Single-photon multiple ionization processes studied by electron coincidence spectroscopy

Per Linusson
Abstract

This thesis is based on studies of multiple ionization of atoms and molecules induced by the absorption of a single photon. For the experimental investigations a time-of-flight magnetic bottle spectrometer has been used to detect the emitted electrons in coincidence. The method of coincidence time-of-flight spectroscopy and the experimental setup used is described. Experimental and theoretical results on molecular double core holes (DCHs) and multiple ionization of atoms are presented.

Molecular DCHs are of considerable interest, as their chemical shifts are predicted to be more sensitive than their single core hole counterparts. Using CH$_4$ and NH$_3$ as examples, it is shown that molecules with two vacancies in the innermost shell can be studied using synchrotron light in combination with our coincidence technique. The chemical shifts of S 2p DCHs are investigated for the molecules CS$_2$, H$_2$S and SO$_2$ and the influence of relaxation effects on the shifts are estimated.

In the studies of atoms, the main focus is on the processes leading to double and higher degrees of ionization, and the final state populations. In cadmium double photoionization in the photon energy region 40-200 eV occurs mainly by indirect ionization via valence ionized satellite states and through Coster-Kronig decay of inner shell hole states. In valence-valence ionization of krypton by 88 eV photons both direct and indirect ionization processes are found to be important. For the indirect pathways strong final state selectivity in the autoionization decays of the intermediate states is observed. Triple ionization of krypton via intermediate core-valence doubly ionized states is investigated. The intermediate states are observed in the energy region 120-125 eV, and their decay to states of the triply charged ion is mapped. Experimental and theoretical results on the formation of 2p double hole states in argon are presented.

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To my family
List of Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

PAPER I: Double core hole creation and subsequent Auger decay of NH\textsubscript{3} and CH\textsubscript{4} molecules

PAPER II: Structure sensitivity of double inner-shell holes in sulfur-containing molecules
P. Linusson, O. Takahashi, K. Ueda, J.H.D. Eland, and R. Feifel

PAPER III: Double ionization of atomic cadmium
P. Linusson, S. Fritzsche, J.H.D. Eland, L. Hedin, L. Karlsson and R. Feifel

PAPER IV: A complete double valence photoionization study of the electron spectra of krypton
In manuscript.

PAPER V: Formation of Kr\textsuperscript{3+} via core-valence doubly ionized intermediate states

PAPER VI: Single photon multiple ionization forming double vacancies in the 2p sub-shell of argon
P. Linusson, S. Fritzsche, J.H.D. Eland, M. Mucke and R. Feifel
PAPER VII: Versatile high-repetition-rate phase-locked chopper system for fast timing experiments in the vacuum ultraviolet and x-ray spectral region

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The following is a list of papers not included in the thesis.

- **Double photoionization of thiophene and bromine-substituted thiophenes**

- **Coincidence technique using synchrotron radiation for triple photoionization: Results on rare gas atoms**

- **Double photoionization of alcohol molecules**

- **A photoelectron and double photoionisation study of the valence electronic structure of 1,4-bromofluorobenzene**
M. Elshakre, F. Heijkenskjöld, P. Linusson, A. Gengelbach, T. Kloda, T. Hansson, L. Karlsson, and R. Feifel

- **Triple ionisation of methane by double Auger and related pathways**
J.H.D. Eland, P. Linusson, L. Hedin, E. Andersson, J.-E. Rubensson,
and R. Feifel


- **Triple ionisation spectra by coincidence measurements of double Auger decay: the case of OCS**

- **Spectra of the triply charged ion CS$_2^{3+}$ and selectivity in molecular Auger effects**

- **Core-valence double photoionization of the CS$_2$ molecule**

- **Strong-field photoionization of O$_2$ at intermediate light intensