected behavior, as lower beam energies tend to lower charge state balances, meaning that, during the downwards scan, the He-like charge state loses population during the scan, only to be refilled later in the upwards scan. This behavior is not present in the 20 and 1 ms scans. In these scans, the baseline of the emissions below the DR resonances is different for each scan direction but, discounting this baseline, the DR structure is consistent when comparing scan directions. This means that a 20 ms duty-cycle period is fast enough for the dynamics of the charge state distribution to be negligible. Since a goal is to extract cross-section data, which depends on the stability of the charge state distribution, only the 20 and the 1 ms scans were considered for further analysis regarding the He-like emissions.

4.1.2 Metastable decay

Apparent differences arise when comparing the downward scan with the upward scan for both the 20 and 1 ms scans. The differences between scan directions become more apparent in the 20 ms period (see Fig. 4.4 (a)). These differences may be given by the

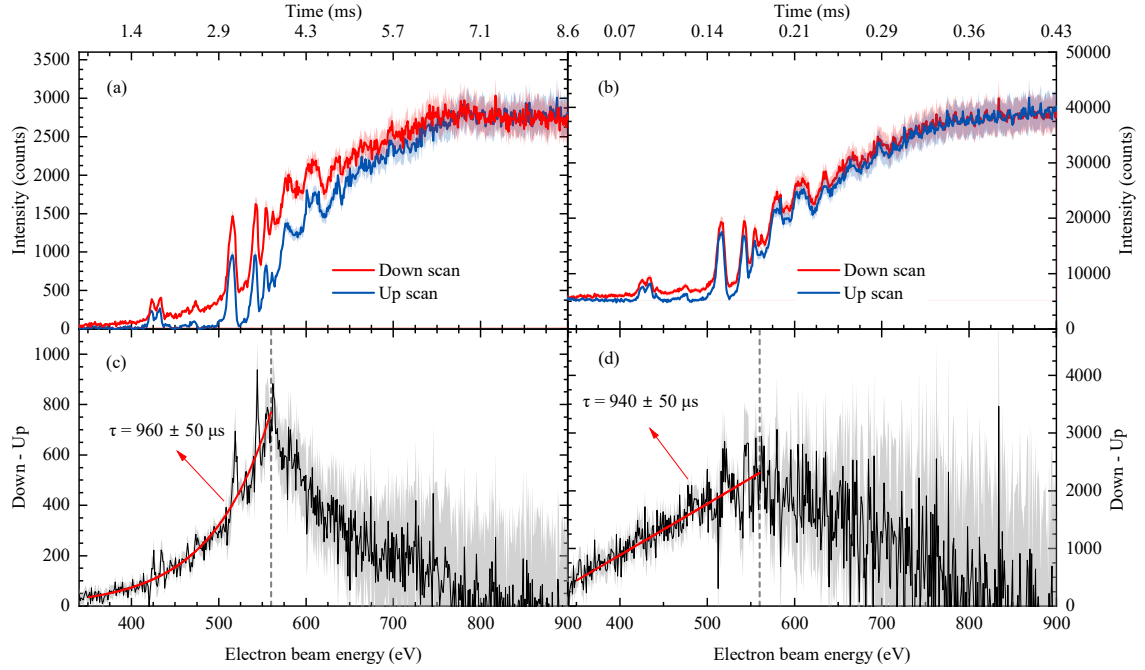


Figure 4.4: Experimental emissions from the downwards (red) and upwards (blue) scans as a function of the electron beam energy for (a) 20 ms scan and (b) 1 ms scan. Subplots (c) and (d) contain the subtraction of the emissions (black) from the downward and upward scans, respectively, along with the exponential fit (red). The dashed line represents the metastable CE threshold.

dynamics of the metastable state $1s2s\ ^3S_1$, which has an excitation threshold of around 560 eV and a lifetime of around 1 ms, a time scale similar to some of the duty cycle periods investigated.

The lifetime of this metastable level is well known, experimentally reported to be $\tau = (956^{+5}_{-4})\ \mu\text{s}$ [101]. This value was previously accurately measured with an EBIT setup designed specifically for this purpose. In this setup, a group of trap He-like oxygen ions was excited with a constant electron beam energy above the metastable state excitation threshold, producing a certain population of the metastable state, emitting the z-line in the process. The electron beam was then turned off, stopping the excitation from the ground to the metastable state. As the excited population decays, the emissions of the z-line were monitored, thus providing a direct observation of the decay of the population, from which a simple exponential fit yielded the high-precision experimental value of the metastable state lifetime. By turning off the beam, the ions are no longer radially confined by the electrons space charge. However the high magnetic field works as a magnetic bottle, being able to confine the ions for a few seconds, which is enough for the measurement of lifetimes in the millisecond order. This older experiment, however, not only provided valuable information for our current experiments, but also demonstrated a different experimental setup that can be done with an EBIT device.

Given the lifetime of the metastable state, the upwards 20 ms scan is expected to start with virtually no metastable population. As the electron beam energy crosses the

excitation threshold during the downwards scan, the metastable population ceases to be excited and start to decay. As the energy scan takes about 3.7 ms to go from the excitation threshold to the end of the down scan, the upwards scan starts with about only 2 % of the metastable population that is available at the beginning of the decay. As result, the upwards scan can be used as a baseline of emissions without the z-line, and the subtraction of the downward scan by the upward scan isolates the emissions of the metastable state in the downwards scan below the threshold energy. Figure 4.4 shows the 20 ms (a) and 1 ms (b) scans in both directions together with their respective subtraction between scans ((c) and (d)). As it becomes clear after the subtraction shown in Figure (c) for 20 ms, an exponential decay pattern is present right before the excitation threshold, marked in the plot with the dashed line. This pattern is the direct observation of the metastable population, as the DR features disappeared in the subtraction due to their intensities being related to the population of the ground state. A simple exponential function fit yielded a decay constant of $(0.01494 \pm 0.00006) \text{ eV}^{-1}$, where the uncertainty is estimated only by fit statistics. Given an electron beam energy sweeping rate of $70 \pm 4 \text{ eVs}^{-1}$, the resulting measured lifetime has a value of

$$\tau_{3S_1} = 0.96 \pm 0.05 \text{ ms.} \quad (4.1)$$

This value is in agreement with the value reported by the older experiment [101] and the calculations therein. This observation, combined with the decay starting at the excitation threshold, strongly suggests that the differences between downward and upward scans are, in fact, mostly due to the metastable population dynamics. Furthermore, the difference between scans vanishes slowly after the excitation energy, an expected behavior since the metastable population starts to replenish in the upward scan after the threshold until it reaches the values present in the downward scan.

Figure 4.4 subplots (b) and (c) show the 1 ms scans with respective upward-downward differences. The 1 ms observation differs from the remaining experiments, as it presents a higher background not seen before at other scans. This is caused by the z-line from an averaged metastable population fraction, as in this case the metastable population does not have time to fully decay. In this case, with an energy scanning speed of about 1400 eVs^{-1} , the metastable population at the end of the downwards scan is about 82 % of the initial population, and about 68 % when it reaches again the excitation threshold in the upwards scan. It is worth noting that the spectra presented in 4.4 (a) and (b) already have their respective backgrounds removed from non-physical events (see Figure 4.2 e.g around the photon energies channel 3700). These random events contribute to a constant background not attributed to metastable emission, as seen in 4.3 (c) at 400 eV. This constant background was estimated by analyzing the signal to noise ratio of the DR resonances in the longer measurements (200 and 400 ms) and deriving the corresponding background present in the faster scans. As the upwards scan still has a significant amount of metastable emissions, the difference between scans cannot be modeled by a simple exponential function. In this case, the difference was fitted by the difference of two time-symmetrical exponential

decays to simulate the decays present in each scan:

$$f(A, E_i, E_\tau; E) = A \left(e^{(E-E_i)/E_\tau} - e^{-(E-E_i)/E_\tau} \right). \quad (4.2)$$

Here, A , E_i and E_τ are the fit parameters exponential amplitude, starting energy and decay constant, while E is the electron beam energy. The fit yielded a final lifetime of

$$\tau_{3S_1} = 0.94 \pm 0.05 \text{ ms}. \quad (4.3)$$

This value is also consistent with the literature, as well as with the 20 ms observation. Although these lifetime measurements do not compare with the older work in terms of accuracy, it is enough to confirm the process behind the differences found between scans, while also supporting the higher precision values already reported in the literature.

4.1.3 Spectral modeling

Since there is a non-linear baseline across all the measurement, given by the dynamics of the metastable state population, differential recombination and excitation cross-sections cannot be directly retrieved from the experimental data. While the emissions below the excitation threshold can be fully explained by fairly simple models, based on the addition of exponential decays, the z-line emissions become non-linear above the threshold. In this region, the metastable population is fed by resonant and non-resonant excitation processes, both directly and through the cascades after excitations above the $n = 3$ threshold. To fully understand the emission spectra, the time dependent CRM described in Chapter 3 was applied with the respective experimental conditions as input parameters.

To model the entire spectrum, the theoretical atomic data for the collisional processes, such as CE, CI, CX, RR and DC, must be calculated and included in the model. Furthermore, the radiative and non-radiative transition rates between all the atomic levels involved must also be calculated, in order to include in the model for the cascades and dynamics of metastable states. The theoretical cross-sections for CI, CE, DC and RR were calculated using FAC. All cross-sections involving one free electron (CI, CE, RR and DC) were calculated with FAC using distorted-wave (DW) approximation. R-matrix-based cross-sections were not possible to implement in the CRM because presently it is complex to identify the levels of each autoionizing channels to address the branching ratios. Since the plasma studied here is mainly composed of He-like ions, the atomic calculations were divided in two parts: a complete part for H-like, He-like and Li-like, and a reduced part for the remaining charge states. All the DW calculations, radiative rates and Auger rates of the complete part have excited configurations up to $n = 10$. These include $n\ell$ for H-like ions, $1sn\ell$ and $2sn\ell$ for He-like ions and $1s^2n\ell$ and $1s2\ell'n\ell$ for Li-like ions. A total of 2576 levels were included in the CRM for this part. CX cross-sections were calculated using the Landau-Zener approximation [134] and using neutral hydrogen as targets, which is sufficient since the observed emission is consistent with a low rate of this process. The reduced part with the other ion charge states contains only CI, CX and RR for

describing the charge state evolution. The corresponding emission occurs exclusively at EBIT plasma ignition, making it unobservable and, therefore, excluded from calculations. Although CI and RR cross-sections can be calculated using FAC with the DW approach, a simpler approximation was adopted in the reduced model. CI and RR cross-sections were determined using the semi-empirical formulas from Lotz [126] and Kim [147], respectively. For CX cross-sections, the formula from Janev [134] was applied.

An example of a result of the simulation, a simulation with a static beam at 800 eV was already presented in Figure 2.8, in Chapter 2. Here we can observe a charge state balance at equilibrium of around 75 % of He-like ions and 25 % of H-like ions. This proportion is consistent with the ratios of the resonance strengths of the KLL DR structures of H-like and He-like, located around 460 and 420 eV, respectively. Moreover, the Li DR resonances are not experimentally observed, showing that with the given the statistical uncertainty of the spectra, the population of this charge state must be lower than 5 %. To make the complete simulations, the electron energy follows a triangular wave with the same conditions and the electron beam energy schemes (see Figure 4.1) used in the experiments. For each of the tested duty-cycle periods, the simulation was performed with enough cycles to reach equilibrium in terms of charge state distribution, as well as resulting in identical population dynamics in consecutive cycles.

As an example of a CRM calculation, Figure 4.5 shows the metastable population and emissivity of the $K\alpha$ lines resulted from the simulation for a 20 ms scan. In the Figure, two periods of the energy scan are represented. Note that, by following the CRM method presented in Chapter 2, only the populations of metastable states are obtained, while the emissivities are reconstructed from the branching ratios in each step. As expected, the metastable population grows and decays exponentially when the electron beam energy crosses the $n = 2$ excitation threshold up and down. Crossing the $n = 3$ excitation threshold also produces the same effect due to higher cascades feeding the metastable population, however with less magnitude (both thresholds are marked in the Figure with vertical dashed lines). The observed peak of population at approximately 750 eV results from a balance between the increasing feeding cascades and the decreasing collisional cross-sections of 3S_1 with the increase in energy. This trend is similarly reflected in the corresponding z -line emission shown in Figure 4.6 (c), where the emissivity is proportional to the metastable state population. Moreover, the collisional excitation cross-section from the ground to the 1P_1 state increases within this energy range, contributing to the enhanced emissivity of the w -line as the energy rises, while the x and y lines emissivities decrease due to the decrease of excitation cross-sections with the increase of electron beam energy. As these lines have fast electric dipole-allowed transitions, the excited states that produce them reach a local equilibrium almost instantly, where all the excited population decays very fast to the ground state. For this reason, and opposed to the case of the emission of the metastable state, these lines are proportional to the excitation cross-sections. Additionally, a faint emission of the $x + y$ lines is observable below the excitation threshold, attributed to the excitation of the metastable state into the $^3P_{1,2}$ levels. This part of the $x + y$ lines

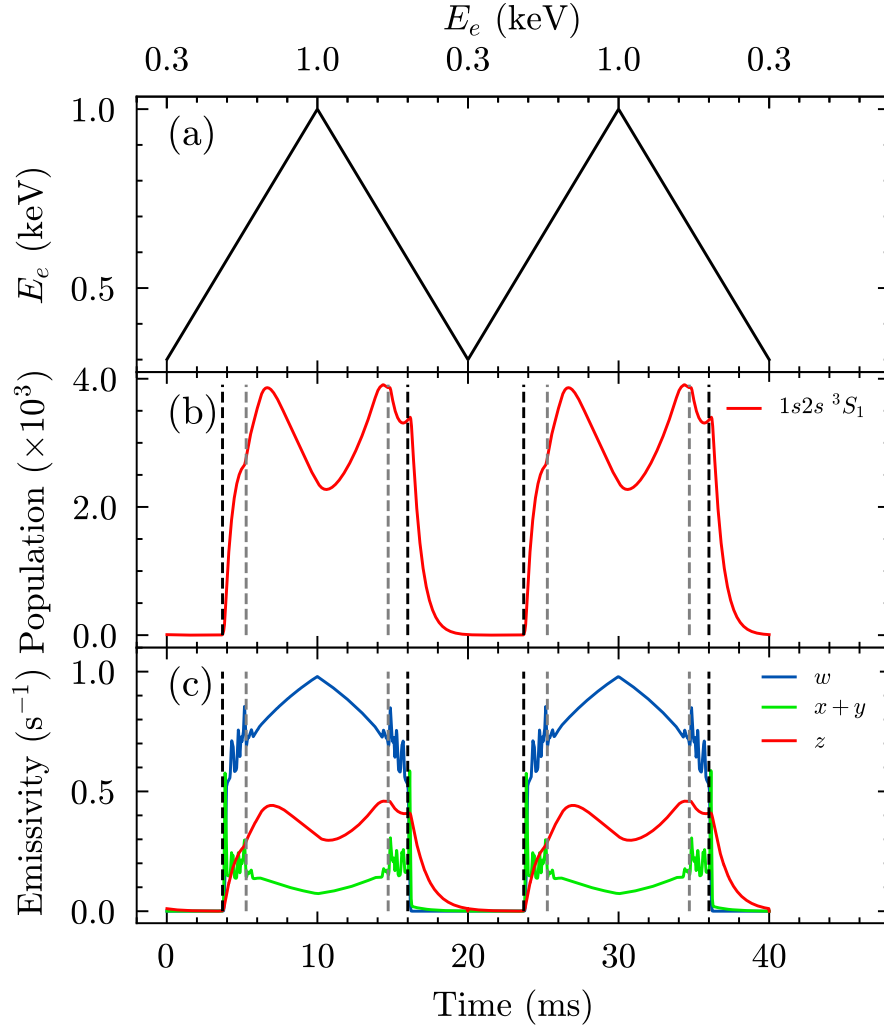


Figure 4.5: Populations of the excited states that produce the K_α calculated with the time-dependent CRM in the experimental conditions for the 20 ms scan. (a) Electron beam energy. (b) Population of the triplet 3S_1 metastable state. (c) Emissivity of the main K_α lines. The vertical dashed lines represent the beam energy crossing the metastable state excitation threshold (black) and the $n = 3$ excitation threshold (grey).

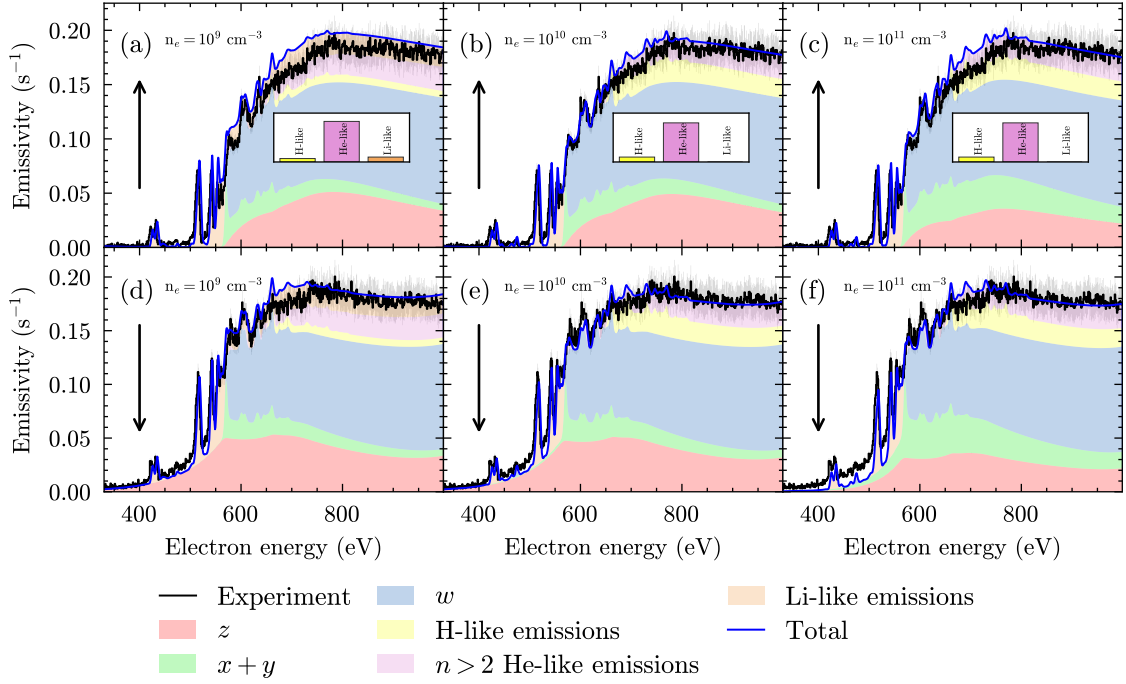


Figure 4.6: Results from the time-dynamical CRM compared to the laboratory measurements for different n_e values. Up (a) and down (d) scans for $n_e = 10 \times 10^9 \text{ cm}^{-3}$. Up (b) and down (e) scans for $n_e = 10 \times 10^{10} \text{ cm}^{-3}$. Up (c) and down (f) scans for $n_e = 10 \times 10^{11} \text{ cm}^{-3}$. Here we distinguish emissions from the z , x , y , and w lines, $n > 2$ excitations from He-like, as well as emissions from both the H-like and the Li-like charge states.

emission is also proportional to the population of the metastable state. Moreover, it is also possible to observe the RE resonances between the $n = 2$ and $n = 3$ excitation thresholds that contribute to the emission of the $K\alpha$ lines. No resonances are observed in the z -line emissivity due to its slow decay, diluting the resonances in the general metastable state population profile.

Figure 4.6 presents the synthetic emissions for the 20 ms scan, sorted by upward and downward directions of the electron beam energy, and compares them with the experimental observations. The different columns show the CRM simulation for different electron densities: 10^9 , 10^{10} , 10^{11} cm^{-3} . The main difference between spectra is the z -line emission baseline given by the 3S_1 population dynamics, as well as the charge state distribution. The higher electron density case shows a growth of the metastable population to values lower than what is observed experimentally, leading to an overestimation of the emissions after the excitation threshold due to a relative increase of the remaining $K\alpha$ lines. An analogous situation is observed in the downward scan, where, for the higher electron density, the emissions of the non-metastable populations have a bigger impact than the z -line emissions. An exponential decay comparable to what is observed experimentally when the electron beam energy crosses the excitation energy downwards is observed for the other electron densities. Both the simulations for the $n_e = 10^9 \text{ cm}^{-3}$ and $n_e = 10^{10} \text{ cm}^{-3}$ are in agreement with the experimental observations regarding the

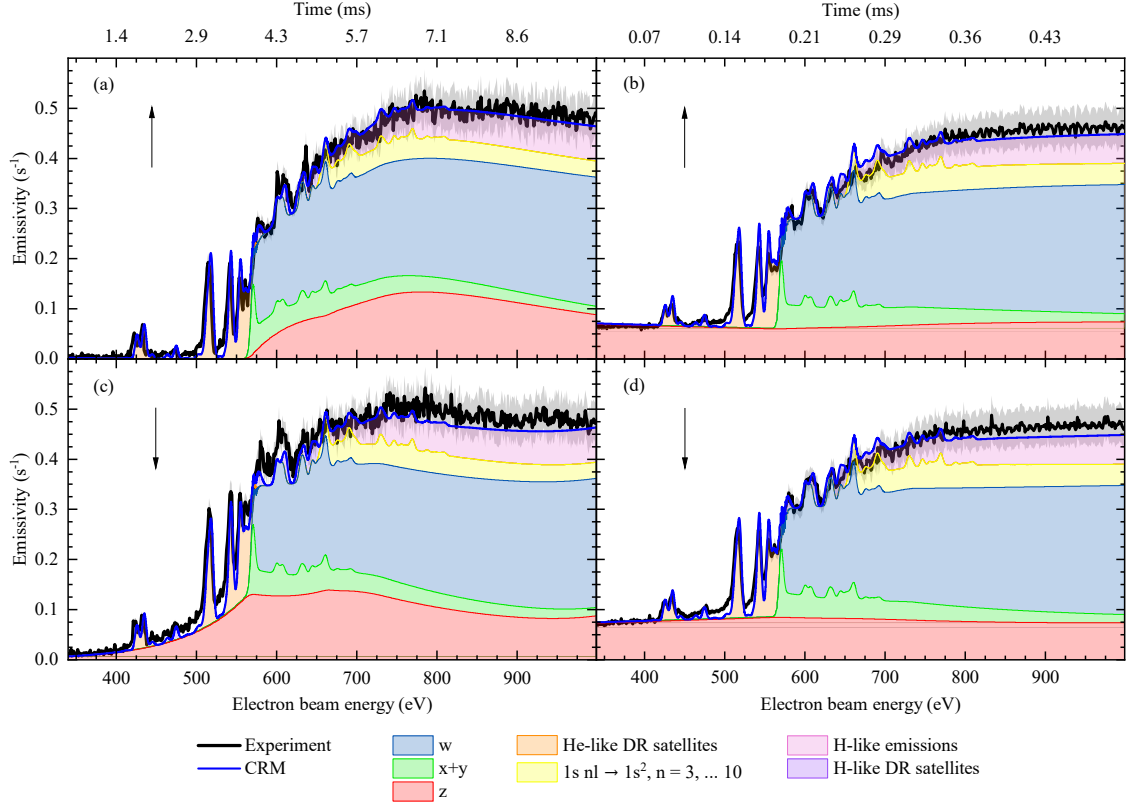


Figure 4.7: Results from the time-dynamical CRM compared to the laboratory measurements. The comparison is made in four different experimental conditions: (a) upward scan with a period of 20 ms, (b) upward scan with a period of 1 ms, (c) downward scan with a period of 20 ms, (d) downward scan with a period of 1 ms. The experimental observations are represented in black with the respective error bars, while the several components of the emission spectrum from CRM are represented in colors.

z-line emission. Nonetheless, in the lower electron density, the charge exchange with the residual gas is enough to compete with the ionization rate, leading to a different charge state balance. In this case, instead of a distribution dominated by He-like and H-like ions, there is a similar proportion between Li-like and H-like ions. This leads to differences in the overall intensity of the direct impact excitation emissions, leading to an overestimation in the case of the upward scan. The resonant features of the H-like charge state are also lost in these conditions, particularly the presence of the KLL and KLM DR structures around 470 and 570 eV, respectively. These characteristics demonstrate the 10^{10} cm^{-3} simulations as the best to represent experimental data for both charge state balance and metastable state population.

The final simulated emission spectra are displayed in Fig. 4.7 along with the experimental data (top of Fig. 4.4) scaled for emissivity. The comparison between spectra and predictions highlights that the metastable time dependence can explain the differences between upwards and downwards in both scans within the experimental uncertainty. In the subplot 4.7 (a), we can see the 20 ms upwards scan, where there is virtually no z-line

emission in the lower end energy range of the spectrum after the 3S_1 collisional threshold. On the other hand the subplot 4.7 (c) shows the 20 ms scan in the downward direction, where an exponential decay of the 3S_1 population is evident when the energy crosses below the excitation threshold. After the 3S_1 energy threshold, there are additional decay channels linked to the excitation thresholds of He-like ions from $1s^2$ to $1sn\ell$ with $n > 2$, where the cascades contribute to the production of the metastable population. As for the case of 1 ms scan in subplots 4.7 (b) and (d), these effects are present, however, they are more spread over the spectra leading to the z-line forming an almost linear baseline. The CRM was able to reproduce the baseline for both experimental conditions reliably and fully predict all of the different emission features present in the experimental results.

4.1.4 Cross-section data

To extract the cross-sections of the collisional data, it is important to understand how it relates with what was measured in the experiments. The emissivity (defined as photon count rate) of an initial-state population N_i while radiatively decaying to a final state f is given by

$$I_{if}(E_e) = N_i A_{if}^r, \quad (4.4)$$

with the initial state i being populated by the various atomic processes. If all populations decay by allowed radiative or Auger transition, they quickly reach local equilibrium ($\frac{dN_j}{dt} = 0$). In such case, and not considering CX, the emissivity is approximately given by

$$I_{if}(E_e) \approx n_e v_e N_0 \left(\sigma_{0i} + \sum_k \sigma_{0k} B_{ki} \right), \quad (4.5)$$

where N_0 is the ground state population and B_{ki} is the total branching ratio probability of a state k reach the state i after all cascades. The direct link between emissivity and cross-sections in Eq. (4.5) has been often assumed in EBIT measurements of cross-sections and resonate strengths, e.g [141, 172]. In the present case with a metastable state, extraction of cross-sections requires a careful analysis of the emissivity generally defined in Eq. (4.4). Nonetheless, as the 3S_1 state is the only metastable state, the rest of the emissions follow the latter approximation, being proportional to the collisional process that populates the excited state, e.g. dielectronic recombination, direct impact excitation and resonant excitation.

After the z-baselines of the entire spectra were modeled, the 1 ms scan was chosen for further analysis. This case was chosen because of the small baseline variations with the electron beam energy. The baseline estimated by the CRM was subtracted from the experimental data, which gives a spectrum free of the z-line. As expected, both upward and downward spectra yielded the same results after the subtraction. After this subtraction both downward and upward counts were added to improve statistics. Furthermore, the emissivity is proportional to cross-sections times electron velocity, following equation

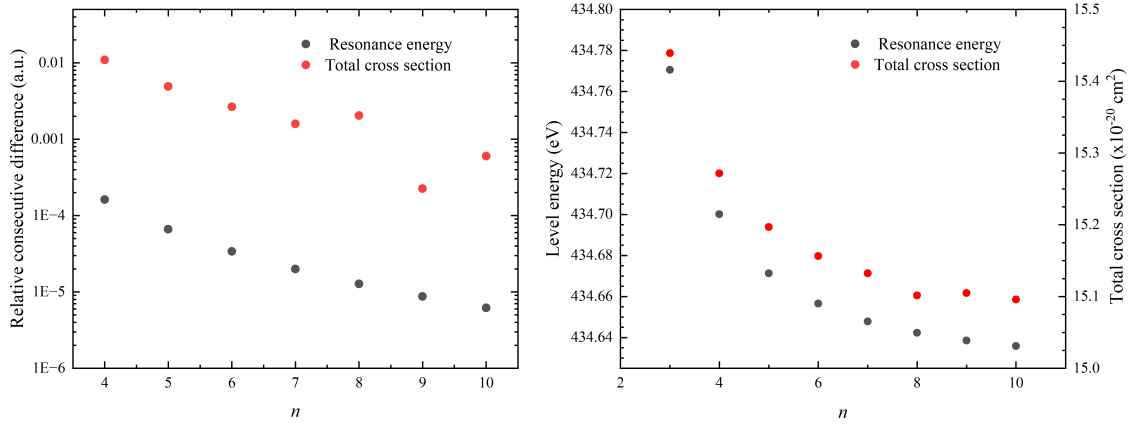


Figure 4.8: Convergence of the FAC calculations of the DR KLL structure. Both plots represent the resonance energy and the resonant strength of the most intense resonance of DR KLL as a function of the maximum allowed principal quantum number n in the configurations included in the calculation. Left plot represents the consecutive differences between increments of n , right plot represents the absolute values.

(4.5). Therefore the summed counts were divided by $\sqrt{E_e}$ (where E_e is the electron energy), resulting in a quantity $I_{\text{exp}}(E_e)$ to be calibrated to cross-sections by a factor.

The experimental spectrum has been normalized with the DR-KLL resonant strength of He-like oxygen calculated with FAC. Following previous works [141, 167], this choice was based on using the DR channel with the simplest atomic structure. As the experimental data is being calibrated with theoretical calculations, the accuracy of the final cross-sections is limited by this theoretical accuracy. Thus, it is important to estimate the uncertainty of the calculation itself. The FAC DR calculations were made within the isolated resonance approximation. This approximation relies on the values of the resonance energy and the Auger and radiative rates from the doubly excited level. Although the cross-section calibration relied on the KLL structure, where the doubly excited state has a maximum principal quantum number of $n = 2$, the increase of the principal quantum number n enlarges the configuration space included in the configuration interaction calculation, thus improving the accuracy of the energies and decay rates of the KLL structure. Figure 4.8 (left) shows the convergence of the energy of the most intense resonance of this structure with the maximum allowed principal quantum number n in the structure calculations. A final variation lower than 0.001% was achieved for $n = 10$. The convergence of the total cross-section of the KLL structure is also represented, with the few final variations being lower than 0.1%. The variation between the values obtained with a lower and higher number of configurations included in the atomic structure was considered as the uncertainty of the DR structure cross-section calculation.

To estimate the total error of cross-sections, the following processes were considered:

1. The square root of the number of counts was taken as the statistical uncertainty for each energy bin of the experimental histogram.

Table 4.2: Discriminated uncertainty budget of cross-section applied to two distinct electron beam energies (580 eV and 620 eV). Cross-sections for those energies with respective uncertainties are also listed.

	Contribution	580 eV	620 eV
1	Statistic	0.6 %	0.6 %
2	ROI	3.0 %	2.7 %
3	Detector filter	3.0 %	3.0 %
4	FAC DR	3.9 %	3.9 %
5	DR fit	0.5 %	0.5 %
6	H-like DR removal	2.4 %	1.0 %
	Total	6.3 %	5.7 %
	Cross-section ($\times 10^{-20} \text{ cm}^2$)	5.7 ± 0.4	4.8 ± 0.3

2. A large region of interest (ROI) of 420 to 720 eV of photon energy was used to account for all emissions, regardless of the slightly different transition centroids. To estimate the uncertainty associated with the limits of the ROI area, we considered the percentage difference of intensities given by choosing different ROIs centered just on $K\alpha$ transitions or including the rest of the transitions at higher photon energies within the chosen ROI, namely $K\beta$ and $K\gamma$ around 665 eV and 695 eV, respectively.
3. The SDD detector has a 1 μm carbon foil filter to block UV emission from the trapped ions. The detector efficiency depends on the X-ray transition profile of this foil, which becomes important for a large ROI. Following a previous work [141], the counts were corrected with photon efficiency¹ before the counts summation over the electron beam energy axis. This correction was also taken into account in the total error budget.
4. The resulting total counts plot was calibrated into units of cross-sections using the DR KLL structure calculated from FAC calculations.
5. On the experimental side, we also considered the statistical error associated with the fit of the DR structure.
6. Residual DR contributions of H-like oxygen were also removed from spectra by subtracting experimental cross-sections of [173]. The uncertainty of this procedure comes from the uncertainty given by the authors.

An explicit example of the estimation of the spectrum uncertainty for two individual electron beam energies is presented in Table 4.2.

¹https://henke.lbl.gov/optical_constants/filter2.html

Anisotropic angular emission distribution for the present observation at 90° was also corrected following the procedure from a previous work [141]. Direct measurement of angular distribution [88, 175] showed overall good agreement with FAC predictions. For the present case, we consider also FAC calculations of polarization (FAC-*pol*) for correcting the angular anisotropy. The cross-section spectra were derived from the experimental data $I_{\text{exp}}(E_e)$ by calibrating with

$$\sigma_{\text{exp}}(E_e) = \frac{S_{\text{KLL}}^{\text{theo}}}{A_{\text{KLL}}^{\text{exp}}} \frac{I_{\text{exp}}(E_e)}{P^{90}(E_e)}, \quad (4.6)$$

where P^{90} is the polarization correction factor at an observation angle of 90° . Here, $A_{\text{KLL}}^{\text{exp}}$ is the integral of the experimental DR KLL structure, while S^{theo} represents the theoretical resonant strength of the DR KLL (integral of cross-section).

As observed in Fig. 4.7 (b) or (d), in the region between the CE thresholds of He-like (575 eV) and H-like (653 eV) oxygen, the final spectrum is only composed of the x , y and w lines fed by the resonant structure of RE and continuum CE. Additionally, as described in the next Section 4.1.5, many theoretical calculations have been done for energies in that region, however, no experimental benchmarks are available, either with absolute or relative measurements. Both these structures and the He-like DR structures were benchmarked in this work.

4.1.5 Theoretical context

Before presenting the resulting experimental cross-sections of this procedure, a state-of-the-art overview of the theoretical work is given, as well as a description of our FAC calculations concerning collisional excitation at the measured energy range. While there are no experimental works regarding the DR, CE and RE of He-like oxygen near the excitation threshold, there is a vast history of theoretical calculations regarding these processes, particularly the CE and RE, with improvements being made over the years by taking into account more details and using more sophisticated methods.

The first approach for calculating collisional cross-sections was based on Born approximation [176], which gives the Van Regemorter formula [177]. This approach provides reasonable predictions at collisional energies far from the excitation threshold. Historical calculations with this method are reviewed in Ref. [178]. On the other hand, distorted-wave (DW) and Coulomb–Born approximation approaches provide good predictions also near the excitation threshold [179–181]. Additionally, the resonance excitation (RE) structure can be added *ad-hoc* as a two-step process [182]. Calculations for He-like oxygen with DW approach were done in Ref. [183, 184] and with Coulomb–Born approximation in Ref. [182, 185]. General reaction theory of Feshbach [186] and close-coupling approaches, often implemented in R-matrix (RM) formalism [187, 188], provide a unified quantum treatment of CE+RE that includes interference between the resonance channels and continuum, i.e. Fano profiles. Calculations with close-coupling for He-like oxygen

VII were first done in Ref. [186] using an attached-excited-target approximation and later in Ref. [189–191] using RM with 6 target $n = 3$ autoionizing states. Later, calculations in Ref. [192] included relativistic fine structure with Breit–Pauli RM, radiation damping, and 26 target autoionizing states ($n \leq 4$). Furthermore, an intermediate-coupling frame transformation (ICFT) was implemented in Ref. [193, 194], which was used in Ref. [195, 196] and, more recently, in [197] to calculate excitation coefficient rates (cross-sections averaged over a Maxwellian) of the main lines of He-like oxygen. Finally, in Ref. [198] both coefficient rates and cross-sections were calculated and listed for electron energies at the collisional threshold using Dirac Atomic R-matrix Code (DARC) package with General Relativistic Atomic Structure Package (GRASP) [199]. Atomic databases contain coefficient rates from most of these references: XSTAR [200] and universal atomic DataBase (uaDB)² adopted recommended values of Refs. [182, 185, 201], while AtomDB, CHIANTI, and OPEN-ADAS³ contain RM calculations of [191–193, 195].

Theoretical cross-sections for DR, DE, and RE were calculated using FAC. FAC provides atomic radial wave functions and the respective eigenvalues from a configuration interaction method with orbitals obtained in a modified electron-electron central potential. This code also employs both the DW approximation to calculate cross-sections of atomic processes involving a free electron, like CI, DE, and RR, as well as R-Matrix approach.

In the case of the DW approximation, resonant processes like DR and RE are included apart in a two-step process. All our FAC calculations included configurations with excited states with a maximum principal number up to $n = 10$. We included CE for He-like oxygen from the ground and the metastable state to all the $1s\ nl$ and $2s\ nl$ configurations, and for the H-like ion we have included excitations from the ground state to all the nl configurations. Convergence for the energy levels and collisional strength was achieved for all the calculations within less than 0.05 %. The DR calculations for the He-like ion include the KLn structure. An equivalent procedure was also done for H-like oxygen. As for RE, we focused on the KNn structure. Although the isolated resonance approximation is valid for cases with a low density of resonances, more complicated regions present interference between resonances, which is not included in this simple approximation. As mentioned before, close-coupling methods take into account quantum interference effects. In this work, the R-matrix module of FAC was also used to calculate the relevant excitation cross-sections and collisional strengths. This module is a numerical implementation of the Dirac R-Matrix method, as in the DARC package, with the ability to use the standard configuration-interaction-based FAC atomic structure calculations (details in [202]).

Collisional excitation calculations made with the DW and RM frameworks sharing the same structure calculations as input were consistent within a few percent. In the present case, that was verified for the excitations from the ground state into the $n = 2$ triplet states. The same, however, cannot be said for the $^1S_0 \rightarrow ^1P_1$, where a significant difference was found between the two methods, regardless of the configurations included

²<https://heasarc.gsfc.nasa.gov/uadb/index.php>

³<https://open.adas.ac.uk/>

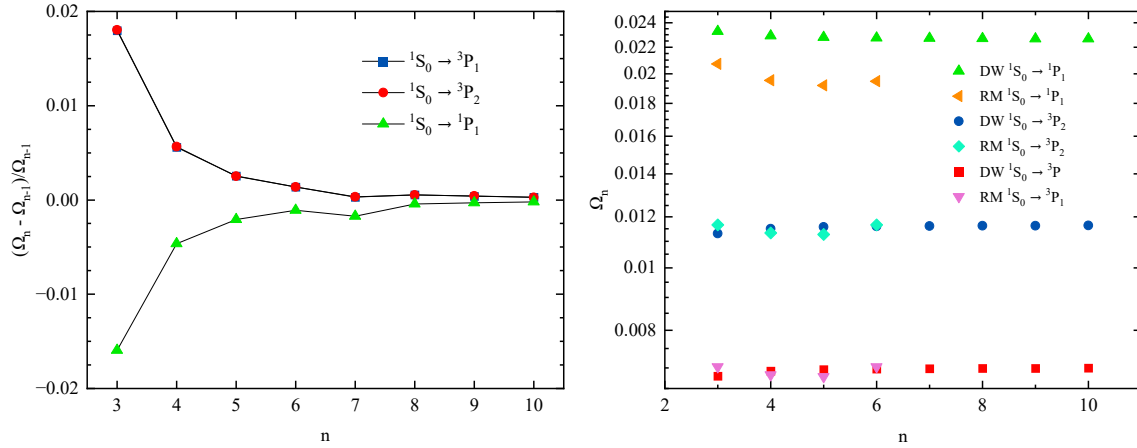


Figure 4.9: Convergence of the collision strength of the excitation of He-like oxygen into $n = 2$. Both plots represent the collision strength of the excitation of these energy levels as a function of the maximum allowed principal quantum number n used in the configurations included in the calculations. Left represents the consecutive differences with the increase of n , right represents the absolute values.

in the structure calculations. Figure 4.9 (right) shows the conversion between methods for the triplet states excitation, while the singlet state excitation consistently deviates by around 16% from each other. Comparing the numerical results with values from previous works with different methods, FAC-DW calculations seem to overestimate the respective collisional strength. Due to the computationally expensive nature of the RM method, it was only possible to perform the calculation with a maximum principal quantum number up to $n = 6$.

4.1.6 Results and Discussion

With the experimental data properly calibrated, and with the He-like DR contribution removed from the data, a direct comparison can be made with theoretical calculations. In Figure 4.10, one can see the result from removing the z-line contributions with the CRM calculations. This plot is dedicated to the dielectronic recombination region, where the DR structures converge into the excitation threshold of $n = 2$, between 560 and 575 eV. In the same plot, the DR FAC isolated resonance distorted wave calculations are also presented. These calculations have been convoluted with a Gaussian function with the respective energy spread of the electron beam. This allows a direct comparison of the theoretical cross-sections with the experimental data. A great agreement was found between the theoretical and experimental data, particularly in the first few resonant structures. These calculations seem to overestimate the recombination cross-section as the resonances converge into the excitation threshold. One explanation for this phenomena could be the fact that the isolated resonance framework does not take into account interference effects between resonances, leading to a small overestimation in regions where there is a big overlap between structures. Other possible cause could be small inaccuracies in the CRM

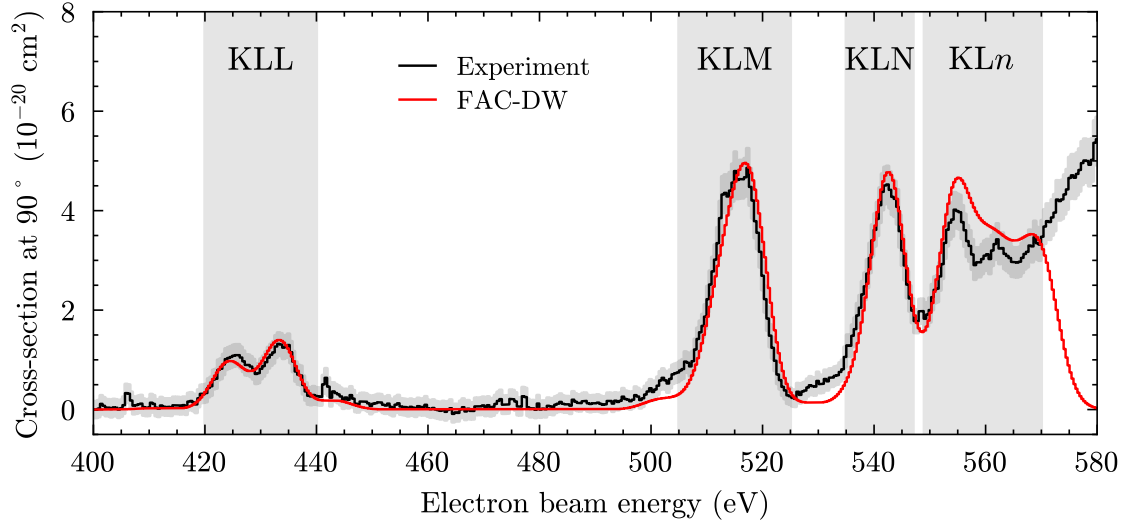


Figure 4.10: Experimental DR KL_n cross-section as a function of the electron beam energy. The main DR structures are highlighted. The red line represents the FAC calculations made within the isolated resonance framework, broadened with the experimental width.

that could be overestimating the presence of z-line emissions at higher energies. This hypothesis is unlikely, as a good agreement was found in the rest of the spectrum at even higher energies. The calculations themselves could also prove to be inaccurate for very high n recombinations. Unfortunately, there is no other DR measurements of this element in the literature to make a good assessment of the discrepancy.

To make a more quantitative comparison of the DR structures, the respective resonant strengths (integral of the cross-sections) of each structure were compared with FAC. Only the KLL and KLM structures are completely isolated, with the KLN structure partially overlapping with the next DR structure and the remaining structures overlapping with themselves and with the direct impact excitation structure. Nonetheless, four electron energy regions were considered to make the integrals. These regions are highlighted in Figure 4.10, with their results being presented in Table 4.3. The same integration procedure was applied to the FAC-DW convoluted calculations. As expected, the KLL, KLM and KLN structures are in agreement with the FAC values, while the rest of the DR structure is slightly below what is predicted by FAC. As part of the KLN and KL_n regions are overlapping, the regions of interest used for the integrations are representative only, meaning that the integrals are not representative of the full resonant strengths of these structures merely suitable for benchmark purposes.

Figure 4.11 (a) shows the excitation cross section near the threshold. In this Figure, the experimental results are compared with the most recently available calculations from Ref. [198]. In their work, the wavefunctions and respective eigenvalues were calculated using GRASP, while the cross-sections were calculated with DARC. The experimental results are also compared with new calculations made with FAC, both with the DW and R-matrix methods. Below, subplot 4.11 (b) shows the theoretical cross-sections not folded with the

Table 4.3: Experimental dielectronic recombination resonant strength of He-like oxygen for different structures in units of $10^{-20} \text{ cm}^2 \text{ eV}$. The experimental values are compared with the theoretical spectrum calculated with FAC-DW. The KLL region was used for the calibration.

Region	Energy Range (eV)	FAC-DW	Experiment
KLL	420-440	16.99	17.0 ± 0.6
KLM	505-525	50.10	50.5 ± 0.9
KLN	535-547	34.14	36.0 ± 0.7
KLn	549-570	73.45	64.6 ± 0.9

experimental width. All the different calculations are in reasonable agreement with the experiment.

While the R-Matrix calculations have the advantage of containing the interference between resonances, they are very computationally intensive and can only include a small number of correlation states. On the other hand, the distorted wave approach is much more efficient, and although it does not account for the interference between resonances, a large number of intermediate energy levels can be included to make a more complete description of the resonant excitation structure. Since all our calculations depend on the same atomic structure package, our theoretical resonances align well with the experimental results, while the Aggarwal calculations have a slight offset. Concerning the baseline (e.g. at 580 eV), the results of the FAC-DW method tend to overestimate predictions, while previous calculations in Ref. [198] seem to slightly underestimate it.

This analysis is quantified in Table 4.4, which compiles the comparison between several calculations of collisional excitation and measurement for two energies outside RE (resonant) region. We observed a tendency for all the FAC calculations to slightly overestimate the collisional excitation values relative to the remaining calculations, which might be partially explained by the precision achievable with the configuration interaction method employed in structure calculations. Moreover, the FAC-DW calculation for the w -line appears to be overestimated, even though it shares similar electron structure calculations as the FAC-RM counterpart. Moreover, the work by Aggarwal also included calculations from FAC that showed that, for our particular energy levels of interest, the latter values were in better agreement with data from NIST than the calculations performed with GRASP. Comparing the FAC calculations within themselves, the DW presents an overestimation of the experimental data compared to the RM calculation. This can be traced to the excitation of $^1S_0 \rightarrow ^1P_1$ feeding the w -line, as can be seen in Table 4.4.

As for a quantitative comparison of the RE part, we present the experimental integrated cross-sections evaluated between 575 and 650 eV in Table 4.5. The RE and CE parts of the theoretical and experimental values were isolated by considering that the CE part is constant over the electron energy range, as in DW method. Although this method does

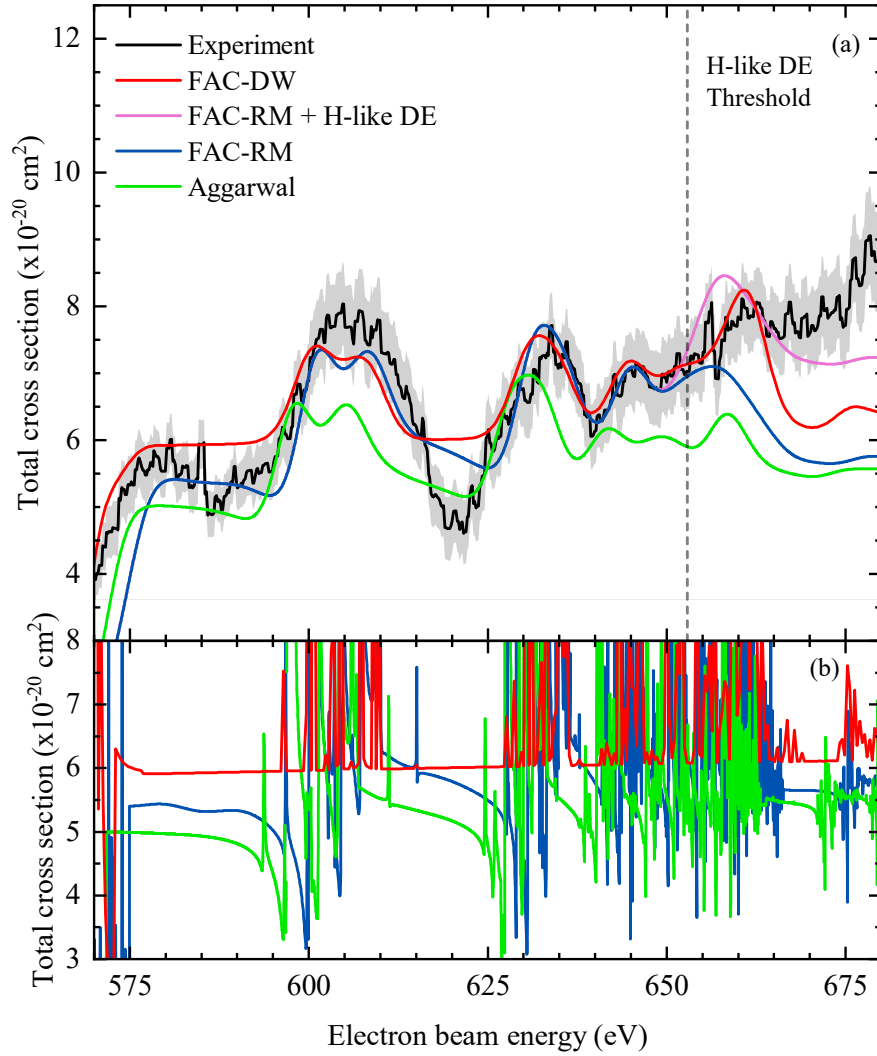


Figure 4.11: Experimental $x + y + w$ cross-sections as a function of the electron beam energy. (a) Experimental results in black taken from the 1 ms scan, after the z-line subtraction, are compared with calculations. The theoretical calculations were convoluted with a Gaussian function of electron-beam FWHM. (b) corresponds to the unconvoluted theoretical cross-sections from Ref. [198], FAC DW, and FAC R-matrix, respectively.

Table 4.4: Theoretical and experimental cross-sections $\sigma(\times 10^{-20} \text{ cm}^2)$ for the formation of the x , y , and w -lines by collisional excitation from the ground state. Collisional energies of 580 eV and 620 eV away from resonances are considered to compare the CE baseline.

	580 eV				620 eV			
	x	y	w	total theo.	x	y	w	total theo.
DW								
Badnell <i>et al</i> [184]			3.886				4.183	
FAC-DW	1.221	0.009	4.609	5.839	1.039	0.008	4.920	5.967
R-Matrix								
Tayal <i>et al</i> [191]			3.775				4.216	
Delahaye <i>et al</i> [192]	1.165	0.009	3.869	5.042	1.013	0.007	4.256	5.276
Aggarwal <i>et al</i> [198]	1.131	0.008	3.818	4.958	0.963	0.007	4.190	5.160
FAC-RM	1.211	0.009	3.969	5.189	1.011	0.007	4.337	5.356
Measurem.	5.7 ± 0.4				4.8 ± 0.3			

Table 4.5: Experimental integrated cross-sections ($\times 10^{-20} \text{cm}^2 \text{eV}$) of the lines $x + y + w$ between 575 eV and 650 eV compared with theoretical calculations made with FAC-DW and FAC R-matrix, as well as in Ref. [198]. Values in parentheses address the relative difference to the edge of the experimental uncertainty.

	FAC-DW	FAC R-matrix	Aggarwal <i>et al</i> [198]	Experiment
DE	441.4	403.7	375.9 (-1%)	420 ± 40
RE	45.5 (-9%)	62.2 (11%)	53.5	53 ± 3
Total	486.8	465.9	429.4 (-0.2%)	470 ± 40

not consider Fano-like profiles that contain the interference between the resonant and continuum part, it still provides a quantity related to the resonant contribution that can be objectively compared among all experimental and theoretical sources. Despite the CE values of [198] being slightly underestimated, the respective resonant contribution is in excellent agreement with the measurements. Concerning the total integrated cross-sections, all calculations are in agreement with measurements. In this regard, the FAC-DW calculation deviates the most. This might be expected since it uses the two-step approximation and does not account for quantum interference between channels. The FAC-RM calculations predict interference features but still show noticeable differences elsewhere. Overall, the FAC-RM calculation describes best the observations and has a good balance between the resonant and non-resonant accuracy of the calculation.

4.2 H-like oxygen DR emission reduction

The He-like oxygen experiment described in the last Section also yielded DR resonances from H-like oxygen. While these resonances have been measured with high accuracy before [173], and this measurement has in fact been used in the last Section to remove the H-like DR contribution from the He-like spectra, a dynamical effect was actually found regarding the DR of H-like ions that warrants a Section on its own. Due to the long life of the first excited state of the He-like ion, part of the cascades that are generated by dielectronic recombination of H-like ions end up at the He-like metastable level. As seen in the previous Section, this can lead to dynamical effects that are highly dependent on the measurement schemes. If a scan is too fast, the z-line emission has a delayed response to the recombination stimuli, diluting it into the background, when the electron beam is probing the recombination resonance. This can lead to an apparent reduction of the H-like DR resonances, depending on the speed of the energy scan and the branching ratios of the respective resonances. In this Section, this effect will be explored with the observed resonances in each of the measurement schemes, as well as constructing a simple theoretical model capable of predicting this suppression effect.

It is worth noting that the term *DR suppression* is usually associated with an already known type of suppression in DR also with metastable resonances. First suggested by [203], the effective DR cross-sections can be suppressed in high density conditions, where the radiative stabilization of recombined highly excited ions competes with electron impact ionization, thus reducing the branching ratio after dielectronic recombination. To accurately model this process, a complete collisional radiative model is required, which was first implemented by [204]. Later, an empirical formula to estimate the overall impact of DR suppression due to density effects was introduced and developed by [205, 206]. The electron density in the EBIT trap is not high enough for this effect to take place, thus it was not generally considered in this work. Moreover, this effect alters the effective recombination cross-section, as a portion of the branching ratio corresponds to an ionization back to the original charge state. In this work, the reduction effect is not related to the recombination cross-section, but rather in the observation of the emissions after the recombination process.

4.2.1 Theoretical Calculations

For H-like oxygen, only the KLL DR structure is isolated. This structure is located between 460 and 480 eV, and is present across all four observations. In this structure, one can observe six main resonances, given by the combination of angular couplings of the configurations $2s^2$, $2s2p$ and $2p^2$. The two more expressive resonances, which are the subject of this study, correspond to the intermediate states $2s2p\ ^3P$ and $2p^2\ ^1D$. Given our experimental energy resolution, only these two main peaks are resolved. A simple level diagram of this process is represented in Figure 4.12. After the dielectronic capture into the doubly

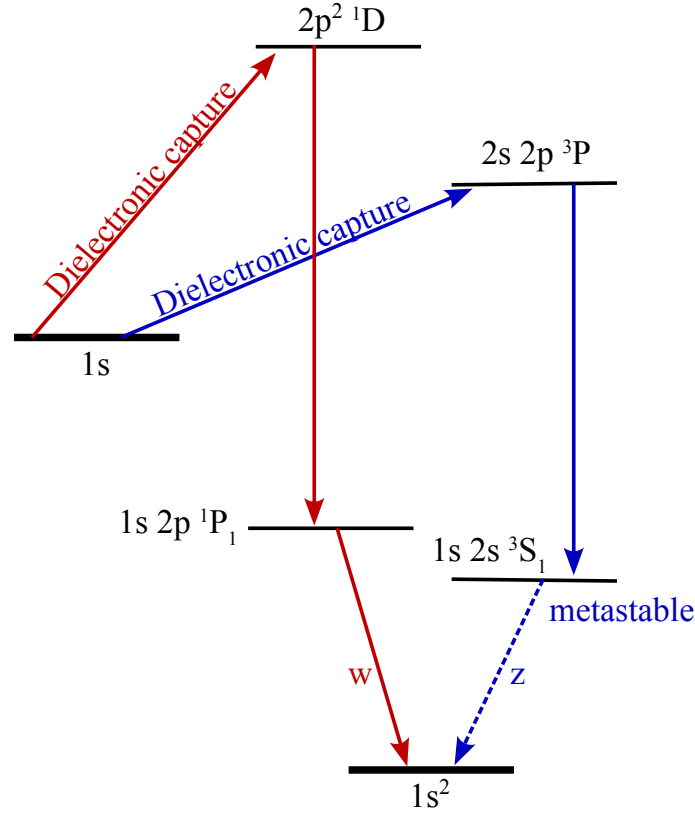


Figure 4.12: Energy level scheme of the main DR KLL resonances of H-like ions. The red and blue lines represent the pathways that decay trough the w and the z -line emissions.

excited $2p^2 \ ^1D$ state, most of the population decays into the $1s2p \ ^1P_1$ state. This state, in turn, can only decay into the ground state via the w -line. Moreover, the population of the $2s2p \ ^3P$ state after dielectronic capture decays mostly to the $1s2s \ ^3S_1$, further decaying to the ground state through the z -line. The transitions between the doubly excited and the singly excited states have photon energies around 650 eV, while the $K\alpha$ complex produces photon energies around 550 eV. Given the poor resolution of the SDD, these two line complexes cannot be resolved, and thus are present together when making a projection along the photon energy axis. In the first DR resonance ($2p^2 \ ^1D$), one recombined ion produces two sequential photons, while in the second case ($2s2p \ ^3P$), the observation of the second photon during the energy scan depends on the speed of the scan. This makes the second line sensitive to the scan speed, while the other main line is insensitive to this experimental parameter.

Following the same procedure as before, the DR structure was calculated within the isolated resonance framework. The level energies, autoionization rates and radiative rates were calculated using the FAC and MCDFGME. To complement the theoretical calculations, the FAC-MBPT module was used to refine the energy levels. For this process, we included virtual levels with configurations of singly excited electrons up to $n = 10$. The previous measurement made at the TSR [173] is presented in Fig. 4.13, along with the calculations made with FAC, FAC-MBPT and MCDF.

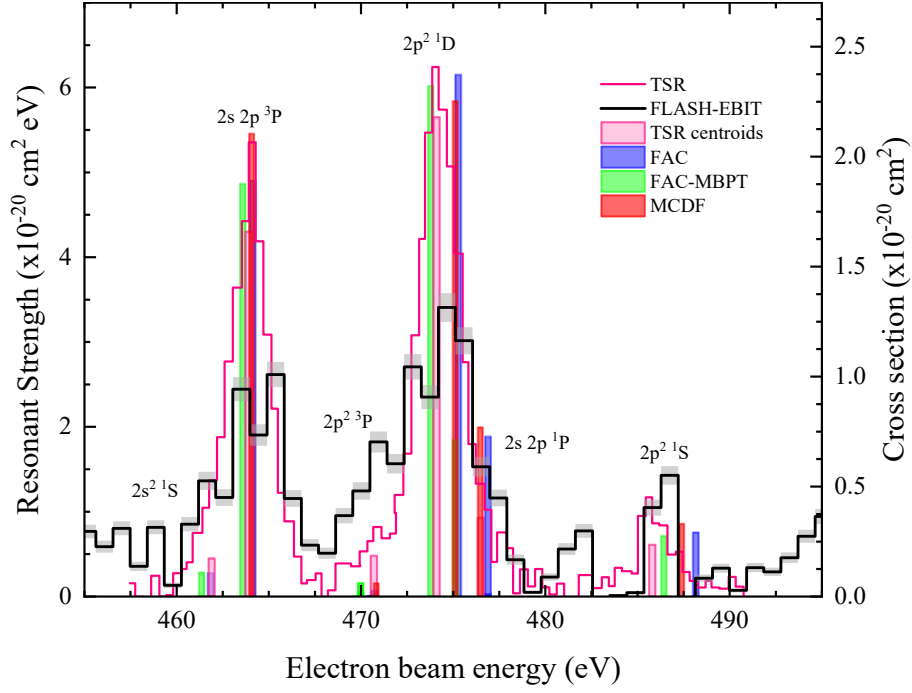


Figure 4.13: DR measurements made with the TSR and the FLASH-EBIT, compared with theoretical calculations made with FAC (blue) and FAC-MBPT (green) and MCDF (red) and the TSR fit centroids (pink).

As observed in Fig. 4.13, while for the first two resonances ($2s^2$ and $2s2p$) both FAC and FAC-MBPT agree with observations, more accurate energy values are attained with the FAC-MBPT correction for the rest of the resonances. A numerical comparison of the resonance energies between the theoretical calculations and the experimental values is presented in Table 4.6.

Table 4.6: Experimental values of the resonance energies taken from [173], compared with the theoretical values obtained with FAC and FAC-MBPT. The configurations presented refer to the intermediate doubly excited state after recombination.

Configuration	E_{TSR}	E_{FAC}	$E_{\text{FAC-MBPT}}$
$2s^2 \ ^1S$	461.9 ± 0.9	461.84	461.35
$2s \ 2p \ ^3P$	463.9 ± 0.1	464.12	463.35
$2p^2 \ ^3P$	470.7 ± 0.4	470.72	469.98
$2p^2 \ ^1D$	474.1 ± 0.1	475.28	473.78
$2s \ 2p \ ^1P$	476.5 ± 0.1	476.89	475.12
$2p^2 \ ^1S$	485.8 ± 0.1	488.16	486.43

4.2.2 Dynamics simulation

Since the energies of DR are below the collisional excitation, the emission of the z-line (from the metastable state) will follow an exponential decay pattern with time. If the electron-energy sweep is towards higher energies, the decay photon is time-delayed and, therefore, detected at higher energies. Likewise, downwards energy scans will produce a resonance with a delayed response at a lower electron beam energies. Although such effect can be modeled with the CRM model, we chose a method that any EBIT user can use for similar experiments without prior access to other CRM calculations. This phenomenon can be simulated by convoluting the DR instrumental steady-state Gaussian profile with the population's exponential decay in electron energy units, according to

$$I^z(E_e) = \int_{-\infty}^{\infty} G(E)P(E - E_e)dE + \int_{-\infty}^{\infty} G(E)P(E_e - E)dE, \quad (4.7)$$

with $G(E_e)$ being the steady-state DR Gaussian profile,

$$G(E_e) = \frac{S}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E_e - E_r)^2}{2\sigma^2}\right), \quad (4.8)$$

and $P(E_e)$ being the exponential decay pattern after DC populating the metastable state at energy E_e , given by

$$P(E - E_e) = \begin{cases} 0 & , E - E_e < 0 \\ \exp\left(-\frac{(E - E_e)T}{1400\tau}\right) & , E - E_e \geq 0 \end{cases} \quad (4.9)$$

Here E_e is the electron beam energy, σ is the experimental instrumentation (electron-beam energy dispersion), E_r is the resonance energy, S is the DR resonant strength, T is the scan period, and τ is the metastable state lifetime. The first and second terms in Eq. (4.7) correspond to the upwards and downwards scan, respectively. An illustration of the DR steady-state resonance and the evaluation of Eq. (4.7) are represented in Fig. 4.14, as well as the individual contributions from each scan directions and the respective exponential decays. Each scan direction produces an off-resonance Gaussian which, when summed, present themselves as an on-resonance, wider peak. The factor $(E - E_e)T/1400$ represents the time that has passed at a certain electron beam energy after passing through the resonance energy. As each energy scan is made between 300 and 1000 eV, a total of 1400 eV is scanned in one period, with the scan speed being defined by $1400/T$ eV s⁻¹. To compare with the experimental results, the z-line emission was simulated for a wide range of scanning periods. In this simulation, the ratio of the two peaks was taken as the main result, as this is adimensional and directly comparable with the experimental data. The simulation yields a smooth curve that ranges from a steady-state DR observation, at very long scanning periods, to a completely suppressed z-line observations at very fast energy scans.

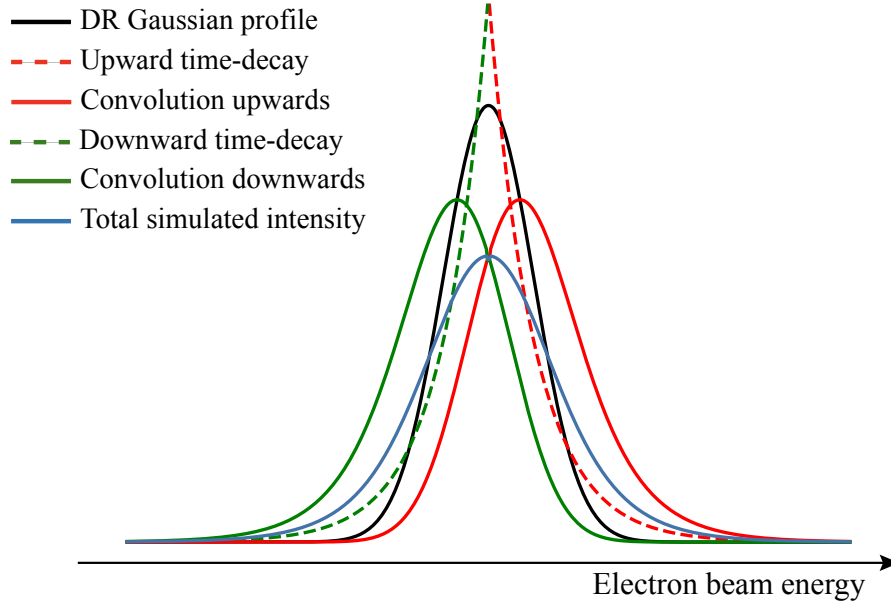


Figure 4.14: Illustration of the method used to model the experimental data. The blue line represents the DC cross-section and in orange is the convolution of the cross-section with the population exponential decay.

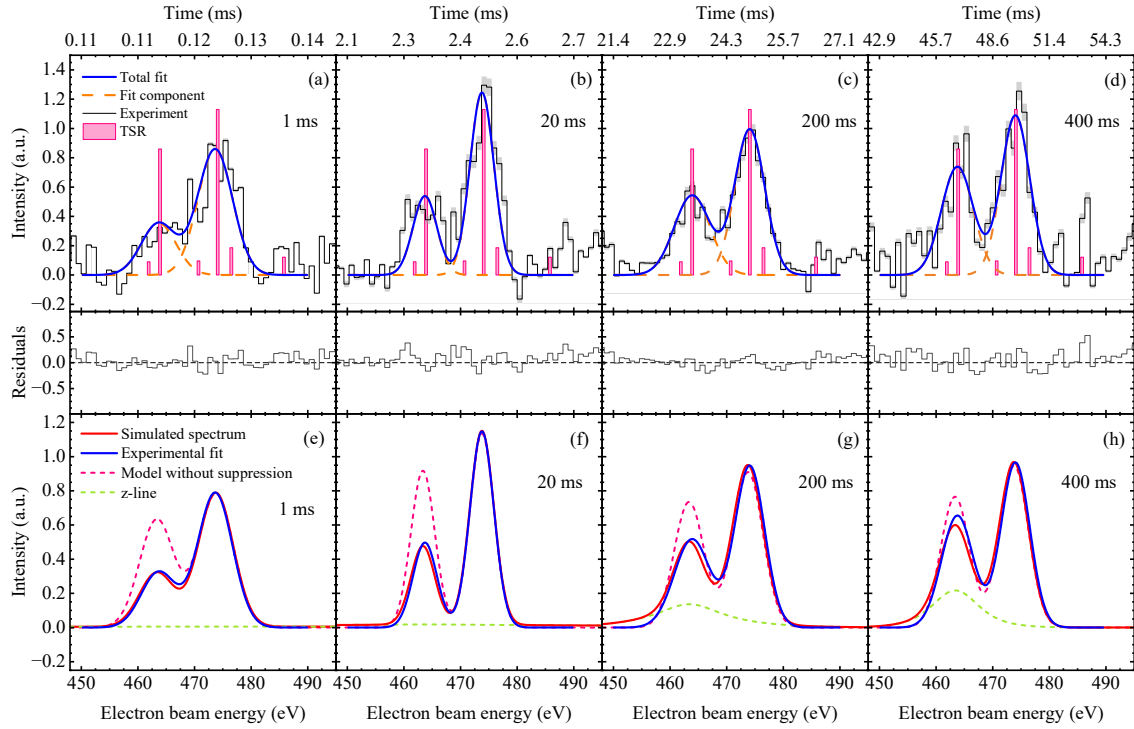


Figure 4.15: Top: Experimental results for the different periods of 1, 20, 200, and 400 ms (black line). The blue line represents the fit. Bottom: Simulation results for the experimental conditions. The pink dashed line represents the two peaks without any DR reduction, the green line represents the simulated z-line contribution to the peaks and the red line is the total simulated peak emission.

4.2.3 Results and Discussion

The DR KLL structure of H-like oxygen was observed across all the experiments. These observations are presented in Figure 4.15 (top). The measurements were fitted with a linear combination of standard Gaussian profiles, represented in Figure 4.15 by the blue lines. For all experiments, the experimental data was fitted with just two Gaussians to account for the two main peaks of the KLL structure. While the previous work with TSR [173] presented a 6-Gaussian fit (used in Table 4.6 for the resonance energy comparison), our experiments yielded a lower free electron energy resolution, thus resulting in a blend of the main peaks with the other small DR features.

The experimental data presented in Fig. 4.15 has been normalized to the theoretical resonant strength of the second peak. In Fig. 4.15 (top), clearly different intensities are observed in the first main peak. The longer energy scans yield a more intense peak than the shorter ones. As mentioned previously, this is due to the fact that part of the cascade after DC in the first peak goes through the $1s2s\ ^3S_1$ metastable state, which has a long lifetime. As the scan gets faster, the electron beam energy spends less time inside the resonance, giving the metastable state increasingly less time to decay within the resonance, contributing mainly to the broadening of the observed peak or increasing the background, depending on the scan period.

The simulation results for the different experimental conditions are shown at the bottom of Figure 4.15. Here the simulated emissions are defined by the regular DR cross-section, but the z-line contribution to the cascade of the first peak is calculated with the convolution method represented by equation 4.7. The green dashed lines represent the contribution to the overall emission profile, while the pink dashed line represents the total emission if there were no effects from the metastable population. At the slower 400 ms scan, we can already observe a broadening of the z-line peak. In the 200 ms scan, the shape of these emissions is large enough to not only decrease the first peak intensity but also slightly enhance the second one. In the cases of 20 and 1 ms, the scan is fast enough for the z-line to effectively contribute to the peaks, leading to an overall increase in the background.

While the EBIT data is obtained by observing photons after exciting the ions with an electron beam, the TSR data was obtained in a storage ring by observing the ion current of ions that change their charge state. Therefore, the long-lived metastable state and the respective slow decay are irrelevant for the observations at the TSR. For this reason, this data can be compared directly with the resonance strength calculations made with FAC and is comparable with an EBIT experiment with longer cycle periods (apart from the polarization factor).

The ratio between peaks obtained from the fits is graphically represented in Figure 4.16. Here we also represent the model described by Eq. (4.7) using a variable value of standard deviation for the Gaussian width, ranging from $\sigma = 4.2$ eV to $\sigma = 6.1$ eV (values obtained from the experimental fits) and a lifetime of $\tau = 0.956$ ms. The blue and

red regions represent the ratio calculated without and with the polarization correction, respectively. The grey region represents the ratio obtained with the TSR data within the respective uncertainty. As expected, the TSR data envelops the value that is expected from an experiment with the scanning period at infinity, which corresponds to the simple ratio S_2/S_1 . As the scan period diminishes, the ratios observed at the EBIT data increase due to the decrease of A_1 . At a period of 1 ms, a value very close to $A_2/(0.5 \times A_1)$ is achieved, corresponding to the case where no z-line is observed within the resonance. The values between the two limits appear to be consistent with the theoretical model. Furthermore, while the simulation itself is enough to fully describe the tendency observed in the experimental data, the polarization correction is needed to obtain correct absolute values for the peak intensity ratio.

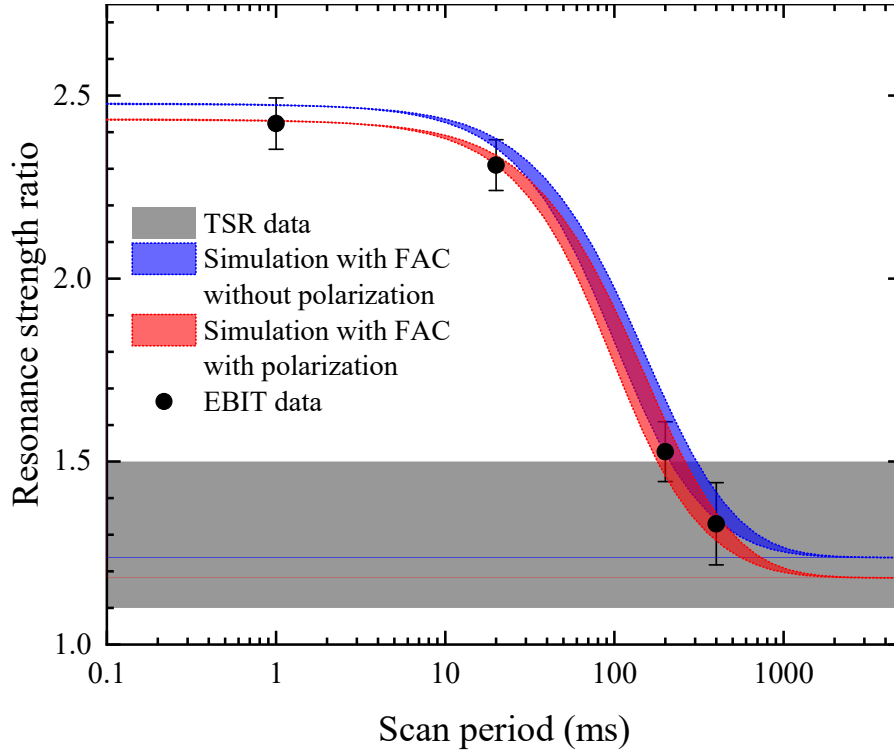


Figure 4.16: Ratio between the two main peaks of DR KLL as a function of the energy scan period. The experimental EBIT data is represented by the dots, while the TSR data is represented by the grey region. The red and blue regions represent the simulations evaluated with the peaks width ranging between the minimum and maximum experimental values with and without the polarization correction, respectively.

All the experimental and theoretical resonance strengths and respective ratios have been compiled in Table 4.7. In the theoretical portion of the Table (bottom part), we included the FAC-MBPT resonance strength for the two resonances (S_1 and S_2) and the respective ratio, as well as the same values discounting the z-line from the subsequent cascades. We also included the resonant strengths of the main peaks mixed with the low-intensity peaks in the vicinity and corrected by the polarization factors (S_1' and S_2'). These values should better represent the EBIT picture, as the electron beam energy resolution is

4.2. H-LIKE OXYGEN DR EMISSION REDUCTION

Table 4.7: Results from the fits applied to the experimental data, including the ratio between the two peaks, as well as a comparison with theoretical ratio. For the TSR, we included numerical data from [173]. A_1 and A_2 represent the area of the Gaussians fitted to the two main peaks. S_1 and S_2 are the theoretical resonance strength ($\times 10^{-20} \text{cm}^2 \text{eV}$) for the two peaks, while the apostrophe denotes the summation of the former with neighboring low intensity resonances and include a polarization factor to directly compare with the lower resolution EBIT data.

	Period (ms)	A_1	A_2	Ratio
TSR		4.3 ± 0.6	5.7 ± 0.9	1.3 ± 0.2
FLASH	400	5.2 ± 0.4	6.9 ± 0.4	1.3 ± 0.1
	200	4.3 ± 0.2	6.6 ± 0.2	1.53 ± 0.08
	20	2.9 ± 0.3	6.6 ± 0.4	2.31 ± 0.07
	1	2.7 ± 0.3	6.6 ± 0.4	2.42 ± 0.07
		S_1	S_2	
FAC		4.87	6.02	1.26
FAC w/o z-line		2.43	6.02	2.47
MCDF		5.46	5.84	1.07
MCDF w/o z-line		2.73	5.84	2.14
		S'_1	S'_2	
FAC		5.59	6.60	1.18
FAC w/o z-line		2.71	6.60	2.43
MCDF		5.95	6.51	1.09
MCDF w/o z-line		2.38	6.51	2.38

not sufficient to individually observe just the two main resonances.

4.3 Calcium

As seen before, calcium is an element with potential to be used in X-ray astrophysics due to its He-like $K\alpha$ line complex being around 3.9 keV. Being closer to iron in terms of mass, it is present in many astrophysical observations, and can potentially be used as an iron alternative when there is a lack of lines from these elements. Yet, there are no good experimental benchmarks of energy lines of HCI of this element, particularly for the DR satellites and excitation cross-section structure near the collision threshold. Similar to the oxygen case, the FLASH-EBIT was used to produce the emissions of calcium when probed with an electron beam. This Section will explore the experimental setup used for the observations of the transition energies and cross-sections.

4.3.1 Experimental setup

A compound of Ca(TMHD)_2 (calcium Bis(2,2,6,6-tetramethyl-3,5-heptanedionate)), in the form of a solid sample, was inserted in the differential pumping injection system of the EBIT. As the vapor pressure of the compound is very low, sublimation of the compound was helped by heating the injection system with an electric resistor. To maintain an homogeneous heating across the injection system, and therefore avoid condensation problems preventing the compound vapor from flowing into the trap, the injection pathway was thermally isolated with fiberglass wool and covered with aluminum foil. A temperature probe was left near the sample to control and maintain the temperature. A signal of calcium emissions at 3.9 keV started being observed when the temperatures reached 80° C, with an optimal count rate around 90 °C. This temperature was maintained through all the experiments. After injection, the molecules were then dissociated by the electron beam, which also ionized and trapped the calcium atoms.

Similar to the oxygen experiments, the electron beam energy scheme followed a triangular wave with an acceleration potential between 2500 eV and 4700 eV. The ionization energies of the calcium charge states between C-like and H-like are presented in Table 4.8. As the ionization threshold of Li-like calcium is around 1158 eV, it is expected that most of the population of calcium, if the trapping is good enough, being in the He-like charge state. Furthermore, as the ionization threshold of He-like calcium is around 5129 eV, a value well above the higher energy of the scanning range, no H-like calcium is present in the trap.

The injection of calcium into the trap with the chosen method was not efficient, leading to a trap filled with contamination that prevented high count rates from calcium emissions. As such, no breeding period was considered to ensure all of the duty-cycle is dedicated to probe the ions. The photon emission from the electron-ion system was recorded using an SDD placed at 90° relative to the electron beam axis, with photon resolution of around 140 eV of FWHM at 3800 eV. The photon detection was also discriminated according to the electron beam energy, allowing the production of two-dimensional spectra of photon

Table 4.8: Ionization energies of each charge state of calcium, as well as the respective ground electronic configurations, from calcium XV to calcium XX. Values taken from the NIST ASD.

Ion species	Charge	Ground configuration	Ionization energy (eV)
Ca XV	14+	$1s^2 2s^2 2p^2 \ ^3P_0$	894.0
Ca XVI	15+	$1s^2 2s^2 2p \ ^2P_{1/2}$	973.7
Ca XVII	16+	$1s^2 2s^2 \ ^1S_0$	1086.8
Ca XVIII	17+	$1s^2 2s \ ^2S_{1/2}$	1157.7
Ca XIX	18+	$1s^2 \ ^1S_0$	5128.9
Ca XX	19+	$1s \ ^2S_{1/2}$	5469.9

intensity with photon and electron beam energy.

At the energy range used in the scans, the entire DR KLn structure of He-like calcium was recorded, as well as the CE and RE structures near the excitation threshold. Scans were made with different ramping speeds with different purposes. A very slow energy scan was made with a period of 500 s, while a faster energy scan was performed with a period of 30 ms. The slower scans obtain charge-state dynamics conversion of He-like into Li-like due to DR depletion [167], thus not being suitable to extract experimental cross-section. Nonetheless, it provided an excellent electron beam energy resolution, making this scan ideal for providing accurate resonant energies for the DR satellites. The faster energy scan reduced the electron beam energy resolution but provided symmetrical measurements for both upward and downward scans, confirming the absence of charge state dynamics. This measurement was used to benchmark theoretical cross-sections for DR, CE and RE.

The SDD spectrum was calibrated by fitting very well known soft X-ray lines of neon and argon for a wide range of energies. For this, neon was injected in the EBIT, where the $K\alpha$ line of the He-like charge state was observed. Argon was also separately injected, and the He-like $K\alpha$ and $K\beta$ were included in the calibration. Finally, lines from oxygen impurities are commonly observed, and the $Ly\alpha$ of oxygen was also considered.

4.3.2 Contaminations

At the scanned energies, the entire DR KLn series of He-like ions was observed, as well as the DR KLL structure of Li-like (illustrated in Figure 4.21). The presence of Li-like ions alludes for the low trapping efficiency of calcium. The experimental conditions produced a calcium charge state balance or around 80 % of He-like, while the remaining population is dominated by Li-like ions.

All the calcium experiments yielded results with emissions from a wide variety of elements that were not the focus of the study. An example for the emissions spectrum of one of the slow scan measurements is presented in Figure 4.17 (a). All the contamination emissions were observed regardless of the energy scan period. At the very low photon

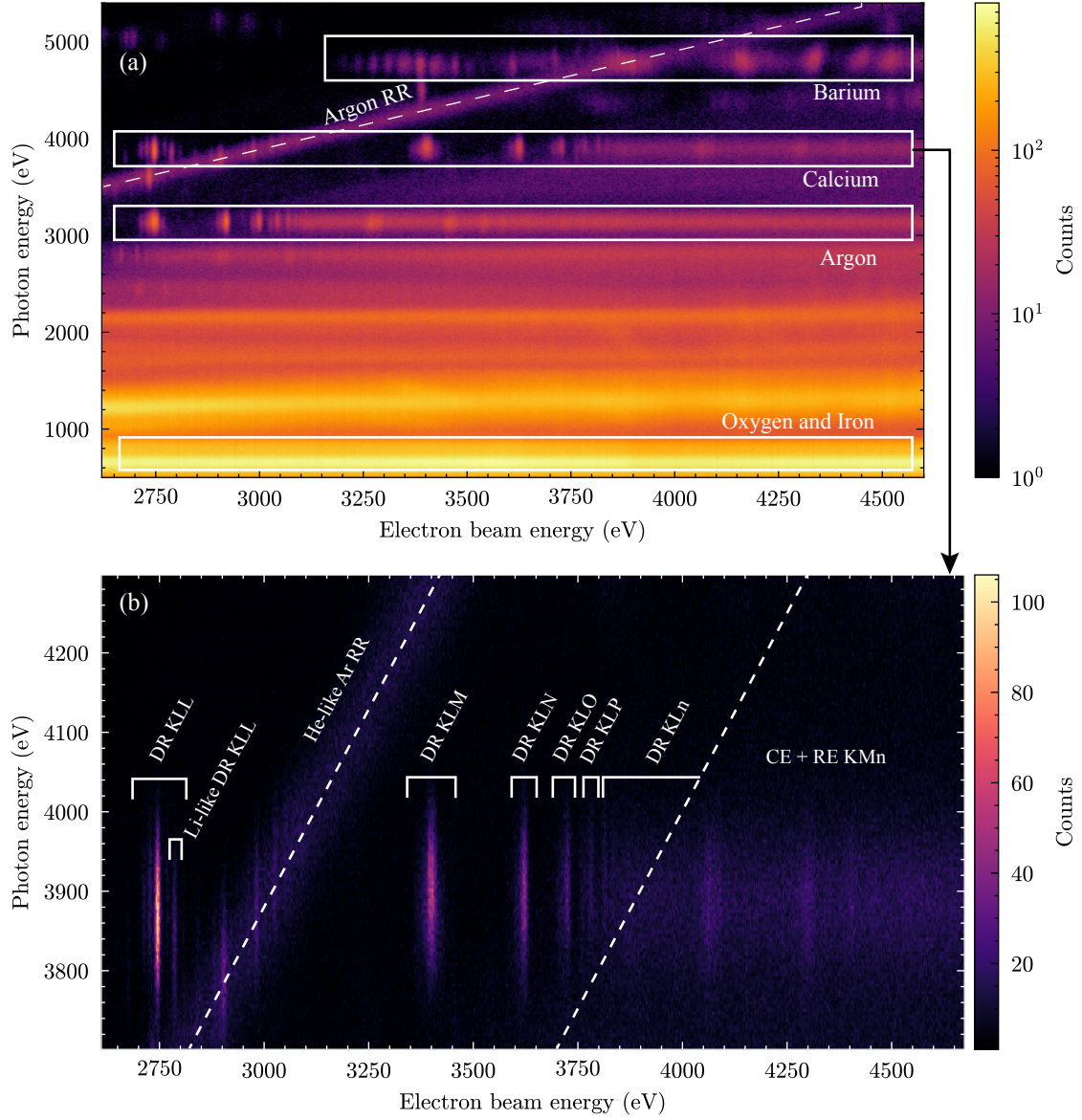


Figure 4.17: Photon intensity as a function of the electron beam and photon energies. The entire DR KL_n structure of He-like Ca, as well as its CE and RE can be observed. There is also a diagonal band of emission corresponding to L-shell RR and DR of an He-like argon contamination. This data corresponds to the slow scan. (a) Wide photon energy range. Emission from contaminations of Ba, Ar, O and Fe can also be observed. (b) ROI around the calcium $K\alpha$ lines.

energy range, there are emissions around 570 eV and 650 eV, corresponding to the $K\alpha$ and the $Ly\alpha$ emissions of He-like and H-like ions of oxygen. The emissions of oxygen are common in any EBIT experiment due to air molecules. Water vapor tends to be adsorbed in vacuum chamber walls, and its outgassing results in a constant presence of oxygen in the trap. Moreover, the Ca(TMHD)_2 molecule has four oxygen atoms to one calcium atom, further increasing the oxygen contamination. Around 820 eV, there are also emission coming from Ne-like iron. The iron contamination likely comes from frozen and adsorbed

material still present in the vacuum chamber from previous experiments. Both the oxygen and the iron lines are found across electron beam energies above the respective excitation thresholds, and do not present any resonant structure. At the very high-end of the photon energy spectrum, there is a presence of a considerable amount of resonant structures around 4800 eV. These resonances may arise from complex L-shell DR structures of barium. The barium emissions are also common in FLASH-EBIT measurements, due to its presence in the cathode of the electron gun. Moreover, there are many lines between 1000 and 2500 eV photon energies, all of which could be attributed to emissions from iron, barium and tungsten. Neither these emissions, nor the ones from oxygen interfere with the calcium emissions at the present charge states, but their presence illustrate the complexity of the different elements present in the trap simultaneously.

The trap was also contaminated with argon ions at a similar quantity as the calcium ions. This can be explained by a potential leak in the injection system, as the argon lines were only visible when the injection gate valve connected to the main trap chamber was open. Nonetheless, the argon and calcium emissions are well separated, around 600 eV apart, making their interference in the calcium lines minimal. Moreover, the RR line of He-like argon into the L shell is prominent in the observations, passing through the He-like calcium emissions region between the KLL and the KLM structures. Counter intuitively, although the DR emissions of argon and calcium were similar in terms of intensity, the RR structure was only observable for argon, but not for calcium. The RR cross-sections are also expected to be similar. This observation was present in all experimental conditions. This behavior is unexpected, as both the RR emission for argon and calcium should be observable, specially given the atomic number proximity of the two elements. No plausible explanation was found for this phenomenon. To confirm the resonances around 3.2 keV of photon energy were, in fact, given by He-like argon, FAC calculations were performed to compare with a projection around this photon energy. The DR structure was calculated within the isolated resonance framework, taking into account singly and doubly excited configurations $1sn\ell$ and $2\ell n\ell'$ up to a maximum principal quantum number of $n_{\max} = 8$. The CE structure includes direct impact excitation cross-sections from the ground state to $1s2\ell$ and the RE structure, calculated in the same framework as the DR structure, also includes doubly excited configurations $3\ell n\ell'$. A projection around the argon ROI from fast-scan data is presented in Figure 4.18, along with the FAC results. Both were normalized to facilitate the comparison. No analysis was performed in this experimental data, as it is a validation of the contamination. There is a gap between the DR and the CE structure due to the relatively low $n_{\max}$ used in the calculations. Nonetheless, an excellent agreement with the theoretical calculations was found across the entire spectrum. The DR KLL structure is outside of the scanning range, but the rest of the DR structure agrees with the theoretical calculations both in resonance energy and in relative intensity. The same can be said about the RE resonances. The relative intensity of DR to RE and CE is also in excellent agreement with the experimental data, confirming that this set of emissions is, indeed given by argon. Given the quality of this experimental

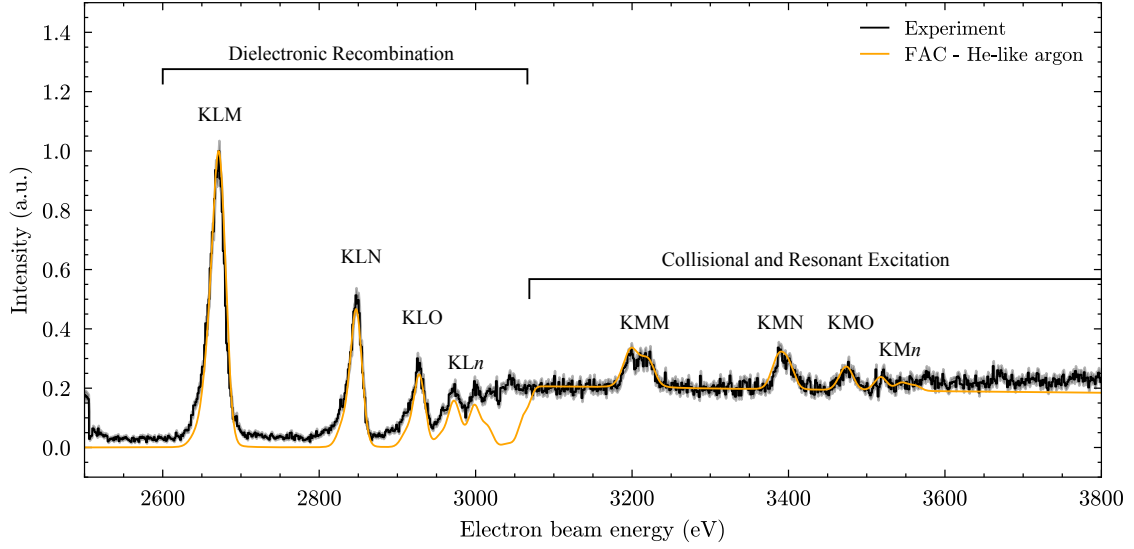


Figure 4.18: Projection of the experimental data for the fast scan around the $K\alpha$ line complex of the He-like Ar contamination. The orange line represents the FAC calculations. The main resonant and non-resonant structures are labeled.

data on the contamination of argon, further studies could be made. Furthermore, a similar dataset is already published in the literature [207].

4.3.3 Theoretical Calculations

The theoretical calculations made for calcium followed a very similar procedure as the ones made oxygen and argon. The isolated resonance framework was used to calculate the DR and RE cross-sections. For the DR calculation the configurations for the ground state, as well as singly and doubly excited state $1sn\ell$ and $2\ell n\ell'$ were included. Unlike the argon calculations, the maximum principal quantum number was increased to $n_{\max} = 15$ to include the region of convergence into the CE structure. The CE structure was calculated using the DW method, and included singly excited configurations up to $n_{\max} = 10$. Although only a region of interest around the $K\alpha$ complex was considered, the higher n excitations were calculated to include their cascade contributions to the $K\alpha$ emissions.

The polarization and anisotropy of the emissions lines were also calculated using the polarization module of FAC. These corrections were included in the calculations to compare directly with the experimental data, i. e. the correction on an observation at 90° was included in the calculations.

A similar set of calculations was also performed for the Li-like charge state. A similar set of configuration was included for the level structure, including the ground state configuration $1s^22s$ and the singly excited and doubly excited state configurations $1s^2n\ell$ and $1s2\ell n\ell'$. In this case, to save time on the configurations, since this charge state does not have a big impact on the numerical computation, a maximum principal quantum number $n_{\max} = 5$ was used. The DW method was also used for the CE calculation. The

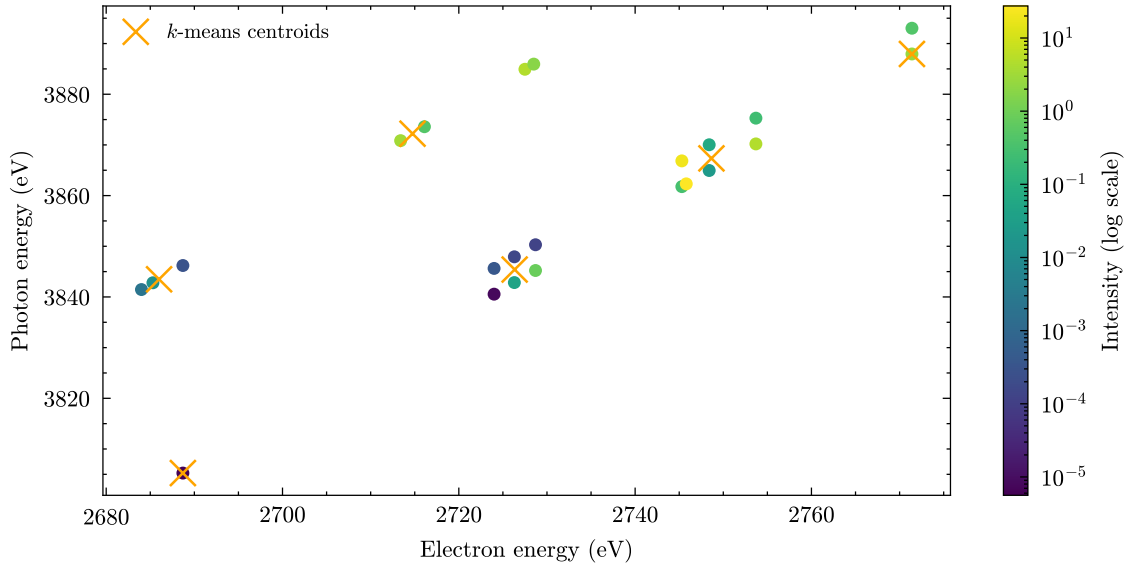


Figure 4.19: Example of the k -means clustering method applied to the theoretical DR KLL resonances of He-like calcium.

Li-like calculations were performed mainly to identify features in the observation that might not belong to the He-like emissions.

4.3.4 Result analysis and Discussion

4.3.5 Slow scan

The slower scan yielded a better electron beam energy dispersion, with a FWHM of around 8 eV at 2700 eV. For this reason, this measurement was chosen to extract experimental electron and photon energy positions for each of the resolved resonances of the KLn structure. The two-dimensional spectrum of the slow scan can be found in Figure 4.17 (b).

A linear combination of two-dimensional Gaussian functions was used as the fitting function to extract the DR resonance energy positions from the experimental data. Thus, an appropriate trial function must be found for the fit. In this regards, the number of Gaussians to use in the fit must be known, as well as initial position values to use in the fit procedure to ensure better convergence. A naive approach would be to use the complete list of theoretical resonances and assign a Gaussian profile to each of the resonances. The full list of theoretical resonances includes thousands of individual peaks, most of which have negligible resonant strengths, so these could be ignored. This would still result in hundreds of peaks, most of them unresolved within the experimental uncertainty. This would yield in a fitting function with too many parameters, resulting in overfitted parameters that could not be representative of the experimental features.

4.3.5.1 K-means algorithm

Since the experimental resolution allows only to observe the general DR structures, with only a few resolved peaks each, the structures should be fitted with a number of Gaussian functions just high enough to represent the general features of the experimental data. As the experimental energies are not directly given by specific resonances, but rather by the center of mass of the superposition of multiple resonances, the k -means clustering algorithm [208] was used to estimate both the number of Gaussians to use in the fit and the respective initial centroids from the theoretical calculations. The k -means algorithm is an unsupervised machine learning clustering method, meaning it is design to classify a dataset into k cluster groups. This is one of the simplest clustering algorithms, and it provides suitable values for the fitting functions, as it groups the theoretical resonances into clusters that can represent the each of the Gaussians to use in the fitting function. This method works by setting an initial set of k cluster centers within the dataset. The dataset points are assigned to each cluster by choosing the one with the least euclidean distance between the cluster center and the point. As the clusters are formed, new cluster centers are found by calculating the center of mass of each cluster. In a new iteration, the euclidean distance between each point and the new center cluster centers are calculated, and the dataset points are assigned to the new clusters, with new centers being calculated with the new centers of mass. This procedure is repeated until there is no variation of centers of mass between iteration (all the data points maintain the same distribution along the same clusters). The simplest way to generate the initial set of cluster centers is to choose k random positions and start the iteration process. As this is prone to find local minima, the same procedure is performed many times, providing a set of cluster centers. By calculating the variance of a cluster, taking into account the euclidean distances between every point of the cluster and the respective center of mass, the set of clusters that better classify the dataset is the one with the lowest sum of the variances of each cluster. In this project, the *SciKit-learn* machine learning *Python* package was used to implement the algorithm. In this package, the k -means algorithm uses the *k-mean++* method to identify suitable initial values for the cluster centers and improve the algorithm. In this method, one of the datasets is chosen to be the first cluster. The data point with the biggest euclidean distance to the first cluster center is chosen to be the second cluster. Then, the distances to all points from the center of both clusters is calculated, and the point with the biggest sum of distances to the first to centers is chosen as the third cluster center. This procedure is carried on until there are k cluster centers. These centers are used as the initial guess. This method is used to avoid repeating the k -means procedure, thus accelerating the clustering process.

To use this method, the dataset consisted in the list of data points given by the photon and resonant electron energies of each resonance. The resonance strength of each resonance is used to weight each data point. The experimental data was divided into regions to analyze separately, namely the rough region where one can find each of the

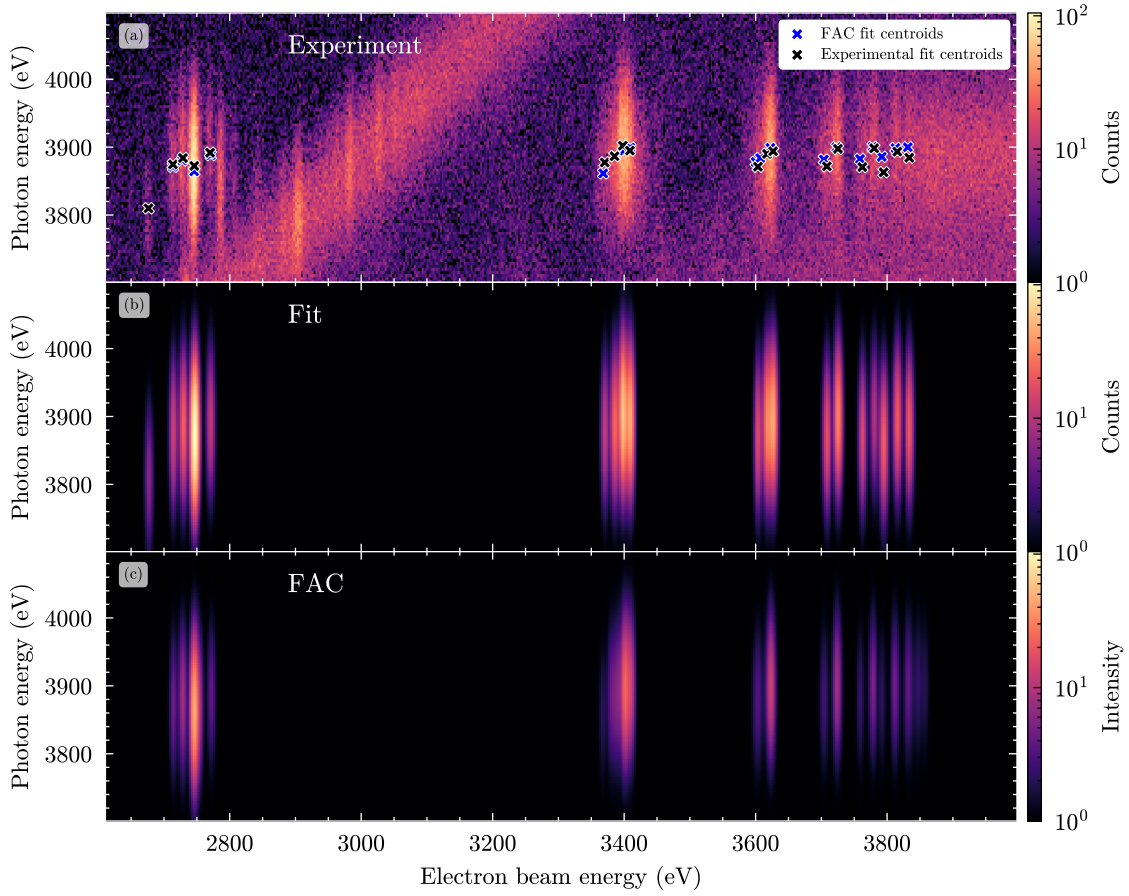


Figure 4.20: Example of the fit procedure applied to the DR structure. (a) Experimental result. The resonances between 2800 and 3200 eV without a fit centroid correspond to Li-like Ca and He-like Ar emissions. (b) Representation of the experimental fit function. (c) Representation of the fits function corresponding to the FAC calculations.

DR structure. As an example, the clustering of the KLL structure is presented in Figure 4.19. In this example, there are clear small structures that are approximated by a single Gaussian after the cluster procedure. One can see that the cluster centroids are not always symmetrical in relation to the cluster distribution, as the each data point has a different weight related to the respective resonance strength. The number of clusters can be defined by how many can be included without the minimum separation between clusters being less than the experimental width. For example, there is a small cluster around 2725 eV of electron energy and 3880 of photon energy that does not have a corresponding centroid because of its proximity of nearby structures. For each region, the k -means procedure is applied with different k values iteratively, until a maximum values of k that fulfills the previous restriction is found. The corresponding k cluster centroids are then used for the fit trial function as initial parameters.

4.3.5.2 Fit procedure

The two-dimensional fit was performed with the *ROOT* data analysis framework [209], developed by CERN. This framework, developed in C++, is a package of tools designed for scientific statistical analysis of large experimental datasets. It also has a *python* interface to run the variety of programs included in the package, which was used to build the fitting procedure with the *k*-means results. The *ROOT* non-linear fit tool uses the *Minuit* program [210], also developed at CERN. This is a *Fortran* program which can use several algorithms to minimize the χ^2 of a user-defined function in relation to a dataset by finding suitable values for the functions free parameters. The statistical error of each parameter after fit is given by the square root of the diagonal of the covariance matrix. This package includes several algorithms to minimize the χ^2 function. The one used by default, also used in this work, is the *MIGRAD*. This algorithm uses a combination of gradient descent and Newton's method to find the minimum of the χ^2 function. These methods require the first derivative of the function, which is computed numerically from finite differences.

The fitting procedure was applied to the KLL, KLM, KLN, KLO and the remaining of the DR structure individually. A comparison of the fit with the experimental results can be found in Figure 4.20. Subfigure (a) shows the experimental data, superimposed with the centroids obtained with the fit procedure (black crosses). The fit procedure was also applied to the theoretical calculations, broadened by the experimental photon energy and electron beam energy spreads for a direct comparison. The centroids obtained from the latter fits were also included in this subfigure (blue crosses). Although not perfect, a good proximity was found between the independently calibrated experimental and theoretical centroids. These appear to be in better agreement at the lower energy structure, and begin to slightly diverge as the electron beam energy increases. This is to be expected, as the number of blended resonances starts to increase, increasing the complexity and, thus, the accuracy of the theoretical calculations. Moreover, the DR resonances start to become unresolved at around the KLQ structure, so no further structures could be fitted. There is also a RR diagonal line emission between 2800 and 3200 eV due to the RR of He-like argon. This line is superimposed with resonances from DR of argon which, not being related to calcium, were not fitted. There is also a DR resonance below 2800 eV that is produced by the DR KLL structure of Li-like calcium. This resonance was also excluded from the fit. Subfigures (b) and (c) are representation of the functions obtained from the fitting procedures for the experimental and theoretical data. As the theoretical calculations included more resonant structures, there are more discernible structures at the higher energies of the subfigure (c) than the subfigure (b). Another apparent disagreement with theory is the relative intensity of each resonance, as the resonances of the experimental data appear to generally be more intense than the theoretical data (relative to the intensity if the strongest peak of the KLL structure). This is partially explained by the fact that this is a slow scan where there are clear signs of charge state dynamics over the scan.

The numerical centroids obtained from the experimental and theoretical data fits

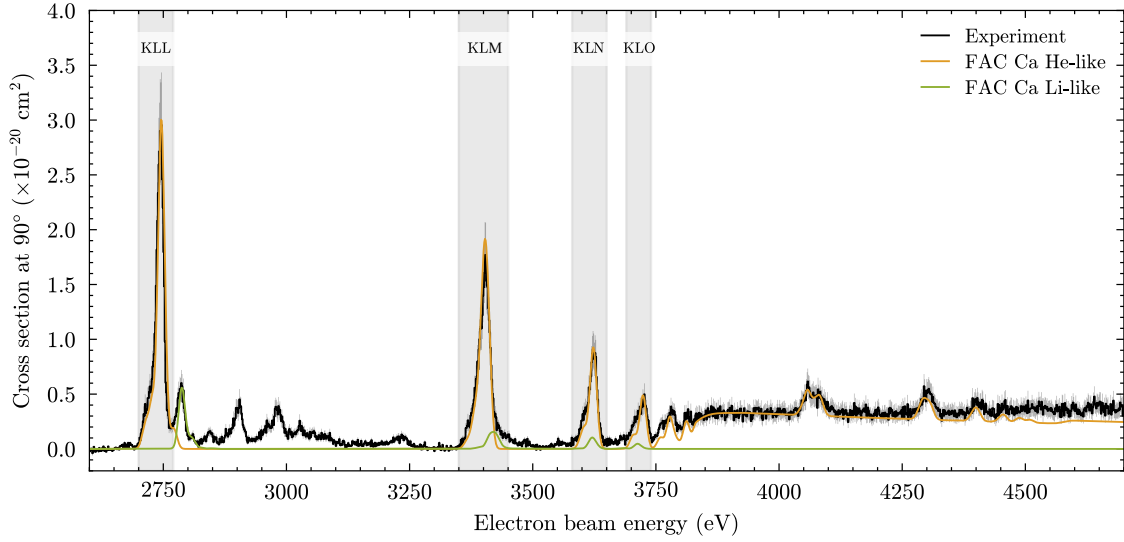


Figure 4.21: Calibrated cross-section (at 90°) of He-like calcium DR KL_n , CE and RE as a function of the electron beam energy, observed with the fast energy scan. The orange and green lines represent the FAC calculations for He-like and Li-like calcium. The main DR structures are labeled.

are presented in Table 4.9. The second column of the Table describes the intermediate configuration of the leading theoretical DR resonance within the energy width of each Gaussian used in the fit. Some peaks are dominated by two similar resonances with different values of J . In those cases, both values of J were provided. The FAC values for the x , y , z and w lines were also presented at the bottom of the Table, compared with a simple Gaussian fit of the emissions after the collisional excitation threshold. The FAC value for the $K\alpha$ line complex was calculated by fitting the emission spectrum obtained with FAC-CRM in the experimental conditions. The relative intensity of fitted resonances was also tabulated, although this should be used for reference only, as they are not directly related to the DR cross-sections due to the charge state dynamics present in the slow measurement. A fit of the main line emission after the excitation threshold is also presented, along with the FAC energy values for the individual $K\alpha$ transitions and a fit of the theoretical calculations broadened by the experimental resolution.

4.3.6 Fast scan

While the slow scan provided better electron beam energy resolution, it also presented a charge state population changing over the scanned range. The 30 ms scans provided an identical spectrum during the upwards and downwards scan, ensuring that the charge state balance is constant over the scan. For this reason, this measurement was used to evaluate experimental cross-sections. The scan scan yielded a FWHM of around 16 eV, while the same quantity was around 8 eV for the slow scans. In this case, and opposed to the slow scan, no individual resonant structures are resolved within each main DR feature, meaning only one peak was observed for KLL, KLM, KLN, KLO. The remaining

DR structures are blended together, and start to overlap with the collisional excitation structure.

Similarly to the slower scans, the RR and DR from the argon contamination are also present the experimental data of the fast scan, which was already presented before, while calcium RR is unobserved. These can be observed in Figure 4.21 between 2800 and 3300 eV. A small contamination of Li-like calcium is also observable by its respective KLL resonance below 2800 eV, as well as a possible trace of Be-like calcium at 2850 eV.

To obtain experimental cross-sections, the two-dimensional experimental data was projected over the electron beam energy axis using a region of interest around the photon energy corresponding to the calcium emissions. The experimental data intensity was calibrated by the DR KLL peak using our FAC calculation broadened by the experimental energy spread. The calculation took into account the polarization and anisotropy correction from the observation at 90 ° in relation to the electron beam axis. The correction from the 1 μm carbon filter transmission was also taken into account.

Both the DR structure and the collisional excitation cross-section, as well as the RE $\text{KM}n$ structure, are in excellent agreement with our experimental results. We were able to resolve the DR $\text{KL}n$ structure up to $n = 8$. At that point, the resonances are blended together, and the respective resonance energies converge into the main lines collisional excitation thresholds.

The experimental resonant strengths of each of the DR structures are presented in Table 4.10. Only the structures of DR KLL, KLM, KLN and KLO were sufficiently isolated to make a comparison with the FAC calculation counterparts. Although there is reasonable agreement between the two, there is a tendency for the FAC to underestimate the experimental results (aside from the KLL structure, which was used for calibration purposes). This can be potentially explained by the contamination of Li-like ions during the measurement. As the DR resonance positions for this charge state are similar to the values for He-like, their presence in the experimental data might be enough to explain the experimental overestimation in relation to the FAC calculations.

Table 4.9: Experimental values of the He-like calcium DR KLn resonances in the electron beam and photon energy (eV) obtained with the fit procedure. The values obtained by making the same applying the same fit procedure to the FAC calculations are also presented. The last column is the relative intensity. The second part of the Table presents the FAC values for the individual main $K\alpha$ lines, along with a fitted value after the excitation threshold broadened to the experimental resolution. A fit of the experimental emissions after the threshold is also presented.

	Leading intermediate conf.	E_e exp	E_e FAC	$E\gamma$ exp	$E\gamma$ FAC	Rel. I
KLL	$[1s_{1/2}2s_{1/2}^2]_{J=1/2}$	2676.5 ± 1.4	2675.20	3810 ± 6	3791.30	5.2
	$[1s_{1/2}2s_{1/2}2p_{1/2}]_{J=1/2}$	2713.6 ± 1.4	2713.61	3875 ± 4	3871.1	12.9
	$[1s_{1/2}2s_{1/2}2p_{3/2}]_{J=1/2, 3/2}$	2728.9 ± 1.4	2727.94	3884 ± 3	3880.5	21.4
	$[1s_{1/2}2p_{1/2}2p_{3/2}]_{J=3/2, 5/2}$	2746.1 ± 1.4	2745.97	3872 ± 3	3864.3	111.2
	$[1s_{1/2}2p_{3/2}^2]_{J=1/2}$	2770.2 ± 1.4	2771.15	3892 ± 4	3888.3	10.6
KLM	$[1s_{1/2}2p_{3/2}3s_{1/2}]_{J=1/2}$	3370.5 ± 1.4	3368.20	3877 ± 4	3861.4	12.1
	$[1s_{1/2}2p_{1/2, 3/2}3s_{1/2}]_{J=1/2, 3/2}$	3385.4 ± 1.4	3385.88	3887 ± 3	3887.1	23.1
	$[1s_{1/2}2p_{3/2}3p_{3/2}]_{J=3/2, 5/2}$	3397.9 ± 1.4	3400.34	3902 ± 3	3895.0	62.2
	$[1s_{1/2}2p_{3/2}3d_{5/2}]_{J=3/2, 5/2}$	3408.8 ± 1.4	3409.16	3895 ± 3	3899.4	45.6
KLN	$[1s_{1/2}2p_{1/2}4p_{3/2}]_{J=5/2}$	3603.5 ± 1.4	3600.02	3871 ± 4	3878.3	15.0
	$[1s_{1/2}2p_{3/2}4s_{1/2}]_{J=1/2}$	3617.4 ± 1.4	3606.99	3890 ± 3	3883.9	34.3
	$[1s_{1/2}2p_{3/2}4p_{3/2}]_{J=5/2, 7/2}$	3626.7 ± 1.4	3622.47	3894 ± 3	3899.1	44.8
	$[1s_{1/2}2p_{3/2}4d_{5/2}]_{J=7/2}$					
KLO	$[1s_{1/2}2p_{1/2}5p_{3/2}]_{J=3/2, 5/2}$	3708.4 ± 1.4	3703.84	3872 ± 4	3881.7	16.8
	$[1s_{1/2}2p_{3/2}5d_{5/2}]_{J=7/2}$	3725.2 ± 1.4	3722.97	3898 ± 3	3899.8	31.9
	$[1s_{1/2}2p_{3/2}5p_{3/2}]_{J=5/2}$					
	$[1s_{1/2}2p_{3/2}5p_{1/2}]_{J=3/2}$					
KLP	$[1s_{1/2}2p_{1/2}6p_{3/2}]_{J=3/2, 5/2}$	3762.3 ± 1.4	3870.66	3871 ± 4	3882.6	15.3
	$[1s_{1/2}2p_{3/2}6d_{1/2}]_{J=5/2, 7/2}$	3780.3 ± 1.4	3898.38	3898 ± 4	3900.5	8.9
KLQ	$[1s_{1/2}2p_{1/2}7p_{3/2}]_{J=3/2, 5/2}$	3794.7 ± 1.4	3863.01	3863 ± 4	3885.8	21.4
	$[1s_{1/2}2p_{3/2}7d_{5/2}]_{J=7/2}$	3815.6 ± 1.4	3812.80	3893 ± 4	3899.9	19.8
	$[1s_{1/2}2p_{3/2}8d_{5/2}]_{J=7/2}$	3833.7 ± 1.4	3831.44	3884 ± 4	3898.8	19.5
z					3859.86	
x					3882.16	
y					3886.57	
w					3901.83	
$K\alpha$				3895 ± 3	3890.53	

Table 4.10: Experimental values of different He-like calcium DR KLn structures resonant strengths in units of $10^{-20} \text{ cm}^2\text{eV}$. The energy range used for the integration are also indicated, as well as the corresponding integrations made to the FAC calculations.

Structure	Energy region (eV)	Exp	FAC He-like	FAC Li-like	FAC Total
KLL	2700-2770	63.0 ± 0.1	62.879	0.107	62.986
KLM	3350-3450	52.3 ± 0.2	47.650	4.604	52.254
KLN	3580-3650	23.1 ± 0.3	19.136	2.155	21.291
KLO	3690-3740	13.1 ± 0.5	10.046	0.892	10.938

EXPERIMENTAL RESULTS - NUCLEAR REACTORS

In this thesis, experiments were made concerning the atomic properties of Ne-like krypton and several charge states of tungsten. As discussed before, these elements are present in tokamak experiments, and the accurate knowledge of their atomic data is essential for accurate plasma diagnostic for fusion reactors. In this Chapter, a spectral decomposition method is used, namely the Non-Negative Matrix Factorization (NNMF), to analyze both the experimental data from krypton and tungsten. Thus, the first Section introduces and explains this method before it can be further applied.

In the second Section, the krypton measurements and results are presented. Here, The DR and excitation structures of Ne-like krypton were measured and analyzed. The DR structures were fitted to provide the electron and photon energy positions. The decomposition technique was also applied to the two-dimensional data to extract the DR and excitation cross-sections as a function of the electron beam energy for different lines. Among them are the so-called 3C and 3D lines, which will be introduced later. The 3C/3D intensity ratio of Ne-like iron has been a central topic in atomic physics and X-ray astronomy, largely due to the persistent discrepancy between advanced theoretical models and experimental results ([211] and references therein). For Ne-like krypton, however, the latest measurements using microcalorimeters align with theoretical predictions [212]. Following our application of the NNMF method, a new line ratio measurement is presented and compared with the current state-of-the-art results.

Finally, the measurement of EUV emissions of open $4f$ -shell tungsten ions will be presented. In this work, the decomposition technique is used to obtain the individual emission spectrum of every charge state from a single measurement. These observations are compared with new calculations, and the main $n = 5$ intrashell transitions are identified and tabulated.

5.1 Non-Negative Matrix Factorization

As it was shown in the last Chapter, it is typical to obtain experimental multi-dimensional data, often with overlap between emission structures, either from the same charge state or from a collection of charge states. While in the last Chapter most structures were completely unresolved, the experimental data for Ne-like krypton, while still presented with blended structures, has enough resolution for a separation between emission structures. Since most structures are still blended, a decomposition method was used to decouple the several processes and obtain either spectra from individual charge states or individual photon emissions regions.

The chosen method was the NNMF. In its essence, this is a method designed to factorize a matrix into a multiplication of two matrices. Let the original matrix be matrix X . The NNMF method uses this matrix as an input, and finds two matrices W and H which follow the relation

$$X = W \times H. \quad (5.1)$$

There are a number of decomposition methods capable of achieving this kind of result, like Principle Component Analysis (PCA) and Singular Value Decomposition (SVD). The main advantages of this method is its simplicity, and the assurance that the resulting W and H matrices are non-negative. The last point is important for these works, since these matrices can represent positive physical quantities, e.g. ion emissions or charge state populations. If one matrix represent for example the charge state, negative values are non-physical. This method has a single free parameter k . Let the matrix X have dimensions (n, m) . The matrices W and H have dimensions of (n, k) and (k, m) , respectively, with k being the common dimension. This dimension is often referred to as the number of features, while the matrices W and H decompose the original matrices into partial matrices describing the features and their locations.

If the number of features is selected as the number of structures that one expects to decompose, and these features change smoothly over one of the axis, then the W and H matrices will provide the shape of the features and their respective location. As an illustrative and simplistic example, let n be the number of bins of an electron beam energy axis and m be the number of bins of a photon energy axis. Let there be three charge states that dominate the population distribution at 300, 500 and 700 eV, respectively, and each has an emission spectrum consisting of three, five and four Gaussian functions, respectively. The population of each charge state is also represented by Gaussian functions centered at 300, 500 and 700 eV, while their emission spectra are a linear combination of Gaussian functions. A synthetic two-dimensional spectrum X is represented in Figure 5.1 (a). This spectrum is the result of the multiplication of the matrices W and H , which have their respective components represented in subplots (b) and (c), each representing the charge states individual emission spectra and population profile. To better represent a real scenario, 15 % (choice) of Gaussian noise was also added to the X matrix. The NNMF method was applied to these synthetic spectra with $k = 3$. The components of

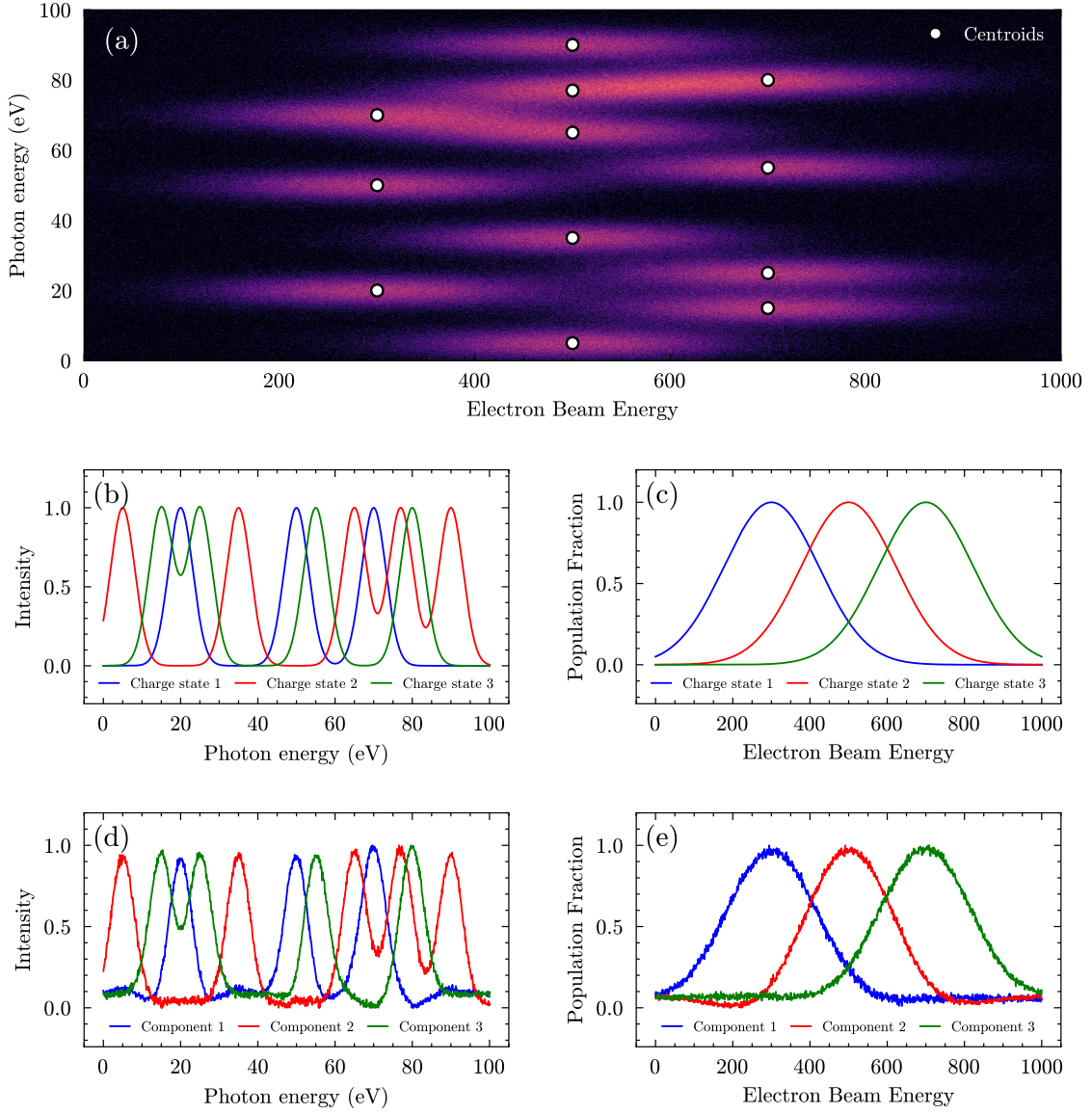


Figure 5.1: Example of the NNMF method applied to synthetic data. (a) Synthetic data comprised of several two-dimensional Gaussian functions. Components of H (b) and W (c) matrices used to produce the spectrum presented in (a). Components of H (d) and W (e) matrices generated by the NNMF method.

the approximated matrices W and H obtained with the method are represented in the subplots (d) and (e). The matrix H follows the initial charge state input, although some residual values persisted in the background outside the original Gaussian. The W matrix also contains every emission feature correctly, aside from a small variability in the peak intensities and the background. While the emission spectra of each charge state could potentially be obtained by a simple projection over the photon energy axis within the electron beam energy region around the center of the Gaussian population distribution, the blended nature of the results means that there would have to be a compromise between a wide ROI with components from other charge states and a narrow ROI with low statistics.

The NMF methods avoids this compromise by obtaining the components of each charge state without loss of statistics. Note that the NMF method has no insights about physical behavior or profiles in general, being designed to numerically approximate the W and H matrices by studying variations at the single bin level. Its results interpretation and applicability therefore must be done by the user.

The use of NMF in this work was done with its implementation in the *scikit-learn* machine learning *python* package [213]. In this application, the objective is to minimize the loss function

$$\begin{aligned}
 L(W, H) = & \frac{1}{2} \|X - W \times H\|_{\text{Fro}}^2 \\
 & + \alpha_W \cdot \text{l1_ratio} \cdot n \cdot \|\text{vec}(W)\|_1 \\
 & + \alpha_H \cdot \text{l1_ratio} \cdot m \cdot \|\text{vec}(H)\|_1 \\
 & + \frac{1}{2} \alpha_W (1 - \text{l1_ratio}) \cdot n \cdot \|W\|_{\text{Fro}}^2 \\
 & + \frac{1}{2} \alpha_H (1 - \text{l1_ratio}) \cdot m \cdot \|H\|_{\text{Fro}}^2.
 \end{aligned} \tag{5.2}$$

The first line is the Frobenius norm of the difference between the original matrix X and the multiplication of the two matrices W and H . This norm is defined as the square root of the sum of every element of the matrix,

$$\|A\|_{\text{Fro}} = \sqrt{\sum_{i,j} A_{i,j}^2}. \tag{5.3}$$

This is the main factor of the loss function, as it is minimal when the multiplication of W and H best approximate X . As there are numerous local minima that can be reached by the condition set in the first line, the remaining lines of the equation are introduced to control features of the optimal solutions. The second and third lines are the L1 norm regularization terms. The L1 norm is simply the sum of the absolute value of the matrix elements,

$$\|\text{vec}(A)\|_1 = \sum_{i,j} |A_{i,j}|. \tag{5.4}$$

These terms penalize the presence of large elements in the respective matrices, thus resulting in the convergence of many elements into zero. These terms, thus, encourage sparsity in the respective matrices. The terms corresponding to the matrices W and H are multiplied by n and m to scale the regularization to the size of each matrix. The fourth and fifth terms are the Frobenius norm regularization terms. In these terms, the Frobenius norm of each matrix penalizes the square root of the elements intensities. As it is more aggressive in the penalization of larger values, it encourages the smoothness of the respective matrix rather than its sparseness. Like the former regularization, these terms are also weighted by the matrix sizes n and m . The coefficients α_W and α_H control the amount of regularization that is to be applied to each of the matrices. Values of $\alpha_W = \alpha_H = 0$ make the first term the only one contributing to the minimization process, while a non-zero coefficient controls how much sparse or smooth should each of the

matrices be. The `l1_ratio`, which can only range between 0 and 1, controls which type of norm is preferred when regularizing. This allows a fine tune between sparseness and smoothness for each of the matrices.

The minimum of the loss function is found by adjusting the W and H matrices iteratively. Several methods can be used to initialize the trial matrices used in the process. In this work, all applications of the NNMF method started with random non-negative matrices of size (n, k) and (k, m) , scaled by $\bar{X}/\sqrt{k}$. As the loss function is separable with respect to W and H , a straightforward optimization method to minimize the function is the Coordinate Descent (CD), which is the default method implemented in this package. This method is characterized by the optimization of each parameter individually, one at a time, repeating a loop of optimizations until convergence is reached. let s be the step count, so that a matrix A in the step s is referred to as $A(s)$. The optimization of a matrix W is done by numerically integrating the equation

$$\frac{\partial X}{\partial W(s)}(X, W(s-1), H(s-1)) = 0 \quad (5.5)$$

in respect to $W(s)$. After optimizing $W(s)$, the new value of W is used to optimize H by integrating the equation

$$\frac{\partial X}{\partial H(s)}(X, W(s), H(s-1)) = 0. \quad (5.6)$$

After each step, the value of X is computed and, if it is lower than a specified tolerance value, the minimization process is complete. If it is higher than the tolerance value, a new step proceeds with a new optimization of the W and H matrices individually. The optimization procedures are always made elementwise, thus ensuring the non-negative nature of every element.

The PCA decomposition methods shares most of its principles with NNMF. While it could be used as an alternative method, it is more complex and allows the optimization with negative values, making it less suitable than the NNMF method for spectral decomposition.

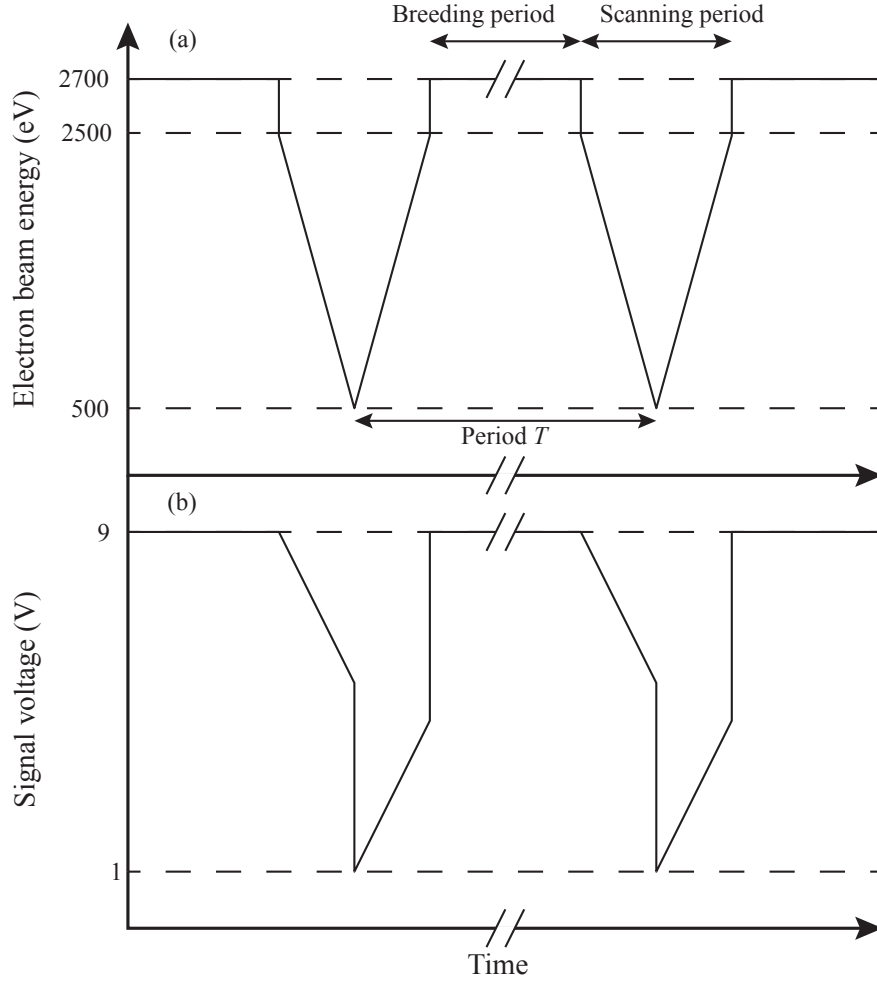


Figure 5.2: Simplified voltage scheme used for the electron beam energy setup use during scans. (a) Nominal electron beam energy given by the difference between the drift tube platform and the electron gun anode voltage. (b) Voltage signal used to discriminate the photon emission detection by the corresponding electron beam energy.

5.2 Krypton

5.2.1 Experimental setup

The FLASH-EBIT was used to produce, store, and probe Ne-like ions of krypton. The krypton gas was introduced in the trap by connecting a bottle of compressed krypton to the injection system. A steady injection pressure from this bottle after the needle valve allowed the formation of a neutral atomic beam directed to the trap. In the trap region, the electron beam had enough energy to ionize the krypton atoms and trap them with its space charge.

Opposed to oxygen and calcium, krypton is a relatively heavy with much higher charge states, with an atomic number $Z = 36$ and a charge of $26+$ for the Ne-like charge state. For these reasons, this ion can be trapped easily, dominating the trap contents by ejecting contaminations of lighter elements from the trap via evaporation cooling (see Section 3.3.3).

This element only competes in the trap with heavier barium and tungsten contaminations from the cathode. These elements are minimized by reducing the cathode current so that the observation lines from these elements is suppressed, but still high enough to produce a beam. The efficient trapping led to high line emission of krypton. Therefore, there was no need of a triangular duty cycle for the electron energy. Instead, the electron beam energy scheme was composed of a breeding period, followed by a scanning period. During breeding, the electron beam energy was set to 2700 eV. The breeding of these ions was set to 0.9 s and was followed by an energy scan between 2500 and 500 eV, followed by another scan with the same range but opposite direction. The downwards and upwards scans were set to take 50 ms each, giving a total of 1.0 s period for the duty cycle. This scheme has been used by several EBIT groups [141, 167, 170–172] and allows for a quick scan of the electron beam energy without a major change of the charge state population balance during the scan. With a triangular wave signal (no breeding time), if the scans are fast enough, the charge state population is given by its average over the electron beam energy, which is determined by the energy scan range. With a breeding period, one can select the energy to breeding the ions, making it easier to optimize the charge state balance, sometimes allowing for the generation of charge state balances dominated by a single charge state. In this case the breeding energy was set to 2700 eV, which is above the ionization threshold of the Na-like charge state, but still below the ionization threshold of the Ne-like charge state. As the ionization cross-section increases with energy, the higher the breeding energy is, without crossing the next ionization threshold, the more efficient is the ionization. The ground state configurations and ionization energy thresholds for the Al-like to O-like charge states of krypton are presented in Table 5.1. As before, one AFG was used to generate the electron beam energy scheme signal before being amplified and controlling the drift tube platform, while another, synchronized to the clock of the first AFG, generated the signal to store the detection events from the downwards and upwards scan separately. The signals from both AFGs are represented in Figure 5.2 for two consecutive periods. As was the case before, the differences between the downwards and upwards scans were used to investigate possible charge state dynamics during the energy scans. A probing time of 0.1 s between breeding periods of 0.9 s yielded no differences between the upwards and downwards scans, indicating that there were no charge state dynamics during scan. As such, the observations from both scan directions were summed during analysis to increase statistics. With this setup, by setting the electron beam current at 11 mA during breeding, an electron beam energy spread of 8 eV at an energy of around 700 eV was achieved.

The photon emissions resulting from the collisional processes during the probing period were observed with the same SDD used in the previous works, still positioned at an angle of 90° relative to the electron beam axis. This detector yielded a FWHM of around 100 eV at 1800 eV of photon energy. As this experiment was performed right before the calcium experiments, the same calibration was used for the photon energy. Once again, the calibration took advantage of the well known $K\alpha$ line of He-like neon, the

Table 5.1: Ionization energies of each charge state of krypton, from XXIV to XXIX, as well as the respective ground electronic configurations. Values taken from the NIST ASD.

Ion species	Charge	Ground configuration	Ionization energy (eV)
Kr XXIV	23+	$1s^2 2s^2 2p^6 3s^2 3p^2 P_{1/2}$	1042
Kr XXV	24+	$1s^2 2s^2 2p^6 3s^2 {}^1S_0$	1155
Kr XXVI	25+	$1s^2 2s^2 2p^6 3s^2 S_{1/2}$	1205
Kr XXVII	26+	$1s^2 2s^2 2p^6 {}^1S_0$	2929
Kr XXVIII	27+	$1s^2 2s^2 2p^5 {}^2P_{3/2}$	3072
Kr XXIX	28+	$1s^2 2s^2 2p^4 {}^3P_2$	3228

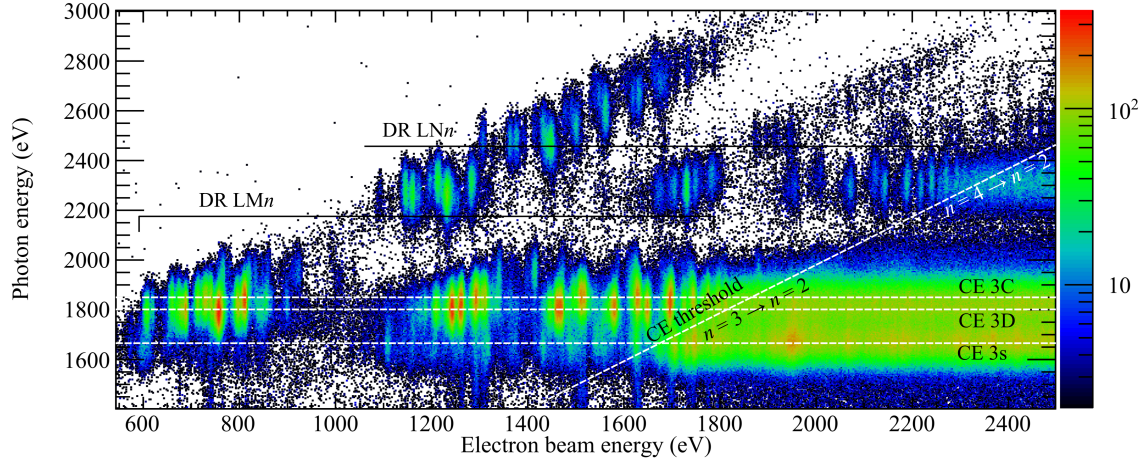


Figure 5.3: Photon intensity as a function of the electron and photon energies for the Ne-like krypton. The DR resonant structures, as well as the excitation structures are labels. The horizontal dashed lines indicate photon energy of the 3C, 3D and 3s line complexes.

$K\alpha$ and $K\beta$ lines of He-like argon, the $Ly\alpha$ line of H-like oxygen and the $K\alpha$ line of He-like oxygen. The electron beam energy axis was calibrated by fitting the DR LMn resonances and calibrating with the corresponding structures calculated with FAC.

The observations allowed the construction of the two-dimensional spectrum represented in Figure 5.3. As it is apparent in the Figure, the observations yielded a wide variety of well resolved resonant and non-resonant structures. Between 600 and 1800 eV of electron beam energy, around 1800 eV of photon energy, one can find the DR LMn structure. In this region, it is possible to resolve the resonant structures of LMM, LMN, LMO, LMP, LMQ and LMR. The remaining DR LMn structures converging into the excitation threshold are blended together. After the excitation threshold, still around the same range of photon energy, there are continuous structures corresponding to the direct impact excitation of the excited states that produce the $3d - 2p$ and $3s - 2p$ line complexes, often abbreviated as $3d$ and $3s$. The $3d$ line complex is composed by the transitions connecting the ground state with the states $[2p_{1/2}^5 3d_{3/2}]_{J=1}$, $[2p_{3/2}^5 3d_{5/2}]_{J=1}$, $[2p_{3/2}^5 3d_{3/2}]_{J=1}$, known as the 3C, 3D

and 3E lines, respectively. The 3s line complex is composed by the transitions connecting the ground state with the states $[2p_{1/2}^5 3s_{1/2}]_{J=1}$, $[2p_{3/2}^5 3s_{1/2}]_{J=1}$, $[2p_{1/2}^5 3s_{1/2}]_{J=2}$, known as the 3F, 3G and M2 lines, respectively. The 3d and 3s line complexes present two different peaks in the collisional excitation regions that can be distinctly resolved, although still presenting a considerable overlap between them. On the 3d complex, the 3C and 3D lines are the most prominent, and their photon energy is represented in the Figure with horizontal dashed lines. While there is not enough resolution to resolve them, there is a clear correspondence between them and their respective DR satellites. On the 3s line complex side, there are only faint DR satellites to compare with. The lines of this complex are also unresolved, so an average photon energy values is represented by an horizontal dashed line in the Figure. There are also several resonant structures after the excitation threshold superimposed to the continuous part corresponding to the LNn RE process.

The $n = 4$ to $n = 2$ emission structures, with the corresponding DR satellites, are also visible in an photon region around 2400 eV. Before the excitation region, there are resolved DR LNn structures from LNN to LNT , with the continuous excitation part after the collisional excitation threshold. As expected, these structures are weaker than the $n = 3$ to $n = 2$ structures. Faint diagonal structures corresponding to the RR into $n = 3$ and $n = 4$ are also present in the data, although not with enough statistics to use for calibration purposes.

5.2.2 Theory

FAC was employed to calculate the atomic level structure, radiative and non-radiative transition rates and collisional cross-sections. The atomic structure and transitions included all configurations for Ne-like krypton ions with ground and singly excited configurations $1s^2 2s^2 2p^6$, $1s^2 2s^1 2p^6 n\ell$ and $1s^2 2s^2 2p^5 n\ell$, where $n = 3, \dots, 15$ and ℓ is every possible orbital angular momentum value. For the recombination processes, the Na-like atomic structure included the configurations for ground state $1s^2 2s^2 2p^6 3s$, singly excited states $1s^2 2s^2 2p^6 n\ell$ and doubly excited states $1s^2 2s^1 2p^6 n\ell n'\ell'$ and $1s^2 2s^2 2p^5 n\ell n'\ell'$, with the same range values for n and n' . The RE cross-section calculations were limited to configurations with the values of n and n' up to 4 and 7, respectively, while for DR we included the values of n and n' up to 3 and 15. The resonant structures were all calculated within the isolated resonance framework, neglecting any quantum interference effects.

The CE cross-sections were also calculated with FAC within the DW method. This atomic data was used to build a small steady-state CRM with the FAC-CRM package in order to understand the main transitions. A small portion of the experimental data was simulated by making a CRM where the electron energy distribution was defined with a Gaussian function with the same width as the experimental electron energy spread, and a centroid around 2300 eV. This value is well above the excitation threshold, but its still within the experimental energy scan range. The collisional excitation cross-sections and radiative decay rates were also included. The line emissivities from the CRM were

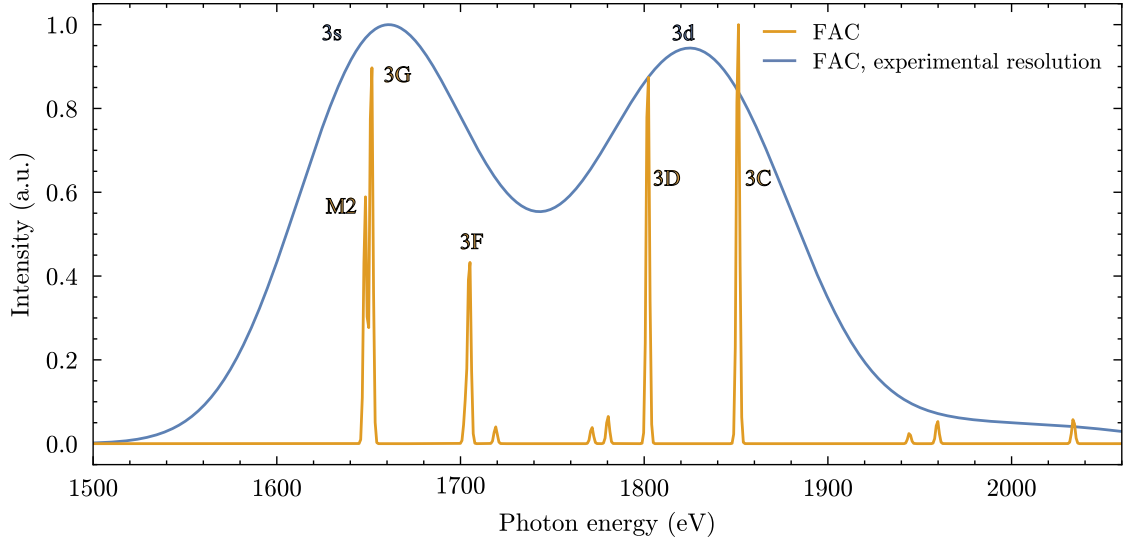


Figure 5.4: Emission spectrum given by a steady-state CRM of the Ne-like krypton plasma for an electron beam energy of 2300 eV. The orange line corresponds to the FAC calculation for a high resolution observation, while the blue line represents the same calculations broadened by the experimental resolution.

used to construct a synthetic emission spectrum, presented in Figure 5.4, by combining Gaussian functions scaled by the respective emissivity values. In this Figure, the emissions spectrum is plotted with both a narrow enough width to resolve the main transitions, as well as with an energy width similar to the experimental resolution. The intensity of both representations was normalized to one to facilitate the comparison. In this Figure, it becomes evident that the $3d$ complex is dominated by the $3C$ and $3D$ lines, while the $3s$ complex has a mixture of the $3F$, $3G$ and $M2$ lines. At the experimental resolution, only the $3s$ and $3d$ line complexes are resolved, but still overlapped.

As for all the previous calculations, all the emitting processes were corrected by the polarization and anisotropy factor given by the excitation by singly directed electrons and the observations at an angle of 90° .

5.2.3 Results Analysis and Discussion

As this dataset provided a great amount of resolved atomic collisional structures, different aspects of it were analyzed with different techniques. The scheme used to analyze the calcium data was applied to this dataset to fit the DR resonances and extract the respective DR satellite line positions. This was compared with the FAC calculations to both identify the structures and benchmark the resonant electron and photon energies. The NNMF method was also applied to decompose the two-dimensional spectrum and study the DR and excitation structures.

Like the calcium analysis, the experimental data was divided into smaller regions to facilitate the convergence of the two-dimensional fit. The trial function was composed of a linear combination of two-dimensional Gaussian functions. Simple projections and

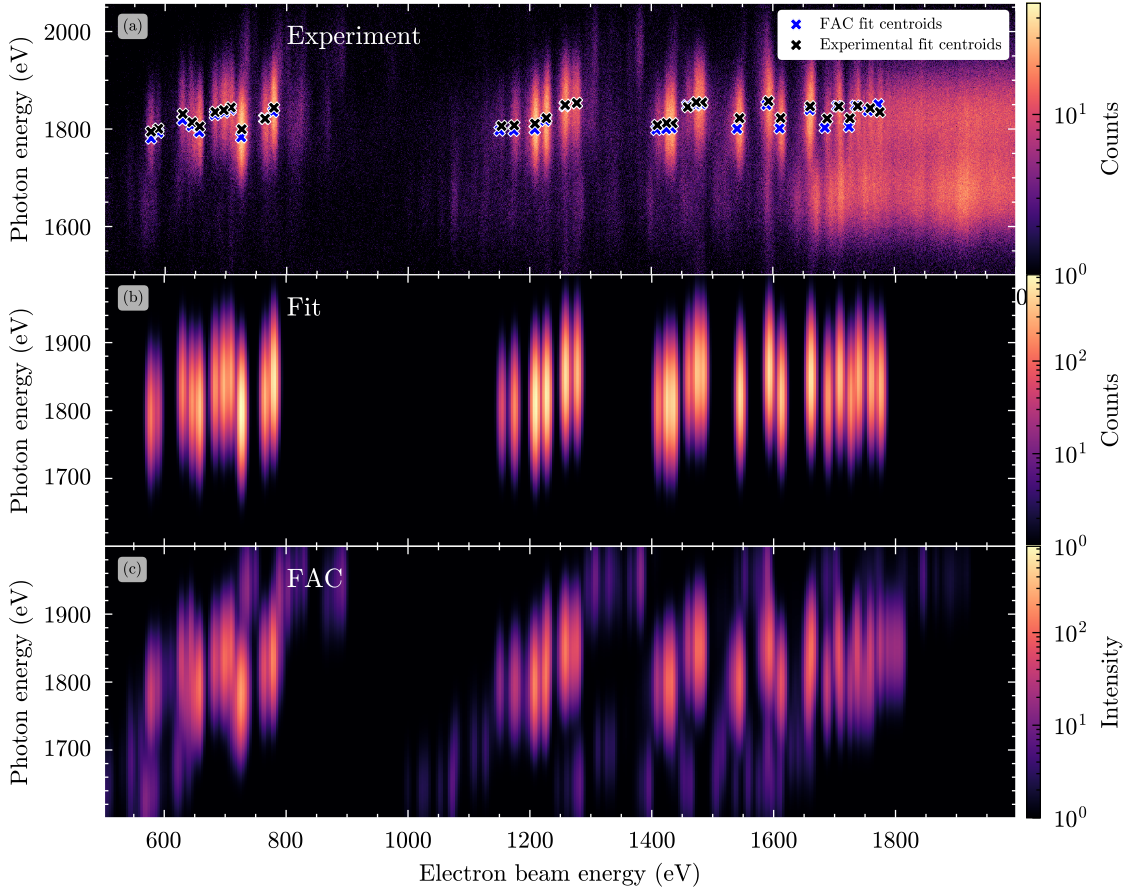


Figure 5.5: Two-dimensional fit of the DR structure of krypton. (a) experimental data, superimposed with the fit centroids represented by crosses. The black crosses correspond to the fit of the experimental data, while the blue crosses represent the fit of the theoretical calculations broadened by the experimental resolution. (b) Two dimensional representation of the fitted function. (c) Theoretical calculations broadened by the experimental resolution.

Gaussian fits were used to determine the experimental resolution, around 8 eV for the FWHM of the electron beam energy and 90 eV for the photon energy. These values were fixed as the width parameters of the two-dimensional Gaussians. The k -means clustering method was once again used to determine the initial centroids to be used in the fitting process. Within each smaller region, the experimental data was fitted with the CERN ROOT framework using the MINUIT program.

The results from the fit procedure are displayed in Figure 5.5. The subplot (a) shows the experimental data, superimposed with the centroids from the fit (black crosses). The same procedure was also applied to the FAC data, broadened by the respective experimental resolutions. The centroids obtained from fitting the theoretical calculations are represented by the blue crosses. In the case of calcium, the DR KL_n satellite photon energies were all around the $K\alpha$ line complex, but no obvious pattern was found. In the case of krypton, within the fitted resonances, there is a clear separation between the

satellite lines connected to the main 3C and 3D emission lines from the Ne-like charge state. This separation is not clear in the LMM region (electron energy below 800 eV), but becomes more apparent as the DR resonances converge into the excitation thresholds. There is a good agreement between the experimental 3C DR satellites and theoretical values. However, there is a slight disagreement between the experimental and theoretical values for the 3D DR satellites. Overall, there is an underestimation in the photon energies predicted by FAC. This disagreement seems to increase with the electron energy, and is not present in the 3C DR satellites.

The subplots (b) and (c) display the minimized fitting function and the FAC calculation, respectively. The 3C and 3D satellites are the ones with higher intensities. The fit was restricted to this set of lines due to difficulties in the convergence of the fit. This restriction is evident when comparing subplots (b) and (c), as the (b) only has lines with photon energies between 1700 eV and 1900 eV. In the (c) subplot, there are lines below 1700 eV corresponding to satellite lines of the 3s line complex. These lines are very faint compared with the 3C and 3D satellites, yet some are still observable in the experimental data. Fewer lines are also observable above 1900 eV. Both line sets have been neglected in the fit procedure.

The fit results are presented in Table 5.2. Here, the centroids of the fits of the experimental and theoretical data are presented. The presented uncertainties include the contributions from the statistical uncertainty in the fit, as well as the uncertainty from the calibrations. The relative intensity from the fit of the experimental data is also presented. The experimental centroids and relative intensity were used as a guide for the identification of each fitted resonance. The leading intermediate configuration after dielectronic capture, as well as the general DR structure, are also presented in the Table. As these are all satellites of the 3d line complex, all the intermediate configurations have an excited electron in the 3d shell. This is expected, as the satellite lines are produced by an intermediate configuration with the same electronic structure and an extra spectator electron. The decay of the electron in the 3d shell into the $n = 2$ produces a photon with an energy similar to the main line with a small offset due to the screening of the spectator electron. As this electron lays in higher n orbitals, its influence in the core and valance electrons is less pronounced, making the satellite lines energies converge, in general, into the energy of the main excitation line. The mains lines from LMM to LMQ were resolved and identified. Some resonances beyond this point were also presented, as long as the respective inferred intermediate configuration. These resonances are already in a region of overlap between each other and with the direct impact excitation structure, so its identification might not be accurate. Nonetheless, their centroids are resolved and presented.

Table 5.2: Experimental values of the Ne-like krypton DR LM*n* resonances in the electron beam and photon energies (eV) obtained with the fit procedure. The values obtained by applying the same fit procedure to the FAC calculations are also presented.

	Leading intermediate conf.	E_e exp	E_e FAC	$E\gamma$ exp	$E\gamma$ FAC	Rel. I
LMM	$\left[2p_{1/2}^2 2p_{3/2}^3 3s_{1/2} 3d_{5/2}\right]_{J=3/2}$	588.7 ± 1.4	588.72	1801 ± 3	1792.6	50
	$\left[2p_{1/2}^2 2p_{3/2}^3 3s_{1/2} 3d_{5/2}\right]_{J=3/2}$	576.7 ± 1.4	576.94	1795 ± 3	1780.7	139
	$\left[2p_{1/2}^1 2p_{3/2}^4 3s_{1/2} 3d_{3/2}\right]_{J=3/2}$	629.0 ± 1.4	643.57	1831 ± 3	1806.1	164
	$\left[2p_{1/2}^2 2p_{3/2}^3 3p_{3/2} 3d_{3/2}\right]_{J=3/2}$	644.4 ± 1.4	628.42	1814 ± 4	1818.5	202
	$\left[2p_{1/2}^2 2p_{3/2}^3 3p_{3/2} 3d_{3/2}\right]_{J=3/2}$	656.9 ± 1.4	656.11	1805 ± 3	1793.7	377
	$\left[2p_{1/2}^1 2p_{3/2}^4 3p_{3/2} 3d_{3/2}\right]_{J=3/2}$	708.2 ± 1.4	696.96	1844 ± 4	1833.9	251
	$\left[2p_{1/2}^1 2p_{3/2}^4 3p_{3/2} 3d_{3/2}\right]_{J=5/2}$	682.5 ± 1.4	681.80	1835 ± 3	1829.0	205
	$\left[2p_{1/2}^1 2p_{3/2}^4 3p_{1/2} 3d_{3/2}\right]_{J=3/2}$	696.5 ± 1.4	707.56	1839 ± 3	1839.8	311
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{1/2} 3d_{5/2}\right]_{J=5/2}$	726.0 ± 1.4	725.11	1800 ± 3	1783.2	932
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{1/2} 3d_{5/2}\right]_{J=5/2}$	764.4 ± 1.4	763.00	1821 ± 3	1821.9	307
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{1/2} 3d_{5/2}\right]_{J=7/2}$	779.0 ± 1.4	777.65	1844 ± 3	1835.2	711
LMN	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 4d_{5/2}\right]_{J=7/2}$	1174.5 ± 1.4	1173.48	1807 ± 3	1796.6	174
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 4d_{5/2}\right]_{J=7/2}$	1153.5 ± 1.4	1150.27	1806 ± 3	1797.0	62
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 4d_{5/2}\right]_{J=7/2}$	1208.6 ± 1.4	1208.10	1811 ± 3	1799.0	860
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 4f_{7/2}\right]_{J=9/2}$	1227.3 ± 1.4	1225.73	1822 ± 3	1817.0	727
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 4d_{5/2}\right]_{J=7/2}$	1258.3 ± 1.4	1277.19	1849 ± 3	1852.9	573
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 4f_{7/2}\right]_{J=9/2}$	1277.4 ± 1.4	1257.43	1853 ± 3	1847.0	340
LMO	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 5d_{5/2}\right]_{J=7/2}$	1435.3 ± 1.4	1473.28	1812 ± 3	1848.7	536
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 5f_{7/2}\right]_{J=9/2}$	1460.0 ± 1.4	1433.38	1845 ± 4	1801.5	145
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 5d_{5/2}\right]_{J=7/2}$	1424.9 ± 1.4	1408.42	1812 ± 3	1798.5	513
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 5d_{5/2}\right]_{J=7/2}$	1484.1 ± 1.4	1459.13	1855 ± 3	1848.5	327
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 5f_{7/2}\right]_{J=9/2}$	1410.0 ± 1.4	1424.55	1808 ± 3	1799.8	159

Table 5.3: Continuation of Table 5.2.

	Leading intermediate conf.	E_e exp	E_e FAC	E_γ exp	E_γ FAC	Rel. I
LMP	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 5p_{3/2}\right]_{J=5/2}$	1474.0 ± 1.4	1482.54	1855 ± 3	1850.8	421
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 6f_{7/2}\right]_{J=9/2}$	1592.9 ± 1.4	1611.17	1857 ± 3	1801.5	578
	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 6f_{7/2}\right]_{J=9/2}$	1545.3 ± 1.4	1541.27	1822 ± 3	1800.4	553
LMQ	$\left[2p_{1/2}^2 2p_{3/2}^3 3d_{5/2} 7f_{7/2}\right]_{J=9/2}$	1612.8 ± 1.4	1589.65	1823 ± 3	1849.4	435
LMn	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 7d_{5/2}\right]_{J=7/2}$	1708.6 ± 1.4	1685.60	1846 ± 3	1802.6	377
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 7d_{5/2}\right]_{J=7/2}$	1661.4 ± 1.4	1705.60	1846 ± 3	1847.1	672
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 8f_{7/2}\right]_{J=9/2}$	1689.4 ± 1.4	1660.78	1821 ± 3	1839.1	225
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 11d_{5/2}\right]_{J=7/2}$	1760.4 ± 1.4	1736.14	1843 ± 3	1847.9	305
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 10f_{7/2}\right]_{J=9/2}$	1776.0 ± 1.4	1756.75	1835 ± 3	1837.1	311
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 8d_{5/2}\right]_{J=7/2}$	1739.7 ± 1.4	1773.71	1847 ± 3	1850.8	284
	$\left[2p_{1/2}^1 2p_{3/2}^4 3d_{3/2} 9f_{7/2}\right]_{J=9/2}$	1726.7 ± 1.4	1725.25	1822 ± 3	1804.6	216

With the centroids for the DR resonances analyzed, attention was given to the DR cross-sections, as well as to the excitation structures. While simple regions of interest could be used to make a projection of certain portions of the DR structure and compare with theoretical calculation, the fact that the DR satellites of different unresolved main lines were clearly separated presented unique conditions to apply decomposition methods to extract more information from the experimental data, not available by simple ROI methods. The NNMF method, described in the last Section, was applied to the experimental data. As seen before, due to the low resolution of the SDD, only the 3s and 3d line complexes are resolved after the collisional excitation threshold, yet, before this limit, and within the 3d line complex energy, the DR satellites of the 3C and 3D lines are effectively resolved from each other. Due to the nature of their satellites, their photon energies are closely related to the main line energies. As such, this fact could be used as a reference for decoupling the 3C and 3D structures across the entire spectrum, including the excitation region. The NNMF method was applied to the experimental data with a number of features $k = 3$.

The components of the matrix H , obtained with the NNMF method, are represented in Figure 5.6. Here, the blue line represents the projection of the entire two-dimensional spectra over the photon energy axis, while the red, green and orange lines representing the three profiles given by the decomposition. The three profiles follow a Gaussian distribution, something to be expected, as that is the profile given by the response of the

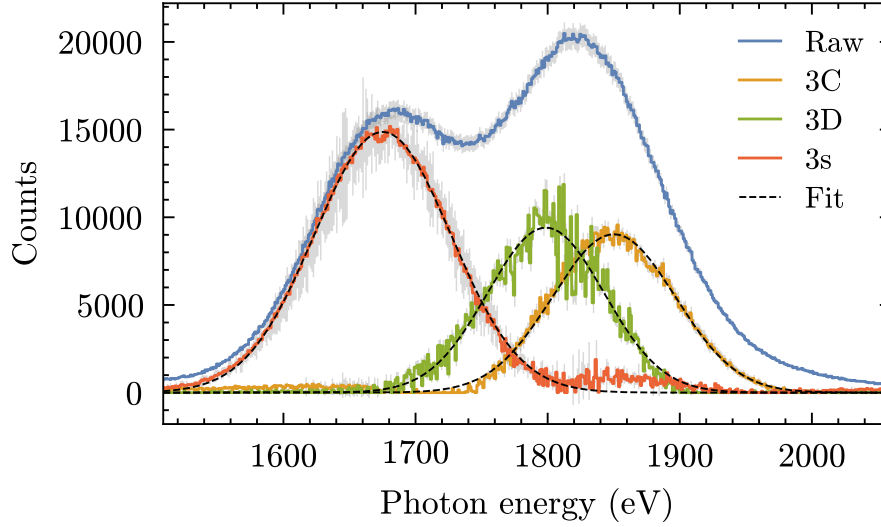


Figure 5.6: Experimental profile of the $L\alpha$ transitions decoupled with the NNMF method. The blue, green and black lines represent the 3s line complex, the 3D and 3C lines, respectively. The red lines represent the Gaussian fits applied to each transition.

SDD. The three histograms were fitted with the *lmfit python* package [214]. The fitted lines centroids are presented in Table 5.4, compared with experimental values from Santana *et al* [215], Rice *et al* [216] and theoretical values from the FAC calculations. The FWHM of the 3D and 3C lines were around 88 eV and 92 eV. The centroid uncertainty takes into account the statistical error from the fit and the uncertainty from the photon energy calibration. A component of uncertainty coming from the NNMF decomposition was also taken into account. To estimate this, a Monte Carlo approach was chosen. In this method, the input data was superimposed with around 5 % of random relative noise, similar to the level of noise present in the experimental data. Dozens of NNMF decompositions were made with different noises applied to the input data, and the standard deviation of each bin from the resulting H and W matrices was taken as the uncertainty of the decomposition method. This approach estimates the variation of the results when perturbing the initial data, leading to an empirical estimate of the uncertainty without the need for an analytically error propagation model. As observed, the centroids found from the fit to the 3C and 3D profiles are close to the expected theoretical values of the 3C and 3D lines, being in agreement within a few electronvolt. This shows that, for the separation between these two lines, the use of their respective DR satellite lines is enough to decouple the photon emission profiles of the two main lines after the excitation threshold.

While the NNMF method also returns the W matrix, which corresponds to the electron beam energy differential spectrum related to the decoupled main lines, one refinement was made before proceeding to the cross-section analysis. The NNMF method is used to generate the W and H matrices from a single X matrix without any prior knowledge from the W and H matrices besides their dimensions. In the current experiment, the photon energy profile is known to be given by a combination of Gaussian functions, where their

Table 5.4: Experimental centroids for the lines decomposed with the NNMF method. The values are compared with experimental values from Santana *et al* [215], Rice *et al* [216] and our theoretical values from FAC.

Line	Experiment	Santana	Rice (NIST)	FAC
3D	1799 ± 3	1802.175	1802.4	1801.90
3C	1851 ± 3	1850.976	1851.3	1851.02

widths are limited by the detector resolution and the centroids given by the transitions energy. Since the H matrix was found to be mostly represented by three components, each with one single Gaussian function, the parameters from the fit were used to generate a new H matrix build with pure Gaussian functions. As now both the X and H matrices are known, the W matrix can be recalculated with the new H matrix with the matrix inversion method,

$$W = X \times H^{-1}. \quad (5.7)$$

The matrix inversion and multiplication were carried out numerically with the *numpy* linear algebra tools. The components from the new W matrix are represented in Figure 5.7. The subplot (a) shows the total projection over the electron beam energy axis, while the components of the W matrix corresponding to the 3C, 3D and 3s line complexes are represented in the subplots (b), (c) and (d). This spectra have been corrected for the emissivity factor and the carbon filter transmission.

All the spectra in the Figure have been calibrated with the theoretical FAC DR LMM resonances. These calculations have been broadened to take into account the experimental electron beam energy spread, and have been corrected for the polarization and anisotropy factors. The 3D and 3C spectra cross-sections are dominated by the DR satellites, presenting a relatively low collisional excitation cross-section, while in the 3s spectrum is the opposite case. For the case of the 3C and 3D decomposition, the DR LM n structure can be observed, followed by collisional excitation of the respective main line. The DR LM n peaks are resolved up to $n = 9$. While the decomposition is enough to obtain good results in the photon energy matrix, there is significant DR peak cross-contamination between the two obtained spectra for the 3C and 3D lines structures. These contaminations are evident in the 3D line spectrum at 775 eV, which corresponds to the main 3C KLL satellites. Moreover, there are a few discrepancies for the case of the 3s at the collision threshold at higher energies that cannot be predicted. These contaminations come from peaks that are sufficiently isolated, so that a benchmark of theoretical calculations is still feasible. Nonetheless, our calculations are in reasonable agreement with the decomposed spectrum, highlighting the viability of the NNMF method to decompose unresolved lines and evaluate their corresponding spectrum individually.

One of the most studied problems of X-ray laboratory astrophysics is the disagreement of state-of-the-art atomic theory and laboratory measurements for the 3C/3D line ratio

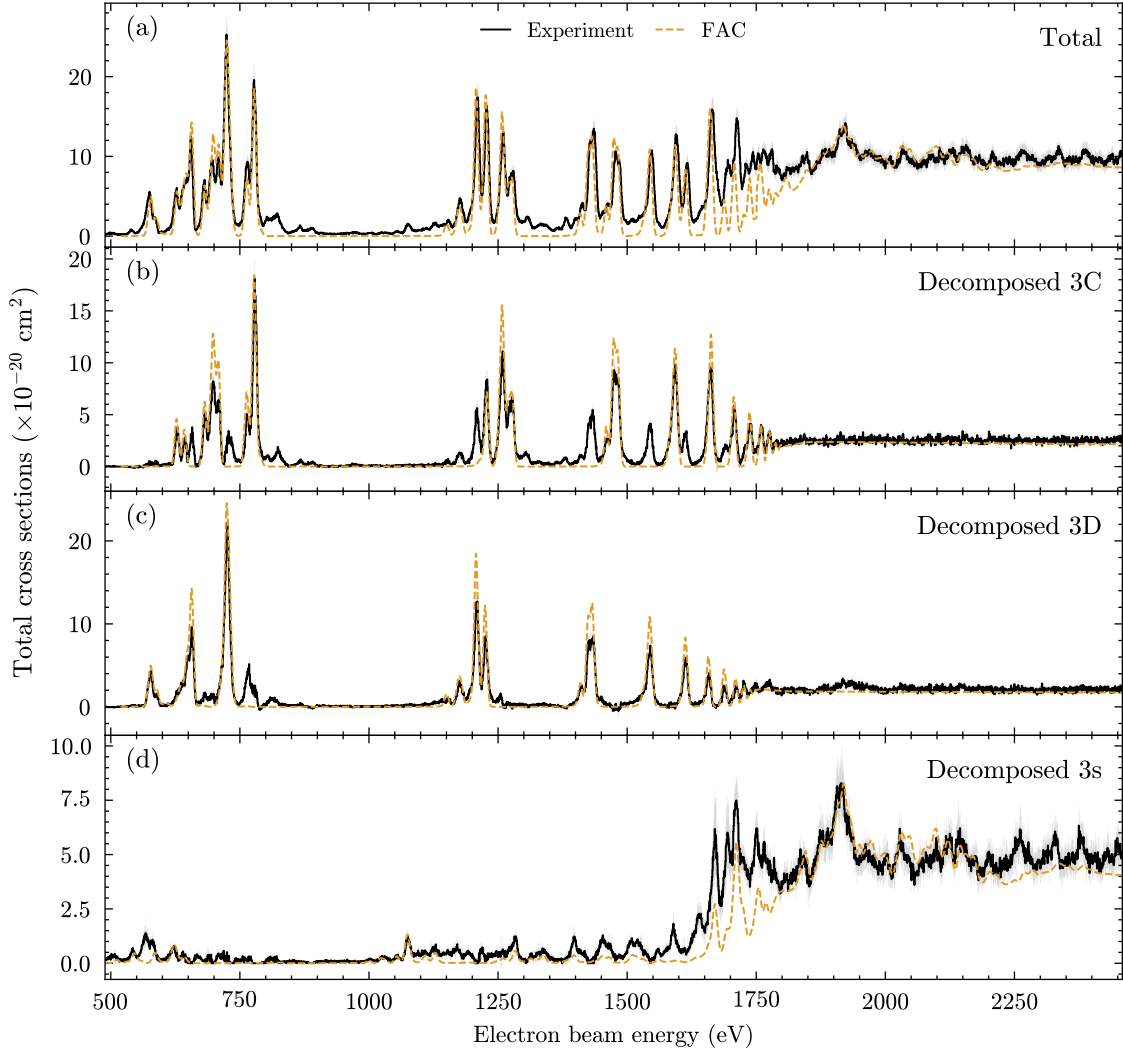


Figure 5.7: Components of the W matrix for the three transitions, 3D, 3C and 3s. The orange line represents the FAC calculations. (a) Total projection around the LM transition region. (b) Decomposed 3C region. (c) Decomposed 3D region. (d) Decomposed 3s region.

of Ne-like iron (see [211] and articles therein). Regardless of the small discrepancies in the decomposed DR satellite lines, the excitation threshold closely agrees with the FAC calculation. In this work, NNMF method was applied to decouple the 3C and 3D collisional excitation structures. This method thus gives the 3C/3D line ratio spectrum, which was compared with other theoretical and experimental results. Note that the spectra of the excitation structures have been normalized to the original blended experimental data by a single factor, so that the intensity ratio between the lines could be recovered regardless of the theoretical calculations. The result from the ratio, with the respective propagated errors, is represented in Figure 5.8. As the excitation cross-section of both structure should have the same shape, the ratio should be almost constant within this energy range. Instead of a constant fit, a linear fit was used to evaluate the a possible variability of the ratio

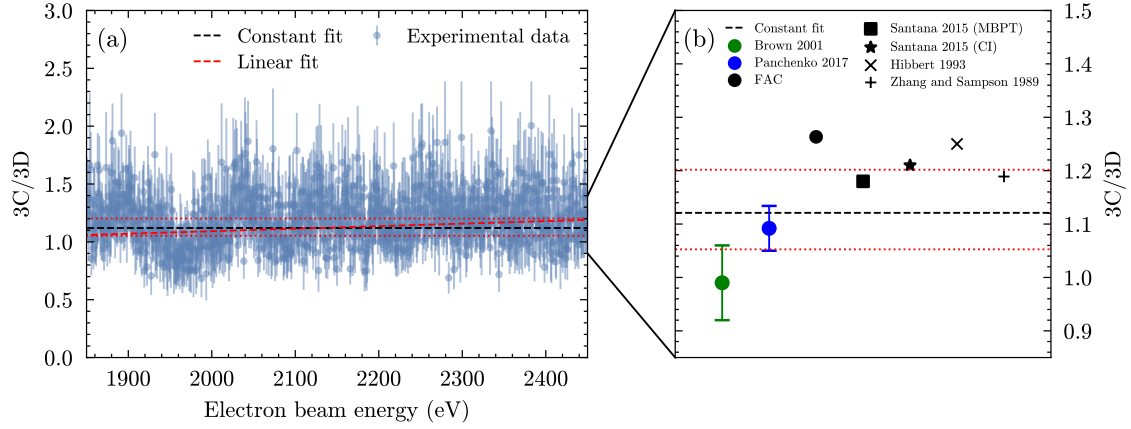


Figure 5.8: Experimental ratio between the 3C and 3D lines after the excitation threshold. The black and red dashed lines represent a constant and linear fit made to the experimental data. In (b), the fit results are compared with previous experimental observations [212, 217], as well as with theoretical results from FAC and other calculations in the literature [215, 218, 219].

with energy. Since the ratio is expected to be constant over these energies, we estimate the uncertainty due to this observed variability as the extreme values of the linear fit. The procedure results are represented in Figure 5.8. A value of 1.12 ± 0.08 was obtained after a linear fit. This value mostly agrees with previous measurements of 0.99 ± 0.07 [217] and 1.092 ± 0.042 [212], as well as state-of-the-art calculations, e.g. 1.18 for MBPT [215]. This comparison is represented in the subplot (b). This method showed positive results in determining experimental values from unresolved structures by decoupling them with a decomposition technique that used their satellite lines as a reference. As such, it could in principle can be applied in the future to heavier elements with potentially more promising results.

5.3 Tungsten

5.3.1 Experimental setup

The FLASH-EBIT was used to investigate the EUV emissions of open $4f$ -shell tungsten ions. The experimental setup followed very similar scheme to the one of the calcium experiment. This work differs from the previous ones, as the main purpose was to study multiple charge states simultaneously. This was done with an electron beam energy scheme comprised of very slow scans crossing the relevant ionization thresholds. The resulting two-dimensional spectrum was decomposed with the NNMF technique to decouple the emissions of each charge state individually. The resulting spectra were fitted and the general features were identified and tabulated.

The injection of tungsten in the EBIT was done by attaching a small container to the injection system. The container was filled with a solid (powder) sample of tungsten hexacarbonyl, $W(CO)_6$. The relatively high vapor pressure of this compound was enough to promote inflow of gas through the differential injection system without any heating. The needle valve was set to maintain a steady injection pressure or around 10^{-7} mbar. This pressure was measured with a pressure gauge attached to the injection system after the needle valve. This was adjusted regularly to maintain the injection pressure stable while the content of the container is being evaporated. As krypton, tungsten is easy to trap due to being a heavy element ($Z = 74$). As such, the trap was saturated with tungsten ions to ensure high emission rates and, thus, improving statistics.

The electron beam energy followed the exact same scheme as the oxygen and calcium experiments. The first AFG was used to generate a very slow triangular wave signal that drives an high voltage amplifier to control the voltage of the drift tube platform. The second AFG, synchronized with the first one, generated the signal to provide to the ADC to store the photon energy events with the respective electron beam scan state to allow the construction of a two-dimensional spectrum of emissions as a function of the electron beam energy and wavelength. The drift tube platform was set to scan the energy between 200 and 1000 eV with a duty cycle period of 30 minutes. This scanning period ensures the plasma has enough time to reach ionization equilibrium at each electron beam energy, so that the different charge states are observed. With this energy range, the tungsten plasma was dominated by charge states between $10+$ and $27+$. The ionization thresholds of the different charge states, with the respective electronic configuration of the ground state, are presented in Table 5.5. The minimum energy is right below the ionization threshold of $10+$ charge state, meaning the charge state of $9+$ could in principle be observed in the lower edge of the experimental data. In the other extreme, the higher energy limit is above the charge state of $27+$ but below the ionization threshold of $28+$, so that the $28+$ charge state could still be observable in the higher energy end. This set of charge states covers the entire open $4f$ -shell, with the charge state $27+$ having only one electron in this shell, and the charge state of $12+$ having this shell completely filled with 14 electrons. The charge

Table 5.5: Ionization energies of each charge state of tungsten with an open $4f$ -shell, as well as the respective ground electronic configurations. Values taken from the NIST ASD.

Ion species	Charge	Ground configuration	Ionization energy (eV)
W X	9+	$[\text{Kr}]4d^{10}4f^{14}5s^25p^3\ ^2P_{3/2}$	179.0
W XI	10+	$[\text{Kr}]4d^{10}4f^{14}5s^25p^2\ ^3P_0$	208.9
W XII	11+	$[\text{Kr}]4d^{10}4f^{13}5s^25p^2\ ^4F_{7/2}$	231.6
W XIII	12+	$[\text{Kr}]4d^{10}5s^24f^{14}\ ^1S_0$	258.3
W XIV	13+	$[\text{Kr}]4d^{10}5s^24f^{13}\ ^2F_{7/2}$	290.7
W XV	14+	$[\text{Kr}]4d^{10}5s^24f^{12}\ ^3H_6$	325.3
W XVI	15+	$[\text{Kr}]4d^{10}5s^24f^{11}\ ^4I_{15/2}$	361.9
W XVII	16+	$[\text{Kr}]4d^{10}5s4f^{11}\ ^5I_8$	387.9
W XVIII	17+	$[\text{Kr}]4d^{10}4f^{11}\ ^4I_{15/2}$	420.7
W XIX	18+	$[\text{Kr}]4d^{10}4f^{10}\ ^5I_8$	462.1
W XX	19+	$[\text{Kr}]4d^{10}4f^9\ ^6H_{15/2}$	502.6
W XXI	20+	$[\text{Kr}]4d^{10}4f^8\ ^7F_6$	543.4
W XXII	21+	$[\text{Kr}]4d^{10}4f^7\ ^8S_{7/2}$	594.5
W XXIII	22+	$[\text{Kr}]4d^{10}4f^6\ ^7F_0$	640.6
W XXIV	23+	$[\text{Kr}]4d^{10}4f^5\ ^6H_{5/2}$	685.6
W XXV	24+	$[\text{Kr}]4d^{10}4f^4\ ^5I_4$	734.1
W XXVI	25+	$[\text{Kr}]4d^{10}4f^3\ ^4I_{9/2}$	784.4
W XXVII	26+	$[\text{Kr}]4d^{10}4f^2\ ^3H_4$	833.4
W XXVIII	27+	$[\text{Kr}]4d^{10}4f\ ^2F_{5/2}$	881.4
W XXIX	28+	$[\text{Kr}]4d^{10}\ ^1S_0$	1132.2

states in between these two have sequentially one more electron in the $4f$ -shell, with the exception of the 15+ and the 16+, where the $5s$ -shell is filled instead of the $4f$ -shell.

The photon emissions were observed with the EUV detector. The MCP position was adjusted to observe wavelengths between 12.5 and 25 nm. Only the first order of diffraction was used for the observation, allowing a resolution of around 0.3 nm of FWHM. While a higher resolution could be achieved by taking advantage of the second order of diffraction, the emissions in this wavelength range did not have high enough count rates to consider this option viable. Nevertheless, some second order emissions from a different wavelength range were detected. An example of what was observed in the MCP for a single electron beam energy is presented in Figure 5.9 (a). To optimize the statistics of the detected signal, an ellipsoid region of interest was used to project the MCP signal into a wavelength axis. An example of the kind of region of interest is represented in the same Figure with a dashed line. The projection was corrected by the height of the ellipsoid to account for the

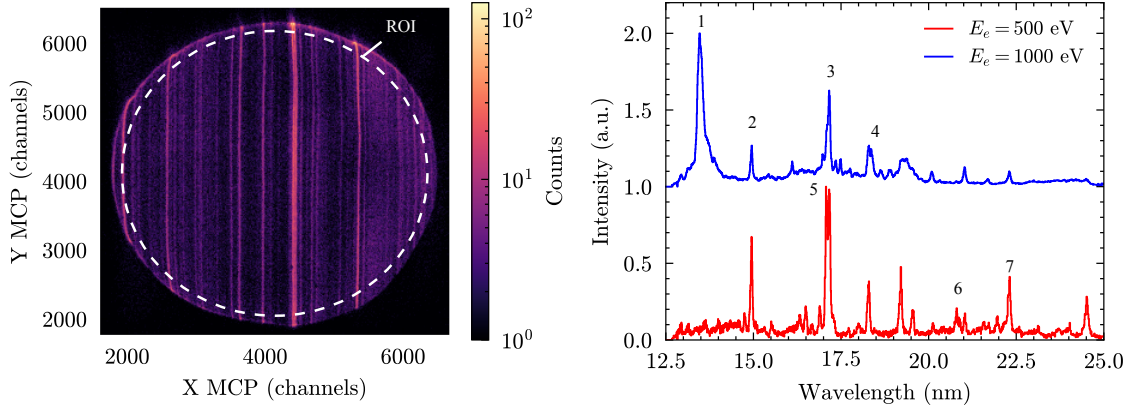


Figure 5.9: Observed EUV oxygen lines for calibration. On the left is one example of the MCP image for one of the oxygen measurements, on the right is the projected spectrum for the two measurements used for the calibration. The specific lines used in the calibration are labeled from 1 to 7. The red and blue lines correspond to an electron beam energy of 500 eV and 1000 eV, respectively.

accumulation of count in the middle when compared to the borders. The MCP signal was rotated to correct for the alignment of the MCP in relation to the reflection plane of the grating. The angle of rotation was found by minimizing the width of the observed lines after the projection. The MCP signal presented in the Figure has the rotation correction already applied. In the Figure, one can also see accumulations effects in the edges of the MCP. For this reason, the radius of the ellipsoid was shorted to avoid the edges of the signal. Moreover, the vertical lines present some wiggle effects due to small misalignments of the delay lines attached to the back of the MCP. These misalignments were not corrected in this work and can contribute to an overall broadening of the lines.

The wavelength axis was calibrated by injecting oxygen in the trap beforehand. This was done by attaching an oxygen bottle to the injection system and observing the resulting emissions with the MCP in the same conditions as the tungsten observations. Multiple measurements were made with a fixed electron beam energy to observe oxygen emission at different charge states. The main two measurements used for the calibration are represented in Figure 5.9 (b). The blue line correspond to an observation with a charge state balance dominated by Li-like oxygen (electron beam at 1000 eV), while the red line corresponds to emissions from a plasma with a charge state distribution with a high content by Be-like oxygen (electron beam at 500 eV). In this wavelength range, most of the observed lines correspond to $4d - 2p$, $3d - 2p$ and $3p - 2s$ transitions. The transitions identified in the Figure are listed in Table 5.6. Only well documented lines available in the NIST ASD were used. It was found that a quadratic relation was better suited for wavelength calibration than a simple linear relation due to geometric factors. This is due to the fact that the relation between the position of an event in the detector surface and angle of dispersion is not linear, since the focal plane after dispersion is curved. The quadratic term of the calibration helps correcting this non-linearity.

Table 5.6: Identification of the EUV oxygen lines used for calibration. The respective initial and final states of the transitions, along with their wavelengths, are listed in the table. Values taken from the NIST ASD.

Id	Ion	Initial configuration	Final configuration	Wavelength (nm)
1	O VI	$[1s_{1/2}^2 4d_{5/2}]_{J=5/2}$	$[1s_{1/2}^2 2p_{3/2}]_{J=3/2}$	12.9871
2	O VI	$[1s_{1/2}^2 3p_{3/2}]_{J=3/2}$	$[1s_{1/2}^2 2s_{1/2}]_{J=1/2}$	15.0089
3	O VI	$[1s_{1/2}^2 3d_{5/2}]_{J=5/2}$	$[1s_{1/2}^2 2p_{3/2}]_{J=3/2}$	17.3079
4	O VI	$[1s_{1/2}^2 3s_{1/2}]_{J=1/2}$	$[1s_{1/2}^2 2p_{3/2}]_{J=3/2}$	18.4117
5	O V	$[1s_{1/2}^2 2s_{1/2} 3p_{3/2}]_{J=1}$	$[1s_{1/2}^2 2s_{1/2}^2]_{J=0}$	17.2169
6	O V	$[1s_{1/2}^2 2p_{1/2} 2s_{3/2} 3d_{3/2}]_{J=3}$	$[1s_{1/2}^2 2p_{1/2} 2p_{3/2}]_{J=2}$	20.7794
7	O V	$[1s_{1/2}^2 2s_{1/2} 3d_{5/2}]_{J=2}$	$[1s_{1/2}^2 2s_{1/2} 2p_{3/2}]_{J=1}$	22.0352

After optimizing the electron beam and trap settings to maximize the emission rates, the data was acquired for two weeks. The resulting two-dimensional spectrum of the intensity as a function of the wavelength and electron beam energy is shown in Figure 5.10. Here, the electron beam energy is the nominal energy given by the voltages of the drift tube platform and the electron gun cathode, not taking into account the energy correction given by the space charge of the ion cloud and the electron beam. As the differential cross-section observation was not an objective of this measurement, the correct calibration of the electron beam energy is not relevant, as long as the emissions of each charge state are identifiable. The ionization thresholds of every charge state of tungsten is also represented in the Figure. These energies have a constant offset of 27 eV to roughly compensate for the space charge correction. The offset value gives a reasonable alignment of the ionization thresholds with the changes of charge state emissions. As the charge state balance is constant for a given electron beam energy, there are clear variations of emission spectrum corresponding to the variation of the dominant charge state for a given energy. These variations occur non-linearly and, with the obtained offset, they agree very well with the ionization thresholds. The main spectral features are similar between spectra of different charge states, and clear tendencies can be observed. This is expected, as most of the charge states observed have a similar electronic configuration with only a different number of electrons in the $4f$ -shell. Even though the excitation thresholds are very close to each other, a very good separation between charge states was found, with each charge state mostly dominating the charge state balance after crossing the previous charge state ionization threshold.

Thinner lines are also observed in the charge states at the higher and lower energy ends of the spectrum. These could be either attributed to charge states with a closed or an empty $4f$ -shell with a simpler emissions structure, or possibly to second order diffraction

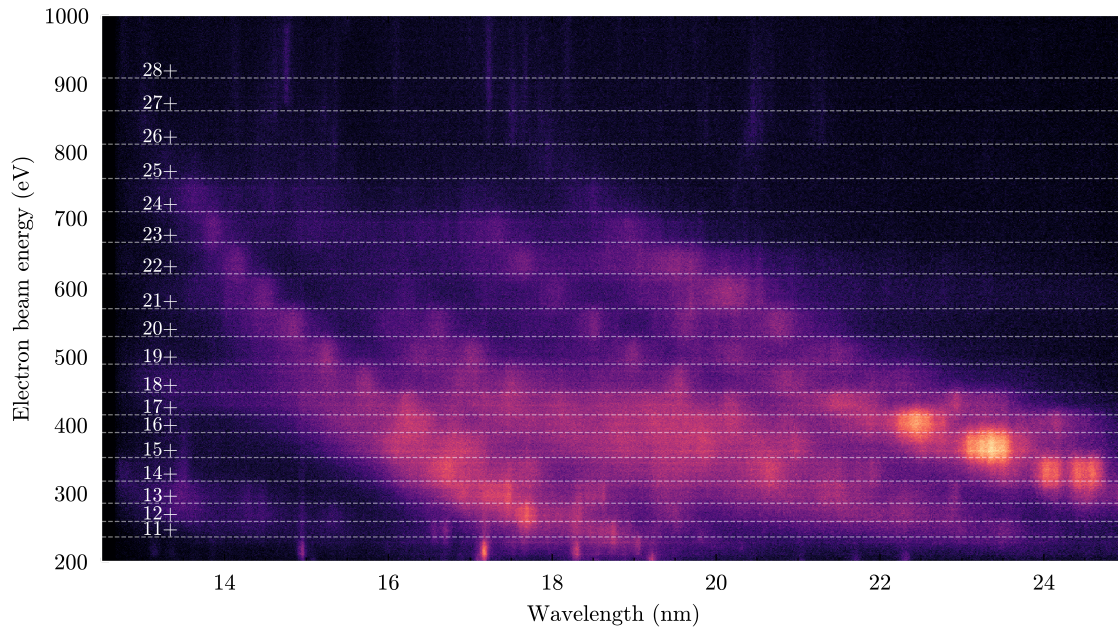


Figure 5.10: Intensity as a function of the electron beam energy and the photon wavelength for the slow scan measurement of tungsten. The ionization threshold of each charge state in the measurements are represented by the dashed lines.

emissions from a different wavelength range. The thin lines are mostly absent from the rest of the scanned electron beam energy range.

5.3.2 Theoretical calculations

As the scan was very slow, the emission spectrum can be simulated with a simple steady-state CRM. As each charge state only emits for a very narrow range of electron beam energy, the average energy can be used to simulate its emission spectrum in the experimental conditions. The FAC-CRM package was used to generate the emission spectra to compare with the experimental observation.

These observations present a different modeling challenge not present in the previous Chapters. Due to the complexity of the electronic structure, difficulties arise when calculating the necessary atomic data to use in the CRM. The observed charge states have the $4f$ shell as the valence orbital. This orbital can accommodate up to 14 electrons. As the number of states grows according to a binomial coefficient with the number of valence electrons m and the number of vacancies $\approx g = 2 \sum (2\ell + 1)$, given by (m, g) , the number of states increases exponentially. An additional complexity is that the observed emissions are actually produced by $n = 5$ intrashell transitions with maximum angular momentum of $\ell = g$, making the structure of every singly excited state vital for the correct simulation of the spectra.

FAC was also used to calculate the electronic structure, transitions rates and direct impact excitation cross-sections. The electronic structure was calculated for all the charge states, including the ground state configurations presented in Table 5.5, as well as singly

excited states from the $4f$ -shell into $n = 5$ and $n = 6$. In all cases, configurations with all the electrons in the $4f$ -shell, one in the $5s$ -shell and two in the $5s$ -shell were included to account for correlations effects between the $4f$ -shell and the $5s$ -shell. The singly excited state configurations included these extra sets of configurations to extend the correlations effects to the excited states. Following this binomial coefficients, the complexity of the structure was the lowest for the cases of only one electron or one vacancy in the $4f$ -shell, with a maximum of complexity in the half-filled shell charge states. The number of energy levels vary from a few hundred in the simplest cases to hundreds of thousands in the most complex cases. With this level of complexity, the calculation for the necessary atomic data becomes increasingly challenging. While the energy levels and radiative transitions were calculated for all charge states, the direct impact excitation was not calculated for the charge states between $18+$ and $24+$. Even though the atomic data for the rest of the cases was calculated with the computer cluster available at the MPIK, the CE calculation for this set of charge states was too computationally intensive, making it unfeasible in a reasonable amount of time. For these charge states, no complete CRM was calculated.

To circumvent this problem, the UTA mode of FAC was used to complement the theoretical calculations. This mode uses the SOSA approximation to simplify the electronic structures. This method is essentially a configuration averaged model, where most spin-orbital angular coupling is avoided without neglecting the relativistic contributions to the energy levels. While this method generally predicts structures at the right energies, details within each structure are lost. The cross-section calculations also present inaccurate results, and, as such, the UTA calculations were only used for structure identification. Due to the relatively low resolution of the spectrometer and the high complexity of the emission structure, only the main unresolved transition arrays were actually experimentally observed. For this reason, the UTA approximation is suitable for the analysis of this experiment. With these approximations, it was possible to include double and triple excitations from $4f$ to $n = 5, 6$ and still have a lower level of complexity. The simpler case had a few hundred energy levels, while the more complex one had tens of thousands of energy levels. The excitation cross-sections were calculated for all the charge state, as well as the relevant radiative transitions. The UTA CRM was calculated for all the charge states. The resulting emission spectra are represented in Figure 5.11.

The most intense emission structures can be found around a wavelength of 5 nm, corresponding to an energy of around 200 eV. These lines correspond to $n = 5$ to $n = 4$ transitions, which have already been studies extensively [111, 114]. The general structures observed experimentally are represented in the UTA plot between 12 and 25 nm. In this calculation, within the relevant wavelength range, there is always a dominant peak, which is not necessarily the case for the experimental observations. Furthermore, the experimental spectra of the lower charge states does present a dominant peak feature, but at the opposite wavelength limit of what is observed in the calculations. There is also a clear change in regime in the calculations between the charge states of $16+$ and $17+$. These are the charge states where the $5s$ -shell is stripped when ionizing this element.

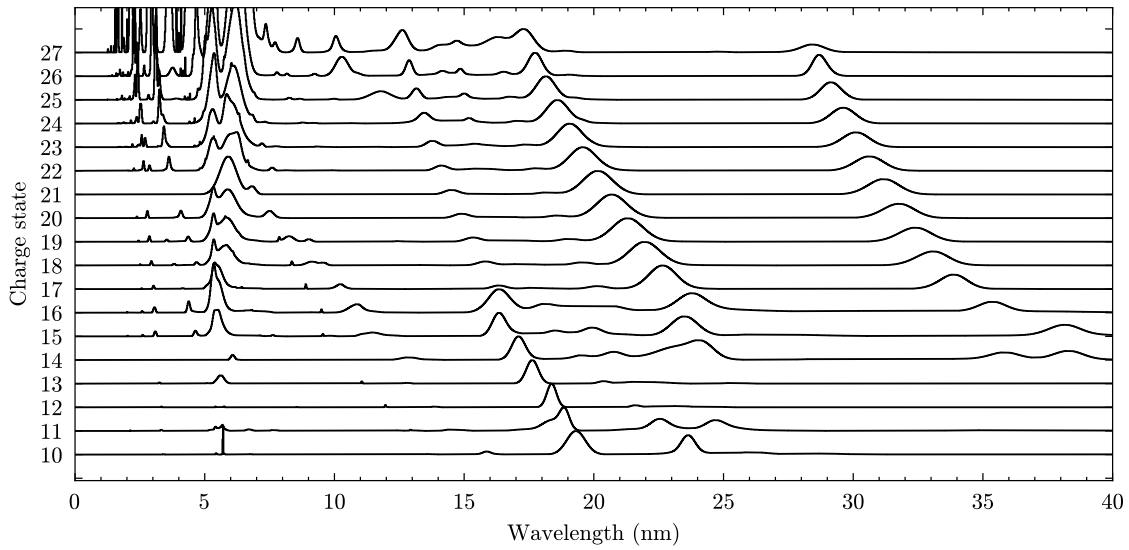


Figure 5.11: Theoretical EUV spectrum obtained with FAC CRM for each of the tungsten charge states. The atomic data was obtained with UTA method.

5.3.3 Results and discussion

The two-dimensional data presents the emission of the different charge states, with those being ionized and replaced by the next charge state as the energy of the electron beam is scanned. While simple rectangular ROI would be enough to retrieve most to the emission features from each charge state, there are small overlaps between charge state populations when their respective profiles are growing and decaying. This leads to cross-contamination of different charge states in each spectra when a wide electron beam energy region of interest is used. On the other hand, a very narrow ROI avoids this issue, but significantly compromises the available statistics. The NNMF decomposition was used to decouple every individual spectra, while maintaining the original statistics available for every emission structure.

In the case of the krypton experiment, the emission structures had smooth profiles over one axis that populated the presence of the remaining structures over the two-dimensional data. A similar situation is found in this experiment, there the spectra are modulated in the electron beam energy axis by the variation of the respective population profiles. While in the previous case, the free parameter corresponded to the number of expected transitions, in this case the free parameter corresponds to the expected number of charge states. As the population profiles are given by the solution of linear coupled differential equations, these are smooth functions, and in order to facilitate the decoupling of the emission spectra with realistic population profiles, a Gaussian filter was applied to the experimental data in the electron beam energy axis direction. This applies an artificial smoothing in this direction without directly affecting the statistical nature of the individual spectra over the wavelength axis. After this filter, the NNMF method from the *scikit-learn* package was applied to the data. The default settings from this package

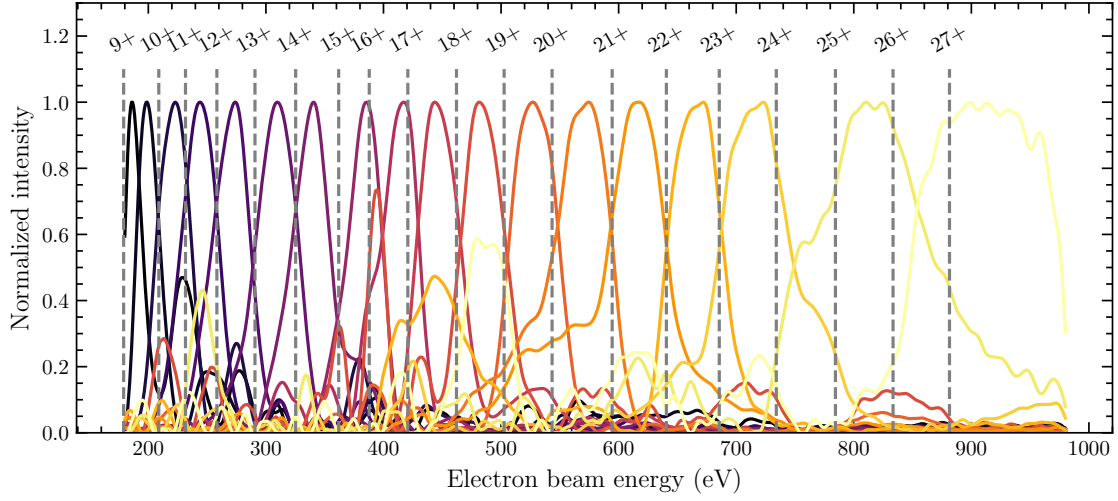


Figure 5.12: Components of the H matrix obtained with the NNMF method applied to the tungsten measurements. These components represent the population profile of each charge state as a function of the electron beam energy. The ionization threshold of each charge state is represented by the dashed lines.

were used, as they already presented the best results. The components of the resulting W matrix are represented in Figure 5.12, all normalize to facilitate the comparison between each other. The corresponding ionization thresholds are also represented by the vertical dashed lines. In this plot, the population profiles were corrected with the 27 eV offset to match the ionization thresholds. The ionization thresholds are around the middle of the growing portion of the next charge state, and a good agreement between the ionization thresholds and the spacing between population profiles was found. This agreement can be seen as an evidence for a correct identification of the charge states. In some cases, like the profile of the 22+ after the 21+ ionization threshold, or the 26+ profile after the 25+ ionization threshold, the respective population profiles start before the respective thresholds, presenting a secondary growth at that point. This can be explained by the potential existence of metastable states in the previous charge state. As these states need less energy to ionize (the energy of the excitation must be accounted for), the ionization of the charge state can happen as soon as the metastable state appears. There are still small artifacts across all the components of the W matrix in the background outside of the main population profile. Nonetheless, the portion of each curve presents a realistic behavior of growing smoothly after an ionization threshold and decaying smoothly after crossing the next one, being replaced by the next population profile. This is enough to draw some conclusions about the content of the individual spectra obtained with the NNMF. For instance, the first two profiles appear to correspond both to the charge state of 10+, while the last two curves appear to accumulate the charge states of 25+ and 26+, as well as 27+ and 28+ respectively.

The components of the H matrix are represented in Figure 5.13. Each component represents the extracted individual emission spectrum of a single charge state, with the

exception of 10+, which is splitted into the first two components, and 25+ to 28+, which are represented by only two components. In order to extract quantitative information from these spectra, the fit procedure was build to analyze each histogram. Due to the structure complexity and lack of reliable theoretical calculations, the k -means strategy was not used in this analysis. Instead, an automated procedure was build to fit a spectrum with a linear combination of Gaussian functions and iteratively determine the best value for the number of Gaussians to include and identify the main features. As the theoretical calculations cannot be done to their fully extent for every charge state, and the UTA calculations only provide a rough approximation of the experimental observations, no theoretical data can be used as a reference for the fitting process. In the beginning of the procedure, an initial number of Gaussians and centroid positions are given by the user. These are determined visually, and serve only as a starting point. The initial Gaussians width is estimated by the number of Gaussians provided. The fitting function is constructed with these parameters. The width variability is set as a parameter of the procedure and can be adjusted accordingly. Instead of using CERN ROOT for the fitting process, the current procedure was developed using the *lmfit python* package. This package stands for *Non-Linear Least-Squares Minimization and Curve-Fitting*, and its build on top of the *scipy.optimize* package to fit any set of datapoints with a user-defined non-linear curve using the least-squares minimization method. After fitting the data with the trial function, the integral of the residues (in this case squared differences between the fit and the experimental data) is computed. The number of Gaussians to include in the model is increased and a new fit is made. The variation of the residuals is tracked again. This procedure is looped with new trials functions and residual values, and the process is only halted when the variation of residuals is less than a user defined threshold. The objective is to find the minimum number of Gaussian functions that minimize the residuals without over fitting the experimental data. As the data initial centroids provided by the user correspond to the most intense peaks, the fitted resonances are matched to the initial user choices by proximity, identifying which Gaussian correspond to the main peaks of each spectrum. The fitted curve for each spectrum is represented in Figure 5.13 by the dashed line. The vertical red lines represent the identified main peaks of each spectrum. These structures are highly complex, and the use of this Gaussians is merely an approximation to correctly fit the curves and support the optimization of the Gaussians representing the main peaks. For this reason, these smaller peaks were not presented nor tabulated, as no useful information can be taken from them.

The most intense peaks of the FAC-UTA calculation were used to identify the main experimental features of each charge state spectrum. The main fitted peaks from the experimental data are represented in Figure 5.14. The experimental data point have already been separated into main groups representing different types of transitions. This was done by grouping the measured transitions according to the observed tendencies when plotted against the charge states. The groups are represented by the different colors. To avoid wrongly assigned transitions, the resonances from the first and last spectra

are not represented in the Figure. Since the peaks from the 25+ and 26+ charge states are present in the same spectrum, these are represented with their average charge state. The experimental data presents clear tendencies of increasing the wavelength with the decreasing of charge state. When observing only the most intense transitions in the FAC-UTA calculations within the same wavelength range, the same patterns as those observed in the experimental data become evident. The observed patterns were used to identify each of the main emission structures. The matched patterns from the UTA calculations are also presented in Figure 5.14. Six different main $n = 5$ intrashell transition groups were identified: $5d_{3/2} \rightarrow 5p_{1/2}$, $5f_{5/2} \rightarrow 5d_{3/2}$, $5f_{7/2} \rightarrow 5d_{5/2}$, $5d_{5/2} \rightarrow 5p_{3/2}$, $5d_{3/2} \rightarrow 5p_{3/2}$ and $5p_{3/2} \rightarrow 5s_{1/2}$. Even though the UTA method is a relatively low accuracy approximation, there is a fairly good agreement between the experimental centroids and the FAC-UTA calculations.

Transitions of type $5d_{3/2} \rightarrow 5p_{1/2}$ were observed across all charge states. While higher charge states agree almost perfectly with the calculations, the same structure for the charge states with an extra electron in the 5s presents some variability, splitting into two peaks. The peaks are still around the value given by the theoretical calculations, but, given the loss of details due to the UTA approximation, these structures were not modeled with full detail. The $5f_{5/2} \rightarrow 5d_{3/2}$ and $5f_{7/2} \rightarrow 5d_{5/2}$ transitions seem to increase in intensity with the decrease of the charge state. They become resolved from the charge state of 20+ and were fitted until the charge state of 17+. Although traces of these transitions are still present in lower charge states, they were not individually resolved and, therefore, not fitted. The ones that were fitted present an excellent agreement with the FAC calculations. The $5d_{5/2} \rightarrow 5p_{3/2}$ transitions were found to increase their intensity with the spectator electrons filling the 4f-shell. The intensity seems to maximize around the half-filled shell point, decreasing again for lower charge states. Resolved resonances were fitted for the charge states between 17+ and 24+. The $5d_{3/2} \rightarrow 5p_{3/2}$ transitions are very faint for higher charge states. These grow in intensity very quickly, becoming the most prominent of all lines observed in this experiment for the lower charge states. The highest charge state to have this line resolved was the 20+, with all the remaining charge states having the respective line fitted until 14+. Lower charge states than this emit lines outside of the observed wavelength range. Finally, the $5p_{3/2} \rightarrow 5s_{1/2}$ transitions were observed for most charge states. Although fainter at the higher charge states, their intensities are more or less steady across the rest charge states. These transitions were observed for the charge states between 26+ and 16+. Like the last case, the transitions of lower charge states were outside of the observed wavelength range.

To provide the experimental observations, the fitted resonances were listed in Table B.1. As the data is too extensive, it is provided in the Appendix B. The FAC-UTA correspondent transitions, as well as the higher and lower configurations that characterize each transition are provided. Although not clear how useful it is due to the complexity of the spectrum, the relative intensity of the observed resonances is also provided.

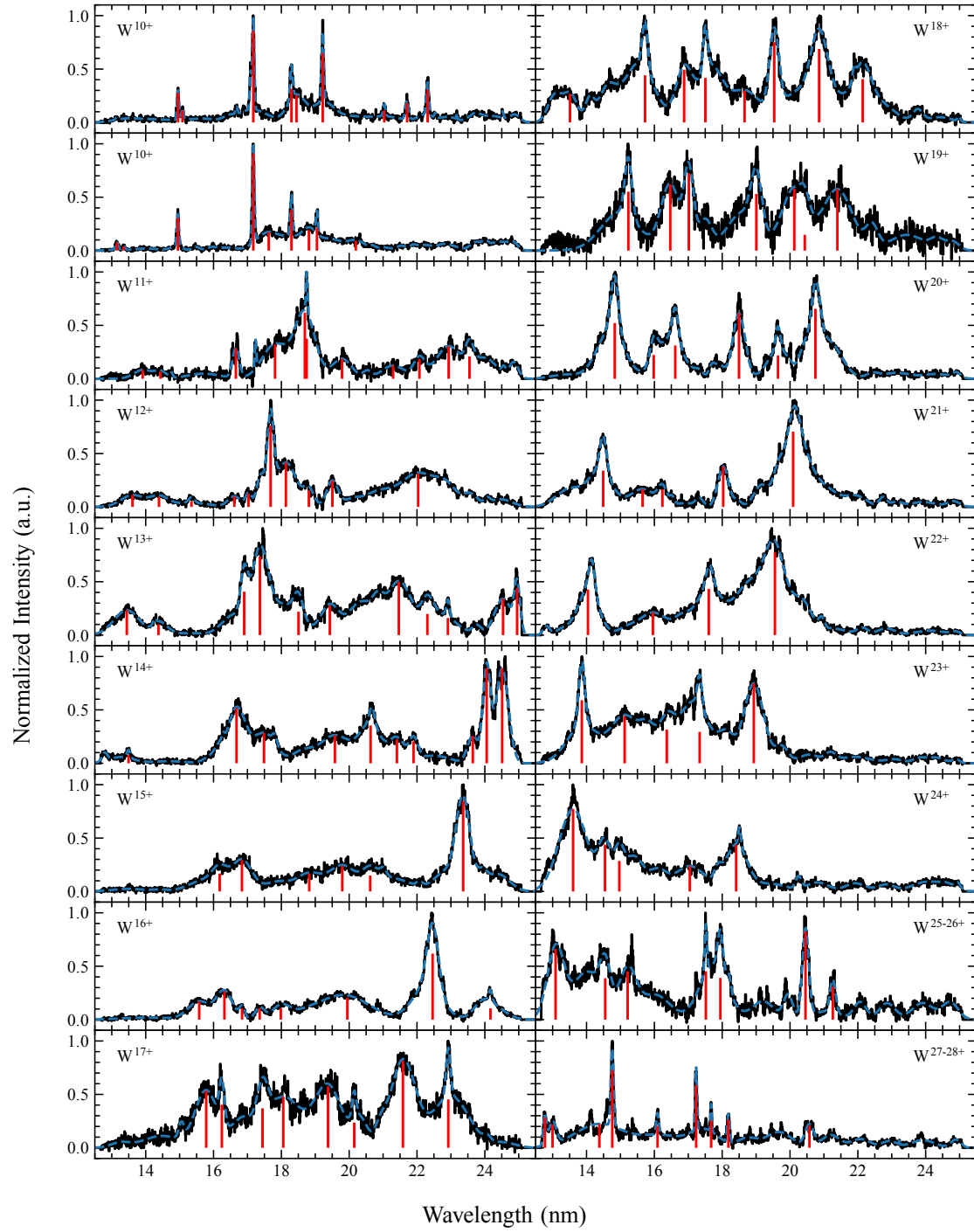


Figure 5.13: Components of the W matrix obtained by applying the NMF method to the tungsten observations. Each component represents a charge state individual emission spectrum as a function of the photon wavelength. The dashed lines represent the total fit, with the vertical red lines representing the main peaks of the fit. The charge state 10+ is represented twice, as it was decomposed into individual components.

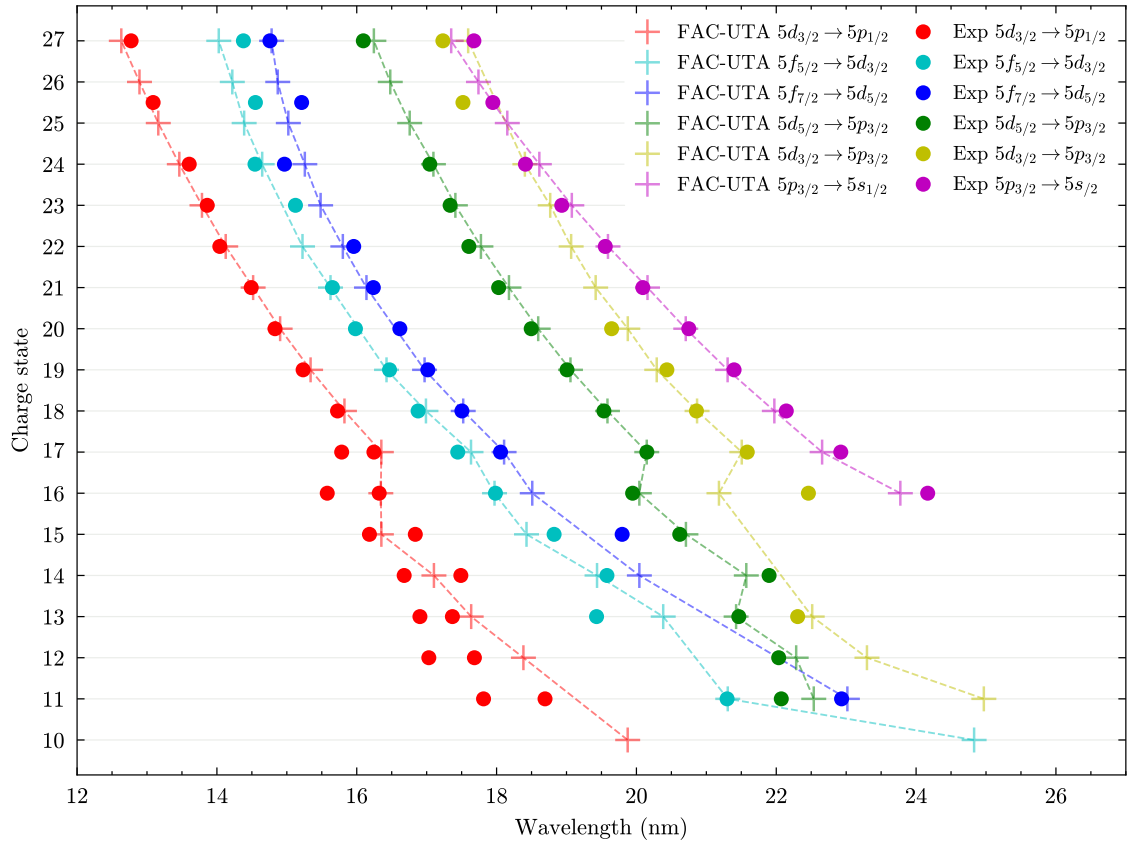


Figure 5.14: Wavelength of the main fitted peaks as a function of the respective charge state. The experimental wavelengths are represented by the circles. Different colors represent different types of $n = 5$ intrashell transitions. The corresponding transitions calculated with FAC-UTA are represented by the crosses.

CONCLUSIONS AND FUTURE PROSPECTS

In this thesis, five different atomic elements have been studied in the laboratory, benchmarking key atomic data that could have further applications in other scientific areas. The chosen elements have known applications in areas of astrophysics and nuclear reactor physics, covering the applicability of the atomic data from purely scientific to highly industrial applications.

The basis of atomic theory was reviewed, along with different approximation methods and codes to calculate atomic data, such as the electronic structure, radiative and non-radiative transition rates and resonant and non-resonant electron-ion collisional excitation, recombination and ionization processes.

The principles of a CRM were also introduced, with a brief history of its development and modern implementations. As a CRM is designed to reproduce the emission spectrum of a general plasma, it is the ideal model to compare to laboratory plasma experiments. Given the specific need of the experiments, a time-dependent implementation of the CRM framework was developed. A brief description of the mathematics behind it, as well as the computational implementation and verification were presented.

All the laboratory experiments in this project were made in an EBIT. A detailed description of this setup, as well as all the main components necessary for the experiment, were presented. It was described how the electron beam is generated, compressed and used to ionize an injected gas, as well as trap the resulting ions. The photon detection systems were also introduced, with a brief explanations about the SDD, the MCP, the EUV detector setup and how these components are used to measure the emission spectrum in the X-ray and EUV energy ranges. A final overview of the entire experimental setup was made, explaining how all the components work together to produce, trap and probe the ions, measure the resulting photon emission and store the experimental data for further analysis.

After introducing all the necessary basis to understand the principles behind the laboratory benchmarking experimental works, the latter were described in detail. Oxygen and calcium were studied due to their relevance for astrophysics. For the case of oxygen, one of the most abundant elements in the universe, the He-like charge state was probed

in the EBIT. As the objective was to study the DR and excitation threshold of this charge state, fast energy scans were performed and the $K\alpha$ line complex was observed. Modeling of metastable population dynamics during the scan allowed extraction of cross-section data. The newly developed time-dependent CRM was successfully used to describe these dynamics, being able to fully describe every detail of the experimental observations. The model was further used to remove the z-line emission component from the experimental data, allowing the benchmark of the resonant and non-resonant excitation structure near the collisional excitation threshold. Furthermore, a peculiar reduction effect was also observed in the DR KLL structure of the H-like charge state. This effect was also given by the He-like metastable state population dynamics, and a simple model was built to describe this phenomenon. Calcium was also injected in the EBIT to study its He-like emissions. The $K\alpha$ line complex of this charge state has been observed by the XRISM telescope, and it might be a good candidate to complement the lack of observation of the L-shell Ne-like iron emissions. The entire DR KLn structure of this ion was observed, as well as the $K\alpha$ excitation structure. The centroids of the DR satellites were fitted and tabulated, and the recombination and excitation cross-sections for this ion were provided.

Krypton and tungsten were also studied to provide useful benchmarked atomic data for nuclear reactor plasma diagnostics. The NNMF decomposition method was introduced as a technique to analyze unresolved structures from the experimental data. As krypton is one of the candidates to be injected in tokamaks for plasma diagnostics, the benchmark of its emission can provide valuable informations. As such, the DR LMn structure, as well as the respective excitation structure, were observed experimentally. As was the case for calcium, the DR resonances were fitted to provide the resonant electron and photon energies for each satellite line. Furthermore, the NNMF method was used to decouple the 3C from the 3D emission structure, providing the DR cross-section for the satellites of these main lines individually. The 3C/3D line ratio was also presented and compared with other references, and a reasonable value was achieved. Tungsten is also an element with an high demand of atomic data for all its charge states due to its use in plasma facing components. Slow energy scans provided observations of $n = 5$ intrashell transitions across all the charge states with an open $4f$ -shell. These transitions have been observed in tokamaks experiments before but, due to the similarity of these charge states, their emissions is always blended. The NNMF method was used to decompose the experimental data, allowing the study of the emission spectra of each charge state individually. It also provided a set of curves related to the population profiles of each charge state, quantity that was used to help identify them. FAC-UTA calculations were used to identify the main emission structures, which were fitted, and the respective wavelengths and transitions identification were tabulated.

In the future, the new CRM could be extended to model plasmas of calcium, krypton and tungsten. The presence and impact of metastable states during EBIT measurements could be studied thoroughly, as well as the respective effects in atomic data benchmarking and plasma diagnostics, particularly for astrophysics and fusion reactors.

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ATOMIC UNITS

All of the atomic theory formalism presented in this thesis follows the use of atomic units to simplify the mathematical formulations and highlight all the relations between quantities in each expression.

Depending on the used case, different unit systems can be devised to simplify the physical expressions that describe a system or phenomenon. The atomic units system is widely used in quantum mechanics, atomic, molecular and plasma physics, as it can greatly simplify their equations. A unit system is characterized by setting a groups of fundamental constants to unity, thereby removing them from the equations. In the case of atomic units, these constants are the electron mass, elementary charge, reduced Planck's constant and Coulomb's constant. The definition of these constants, along with their value in SI units, is represented in Table A.1.

Table A.1: Fundamental physical constants in SI units.

Quantity	Symbol	Value in SI Units
Electron mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
Elementary charge	e	$1.602 \times 10^{-19} \text{ C}$
Reduced Planck's constant	$\hbar$	$1.055 \times 10^{-34} \text{ J}\cdot\text{s}$
Coulomb's constant	$\frac{1}{4\pi\epsilon_0}$	$8.987 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2$

Using these four constants, one can construct the basis of the atomic units system. This basis is composed of the definitions of length, time, energy and charge. The units of length and energy are represented by new constants, known as the Bohr radius a_0 and the Hartree energy E_h . The expressions for each of the units, as well as the respective symbols and SI values, are represented in Table A.2.

As an example, let's apply the atomic units system to the Schrödinger equation for an H-like ion of atomic number Z , given by

$$i\hbar \frac{\partial}{\partial t} \psi = \left[-\frac{\hbar^2}{2m_e} \nabla^2 - \frac{Ze^2}{4\pi\epsilon_0 r} \right] \psi. \quad (\text{A.1})$$

Table A.2: Base atomic units.

Quantity	Symbol	Expression	SI Value
Length (Bohr radius)	a_0	$\frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	$0.529 \times 10^{-10} \text{ m}$
Time	t_a	$\frac{\hbar}{E_h}$	$2.42 \times 10^{-17} \text{ s}$
Energy (Hartree energy)	E_h	$\frac{m_e e^4}{4\pi\epsilon_0\hbar^2}$	$4.36 \times 10^{-18} \text{ J} = 27.2 \text{ eV}$
Charge	e	Elementary charge	$1.602 \times 10^{-19} \text{ C}$

By defining some physical constants as unitary, the previous equation simplifies to

$$i\frac{\partial}{\partial t}\psi = \left[-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right]\psi. \quad (\text{A.2})$$

As most of the physical constants are absent from the equation, it is easier to understand how the potential depends of the values of Z and r , as well and the general formulation of the kinetic energy term.

Every physical quantity can be derived from the units and physical constants presented in the Tables A.1 and A.2. A few examples quantities derived from these are presented in Table A.3.

Table A.3: Derived atomic units. The respective SI values are also represented.

Quantity	Symbol	Expression in a.u.	SI Value
Velocity (Bohr velocity)	v_0	$\frac{\hbar}{m_e a_0}$	$2.19 \times 10^6 \text{ m/s}$
Momentum	p_0	$m_e v_0$	$1.99 \times 10^{-24} \text{ kg}\cdot\text{m/s}$
Force	F_0	$\frac{E_h}{a_0}$	$8.24 \times 10^{-8} \text{ N}$
Frequency	ω_0	$\frac{E_h}{\hbar}$	$4.13 \times 10^{16} \text{ Hz}$
Electric field	E_0	$\frac{E_h}{e a_0}$	$5.14 \times 10^{11} \text{ V/m}$
Magnetic field	B_0	$\frac{\hbar}{e a_0^2}$	$2.35 \times 10^5 \text{ T}$
Temperature	T_0	$\frac{E_h}{k_B}$	$3.16 \times 10^5 \text{ K}$

There are other units systems that are often used in other fields. For example, natural units are usually used in particle physics, statistical physics and cosmology. In this system, the speed of light is set to be unitary, the length scale is defined by the Compton wavelength and the basic unit of energy is the electronvolt (eV).

TUNGSTEN EUV EMISSIONS FIT TABLE

Table B.1: Experimental values of the fitted emission structures for open $4f$ -shell ions of tungsten, compared with the identified structures given by FAC-UTA. The relative intensities of the fitted features are also presented.

Ion	λ_{Exp}	$\lambda_{\text{FAC-UTA}}$	Up conf.	Down conf.	Rel. Int.
W^{10+}	14.95 ± 0.06				0.02
	15.08 ± 0.03				0.01
	17.17 ± 0.40				0.06
	18.30 ± 0.58				0.03
	18.45 ± 0.18				0.17
	19.22 ± 0.01	19.322	$4f_{7/2}^7 5p_{1/2}^1 5p_{3/2}^1 5d_{3/2}^1$	$4f_{7/2}^7 5p_{3/2}^1$	0.05
	21.04 ± 0.01	20.751	$4f_{7/2}^7 5d_{5/2}^1$	$5p_{1/2}^2$	0.01
	21.71 ± 0.04				0.02
	22.31 ± 0.01				0.03
W^{10+}	13.15 ± 0.04				0.01
	13.35 ± 0.01				0.01
	14.95 ± 0.01				0.02
	17.17 ± 0.06				0.07
	17.63 ± 0.03				0.16
	18.30 ± 0.01				0.03
	18.81 ± 0.02				0.11
	19.05 ± 0.07	19.322	$4f_{7/2}^7 5p_{1/2}^1 5p_{3/2}^1 5d_{3/2}^1$	$4f_{7/2}^7 5p_{3/2}^1$	0.02

Ion	λ_{Exp}	$\lambda_{\text{FAC-UTA}}$	Up conf.	Down conf.	Rel. Int.
W ¹¹⁺	20.20 ± 0.09				0.06
	13.91 ± 0.02				0.05
	14.44 ± 0.07				0.03
	16.66 ± 0.05				0.07
	17.81 ± 0.02	17.362	$4f_{7/2}^6 5d_{5/2}^1$	$4f_{7/2}^7$	0.30
	18.69 ± 0.06	18.391	$4f_{7/2}^6 5p_{1/2}^1 5p_{3/2}^1 5d_{3/2}^1$	$4f_{7/2}^6 5p_{3/2}^1$	0.46
	18.75 ± 0.01	18.882	$4f_{7/2}^7 5p_{1/2}^1 5d_{3/2}^1$	$4f_{7/2}^7$	0.02
	19.79 ± 0.01				0.13
	21.30 ± 0.02	21.306	$4f_{5/2}^5 4f_{7/2}^7 5f_{5/2}^1$	$4f_{5/2}^5 4f_{7/2}^7 5d_{3/2}^1$	0.10
	22.07 ± 0.01	22.536	$4f_{7/2}^6 5d_{5/2}^1$	$4f_{7/2}^6 5p_{3/2}^1$	0.08
	22.93 ± 0.01	23.017	$4f_{7/2}^6 5f_{7/2}^1$	$4f_{7/2}^6 5d_{5/2}^1$	0.28
	23.55 ± 0.02				0.06
	13.61 ± 0.05	13.885	$4f_{7/2}^7 5f_{5/2}^1$	$4f_{7/2}^7 5p_{3/2}^1$	0.09
	14.39 ± 0.04				0.06
W ¹²⁺	15.35 ± 0.03				0.01
	16.61 ± 0.02				0.05
	17.03 ± 0.12				0.03
	17.68 ± 0.02				0.18
	18.13 ± 0.01	18.384	$4f_{7/2}^7 5d_{3/2}^1$	$4f_{7/2}^7 5p_{1/2}^1$	0.32
	18.81 ± 0.01				0.06
	19.51 ± 0.01				0.10
	22.03 ± 0.01	22.285	$4f_{7/2}^7 5d_{5/2}^1$	$4f_{7/2}^7 5p_{3/2}^1$	0.39
	13.44 ± 0.02				0.22
	14.38 ± 0.02				0.04
	16.90 ± 0.53				0.10
	17.37 ± 1.71	17.637	$4f_{7/2}^6 5d_{3/2}^1$	$4f_{7/2}^6 5p_{1/2}^1$	0.44
	18.51 ± 0.52				0.08
	19.43 ± 0.09	20.383	$4f_{7/2}^7 5s_{1/2}^1 5f_{5/2}^1$	$4f_{7/2}^6 5d_{3/2}^1$	0.18

APPENDIX B. TUNGSTEN EUV EMISSIONS FIT TABLE

Ion	λ_{Exp}	$\lambda_{\text{FAC-UTA}}$	Up conf.	Down conf.	Rel. Int.
W^{14+}	21.46 ± 0.01	21.426	$4f_{7/2}^6 5d_{5/2}^1$	$4f_{7/2}^6 5p_{3/2}^1$	0.45
	22.31 ± 0.01	22.514	$4f_{7/2}^6 5d_{3/2}^1$	$4f_{7/2}^6 5p_{3/2}^1$	0.08
	22.91 ± 0.08				0.02
	24.54 ± 0.01				0.21
	24.95 ± 0.02				0.09
	13.49 ± 0.07				0.01
	16.68 ± 0.01				0.34
	17.49 ± 0.07	17.104	$4f_{7/2}^5 5d_{3/2}^1$	$4f_{7/2}^5 5p_{1/2}^1$	0.23
	19.58 ± 0.15	19.437	$4f_{5/2}^5 4f_{7/2}^6 5f_{5/2}^1$	$4f_{5/2}^5 4f_{7/2}^6 5d_{3/2}^1$	0.30
	20.63 ± 0.63	20.783	$4f_{7/2}^5 5d_{5/2}^1$	$4f_{7/2}^5 5p_{3/2}^1$	0.28
	21.41 ± 0.02	21.116	$4f_{7/2}^5 5s_{1/2}^1 5p_{1/2}^1 5d_{5/2}^1$	$4f_{7/2}^5 5s_{1/2}^1 5p_{1/2}^1 5p_{3/2}^1$	0.12
	21.90 ± 0.02	21.571	$4f_{7/2}^6 5s_{1/2}^1 5d_{5/2}^1$	$4f_{7/2}^6 5s_{1/2}^1 5p_{3/2}^1$	0.07
	23.65 ± 0.03	23.154	$4f_{7/2}^5 5s_{1/2}^1 5p_{1/2}^1 5p_{3/2}^1$	$4f_{7/2}^5 5p_{1/2}^1$	0.10
	24.06 ± 0.02	24.192	$4f_{7/2}^6 5s_{1/2}^1 5p_{3/2}^1$	$4f_{7/2}^6$	0.25
	24.51 ± 0.08				0.41
W^{15+}	16.18 ± 0.02	16.352	$4f_{7/2}^4 5d_{3/2}^1$	$4f_{7/2}^4 5p_{1/2}^1$	0.09
	16.84 ± 0.13	16.932	$4f_{7/2}^5 5s_{1/2}^1 5d_{3/2}^1$	$4f_{7/2}^5 5s_{1/2}^1 5p_{1/2}^1$	0.22
	18.82 ± 0.12	18.428	$4f_{5/2}^3 4f_{7/2}^7 5f_{5/2}^1$	$4f_{5/2}^5 4f_{7/2}^5 5d_{3/2}^1$	0.16
	19.80 ± 0.31	18.981	$4f_{5/2}^3 5s_{1/2}^1 5f_{5/2}^1$	$4f_{7/2}^4 5d_{5/2}^1$	0.22
	20.62 ± 0.03	20.708	$4f_{7/2}^5 5s_{1/2}^1 5d_{5/2}^1$	$4f_{7/2}^5 5s_{1/2}^1 5p_{3/2}^1$	0.09
	23.36 ± 0.02				0.44
W^{16+}	15.58 ± 0.01				0.14
	16.32 ± 0.13	16.344	$4f_{7/2}^4 5s_{1/2}^1 5d_{3/2}^1$	$4f_{7/2}^4 5s_{1/2}^1 5p_{1/2}^1$	0.15
	16.84 ± 0.02	16.921	$4f_{7/2}^5 5d_{3/2}^1$	$4f_{7/2}^5 5p_{1/2}^1$	0.02
	17.36 ± 0.01				0.04
	17.98 ± 0.01	17.971	$4f_{5/2}^5 4f_{7/2}^5 5s_{1/2}^1 5f_{5/2}^1$	$4f_{5/2}^5 4f_{7/2}^5 5s_{1/2}^1 5d_{3/2}^1$	0.07
	19.95 ± 0.01	20.042	$4f_{7/2}^4 5s_{1/2}^1 5d_{5/2}^1$	$4f_{7/2}^4 5s_{1/2}^1 5p_{3/2}^1$	0.36
	22.46 ± 0.03	21.328	$4f_{7/2}^4 5s_{1/2}^1 5d_{3/2}^1$	$4f_{7/2}^4 5s_{1/2}^1 5p_{3/2}^1$	0.26

Ion	λ_{Exp}	$\lambda_{\text{FAC-UTA}}$	Up conf.	Down conf.	Rel. Int.
W ¹⁷⁺	24.17 ± 0.49	23.775	$4f_{7/2}^5 5p_{3/2}^1$	$4f_{7/2}^5 5s_{1/2}^1$	0.01
	15.78 ± 0.03				0.44
	16.25 ± 0.10	16.352	$4f_{7/2}^4 5d_{3/2}^1$	$4f_{7/2}^4 5p_{1/2}^1$	0.08
	17.44 ± 0.08	17.634	$4f_{7/2}^4 5f_{5/2}^1$	$4f_{7/2}^4 5d_{3/2}^1$	0.15
	18.06 ± 0.02	18.107	$4f_{7/2}^4 5f_{7/2}^1$	$4f_{7/2}^4 5d_{5/2}^1$	0.64
	19.38 ± 0.02				0.57
	20.15 ± 0.01	20.148	$4f_{7/2}^4 5d_{5/2}^1$	$4f_{7/2}^4 5p_{3/2}^1$	0.03
	21.58 ± 0.01	21.507	$4f_{7/2}^4 5d_{3/2}^1$	$4f_{7/2}^4 5p_{3/2}^1$	0.75
W ¹⁸⁺	22.92 ± 0.03	22.656	$4f_{7/2}^4 5p_{3/2}^1$	$4f_{7/2}^4 5s_{1/2}^1$	0.07
	13.51 ± 0.05				0.14
	15.73 ± 0.05	15.824	$4f_{5/2}^5 4f_{7/2}^4 5d_{3/2}^1$	$4f_{5/2}^5 4f_{7/2}^4 5p_{1/2}^1$	0.09
	16.88 ± 0.02	16.990	$4f_{5/2}^5 4f_{7/2}^4 5f_{5/2}^1$	$4f_{5/2}^5 4f_{7/2}^4 5d_{3/2}^1$	0.30
	17.50 ± 0.02	17.523	$4f_{5/2}^5 4f_{7/2}^4 5f_{7/2}^1$	$4f_{5/2}^5 4f_{7/2}^4 5d_{5/2}^1$	0.07
	18.66 ± 0.01				0.34
	19.53 ± 0.02	19.586	$4f_{5/2}^5 4f_{7/2}^4 5d_{5/2}^1$	$4f_{5/2}^5 4f_{7/2}^4 5p_{3/2}^1$	0.26
	20.86 ± 0.02	20.867	$4f_{5/2}^5 4f_{7/2}^4 5d_{3/2}^1$	$4f_{5/2}^5 4f_{7/2}^4 5p_{3/2}^1$	0.43
W ¹⁹⁺	22.14 ± 0.01	21.973	$4f_{5/2}^5 4f_{7/2}^4 5p_{3/2}^1$	$4f_{5/2}^5 4f_{7/2}^4 5s_{1/2}^1$	0.26
	15.23 ± 0.06	15.340	$4f_{5/2}^4 4f_{7/2}^4 5d_{3/2}^1$	$4f_{5/2}^4 4f_{7/2}^4 5p_{1/2}^1$	0.15
	16.47 ± 0.02	16.426	$4f_{5/2}^4 4f_{7/2}^4 5f_{5/2}^1$	$4f_{5/2}^4 4f_{7/2}^4 5d_{3/2}^1$	0.43
	17.02 ± 0.01	16.970	$4f_{5/2}^5 4f_{7/2}^3 5f_{7/2}^1$	$4f_{5/2}^5 4f_{7/2}^3 5d_{5/2}^1$	0.25
	19.01 ± 0.02	19.057	$4f_{5/2}^5 4f_{7/2}^3 5d_{5/2}^1$	$4f_{5/2}^5 4f_{7/2}^3 5p_{3/2}^1$	0.21
	20.13 ± 0.01				0.53
	20.44 ± 0.02	20.291	$4f_{5/2}^4 4f_{7/2}^4 5d_{3/2}^1$	$4f_{5/2}^4 4f_{7/2}^4 5p_{3/2}^1$	0.05
	21.40 ± 0.01	21.304	$4f_{5/2}^5 4f_{7/2}^3 5p_{3/2}^1$	$4f_{5/2}^5 4f_{7/2}^3 5s_{1/2}^1$	0.63
W ²⁰⁺	14.83 ± 0.03	14.904	$4f_{5/2}^4 4f_{7/2}^3 5d_{3/2}^1$	$4f_{5/2}^4 4f_{7/2}^3 5p_{1/2}^1$	0.14
	15.98 ± 0.08	15.987	$4f_{5/2}^5 4f_{7/2}^2 5f_{7/2}^1$	$4f_{5/2}^4 4f_{7/2}^3 5d_{3/2}^1$	0.06
	16.62 ± 0.01	16.538	$4f_{5/2}^4 4f_{7/2}^3 5f_{5/2}^1$	$4f_{5/2}^4 4f_{7/2}^3 5d_{5/2}^1$	0.07
	18.50 ± 0.01	18.595	$4f_{5/2}^4 4f_{7/2}^3 5d_{5/2}^1$	$4f_{5/2}^4 4f_{7/2}^3 5p_{3/2}^1$	0.28

APPENDIX B. TUNGSTEN EUV EMISSIONS FIT TABLE

Ion	λ_{Exp}	$\lambda_{\text{FAC-UTA}}$	Up conf.	Down conf.	Rel. Int.
W^{21+}	19.65 ± 0.01	19.876	$4f_{5/2}^4 4f_{7/2}^3 5d_{3/2}^1$	$4f_{5/2}^4 4f_{7/2}^3 5p_{3/2}^1$	0.04
	20.75 ± 0.01	20.706	$4f_{5/2}^4 4f_{7/2}^3 5p_{3/2}^1$	$4f_{5/2}^4 4f_{7/2}^3 5s_{1/2}^1$	0.22
	14.49 ± 0.02	14.518	$4f_{5/2}^3 4f_{7/2}^3 5d_{3/2}^1$	$4f_{5/2}^3 4f_{7/2}^3 5p_{1/2}^1$	0.09
	15.65 ± 0.05	15.625	$4f_{5/2}^4 4f_{7/2}^2 5f_{5/2}^1$	$4f_{5/2}^4 4f_{7/2}^2 5d_{3/2}^1$	0.15
	16.24 ± 0.03	16.139	$4f_{5/2}^4 4f_{7/2}^2 5f_{7/2}^1$	$4f_{5/2}^4 4f_{7/2}^2 5d_{5/2}^1$	0.05
	18.03 ± 0.01	18.177	$4f_{5/2}^4 4f_{7/2}^2 5d_{5/2}^1$	$4f_{5/2}^4 4f_{7/2}^2 5p_{3/2}^1$	0.15
W^{22+}	20.09 ± 0.02	20.159	$4f_{5/2}^4 4f_{7/2}^2 5p_{3/2}^1$	$4f_{5/2}^4 4f_{7/2}^2 5s_{1/2}^1$	0.34
	14.04 ± 0.04	14.126	$4f_{5/2}^3 4f_{7/2}^2 5d_{3/2}^1$	$4f_{5/2}^3 4f_{7/2}^2 5p_{1/2}^1$	0.33
	15.96 ± 0.01	15.801	$4f_{5/2}^3 4f_{7/2}^2 5f_{7/2}^1$	$4f_{5/2}^3 4f_{7/2}^2 5d_{5/2}^1$	0.23
	17.60 ± 0.01	17.776	$4f_{5/2}^3 4f_{7/2}^2 5d_{5/2}^1$	$4f_{5/2}^3 4f_{7/2}^2 5p_{3/2}^1$	0.43
	19.55 ± 0.06	19.593	$4f_{5/2}^3 4f_{7/2}^2 5p_{3/2}^1$	$4f_{5/2}^3 4f_{7/2}^2 5s_{1/2}^1$	0.60
W^{23+}	13.86 ± 0.11	13.786	$4f_{5/2}^3 4f_{7/2}^1 5d_{3/2}^1$	$4f_{5/2}^3 4f_{7/2}^1 5p_{1/2}^1$	0.13
	15.12 ± 0.01	14.888	$4f_{5/2}^2 4f_{7/2}^2 5f_{5/2}^1$	$4f_{5/2}^2 4f_{7/2}^2 5d_{3/2}^1$	0.45
	16.37 ± 0.03				0.17
	17.34 ± 0.03	17.411	$4f_{5/2}^3 4f_{7/2}^1 5d_{5/2}^1$	$4f_{5/2}^3 4f_{7/2}^1 5p_{3/2}^1$	0.05
	18.93 ± 0.03	19.076	$4f_{5/2}^3 4f_{7/2}^1 5p_{3/2}^1$	$4f_{5/2}^3 4f_{7/2}^1 5s_{1/2}^1$	0.55
W^{24+}	13.60 ± 0.01	13.462	$4f_{5/2}^2 4f_{7/2}^1 5d_{3/2}^1$	$4f_{5/2}^2 4f_{7/2}^1 5p_{1/2}^1$	0.80
	14.54 ± 0.01	15.257	$4f_{5/2}^2 4f_{7/2}^1 5f_{7/2}^1$	$4f_{5/2}^2 4f_{7/2}^1 5d_{5/2}^1$	0.22
	14.97 ± 0.10	14.648	$4f_{5/2}^2 4f_{7/2}^1 5f_{5/2}^1$	$4f_{5/2}^2 4f_{7/2}^1 5d_{3/2}^1$	0.09
	17.04 ± 0.03	17.096	$4f_{5/2}^2 4f_{7/2}^1 5d_{5/2}^1$	$4f_{5/2}^2 4f_{7/2}^1 5p_{3/2}^1$	0.27
	18.41 ± 0.01	18.404	$4f_{5/2}^2 4f_{7/2}^1 5d_{3/2}^1$	$4f_{5/2}^2 4f_{7/2}^1 5p_{3/2}^1$	0.35
	13.09 ± 0.02	13.161	$4f_{5/2}^1 4f_{7/2}^1 5d_{3/2}^1$	$4f_{5/2}^1 4f_{7/2}^1 5p_{1/2}^1$	0.41
$\text{W}^{25+/26+}$	14.55 ± 0.05	14.390	$4f_{5/2}^1 4f_{7/2}^1 5f_{5/2}^1$	$4f_{5/2}^1 4f_{7/2}^1 5d_{3/2}^1$	0.15
	15.21 ± 0.01	15.021	$4f_{5/2}^2 5f_{7/2}^1$	$4f_{5/2}^2 5d_{5/2}^1$	0.29
	17.52 ± 0.02	17.741	$4f_{5/2}^1 5p_{3/2}^1$	$4f_{5/2}^1 5s_{1/2}^1$	0.04
	17.95 ± 0.05	18.153	$4f_{5/2}^2 5p_{3/2}^1$	$4f_{5/2}^2 5s_{1/2}^1$	0.08
	20.46 ± 0.02				0.20
	21.26 ± 0.01				0.06

Ion	λ_{Exp}	$\lambda_{\text{FAC-UTA}}$	Up conf.	Down conf.	Rel. Int.
W^{27+}	12.77 ± 0.01	12.633	$5d_{3/2}^1$	$5p_{1/2}^1$	0.03
	13.00 ± 0.01				0.06
	14.38 ± 0.06	14.027	$5f_{5/2}^1$	$5d_{3/2}^1$	0.40
	14.76 ± 0.01	14.782	$4d_{5/2}^5 4f_{5/2}^1 5f_{7/2}^1$	$4d_{5/2}^5 4f_{5/2}^1 5d_{5/2}^1$	0.07
	16.09 ± 0.08	16.245	$4d_{5/2}^5 4f_{5/2}^1 5d_{5/2}^1$	$4d_{5/2}^5 4f_{5/2}^1 5p_{3/2}^1$	0.02
	17.23 ± 0.01	17.351	$5p_{3/2}^1$	$5s_{1/2}^1$	0.04
	17.68 ± 0.01	17.594	$5d_{3/2}^1$	$5p_{3/2}^1$	0.01
	18.18 ± 0.01				0.03
	20.57 ± 0.01				0.07

SCIENTIFIC OUTPUT

First author publications

- Grilo, F., Shah, C., Marques, J., et al. "Measurement of differential collisional excitation cross sections for the K emission of He-like oxygen." *Physical Review A*, vol. 110, no. 4, p. 042827, 2024. doi: <https://doi.org/10.1103/PhysRevA.110.042827>.
- Grilo, F., Shah, C., Kühn, S., et al. "Comprehensive Laboratory Measurements Resolving the LMM Dielectronic Recombination Satellite Lines in Ne-like Fe xvii Ions." *The Astrophysical Journal*, vol. 913, p. 140, 2021. doi: <https://doi.org/10.3847/1538-4357/abf737>.

Other publications

- Biela-Nowaczyk, W., Grilo, F., Amaro, P., et al. "L-Mn dielectronic recombination of cerium ions in a room-temperature EBIT." *Journal of Physics B: Atomic, Molecular and Optical Physics*, vol. 57, no. 5, p. 055201, 2024. doi: <https://doi.org/10.1088/1361-6455/ad2b72>.
- Biela-Nowaczyk, W., Amaro, P., Grilo, F., La Mantia, D. S., Tanis, J., and Warczak, A. "Hypersatellite $K\alpha$ Production in Trapped Ar Ions at KK Trielectronic Recombination Energies." *Atoms*, vol. 11, no. 3, p. 58, 2023. doi: <https://doi.org/10.3390/atoms11030058>.
- Pinheiro, D., Fernandes, A., Godinho, C., et al. "K- and L-shell theoretical fluorescence yields for the Fe isonuclear sequence." *Radiation Physics and Chemistry*, vol. 203, p. 110594, 2023. doi: <https://doi.org/10.1016/j.radphyschem.2022.110594>.
- Biela-Nowaczyk, W., Amaro, P., Grilo, F., and Warczak, A. "Higher-Order Recombination Processes in Argon Ions Observed via X-ray Emission in an EBIT." *Atoms*, vol. 11, no. 1, pp. 1, 2022. doi: <https://doi.org/10.3390/atoms11010001>.

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Manuscripts in preparation

- Grilo, F., Shah, C., Santos, J., et al. "Two-step approach to local time-equilibrium in dynamic collisional-radiative emission." Manuscript in preparation.
- Grilo, F., Shah, C., Marques, J., et al. "Reduction of the dielectronic recombination emissivity by a metastable cascade in H-like oxygen." Manuscript in preparation.
- Grilo, F., Shah, C., Botz, M., et al. "Non-Negative Matrix Factorization on L-Complex of Ne-like Kr." Manuscript in preparation.
- Grilo, F., Shah, C., Crespo López-Urrutia, J., et al. "EUV emissions from open 4f-shell W ions." Manuscript in preparation.
- Grilo, F., Botz, M., Shah, C., et al. "Precise energy measurement of the KLn dielectronic satellites of He-like Ca." Manuscript in preparation.





2025 Precision Benchmarking of Atomic Data of Highly Charged Ions

Filipe Grilo

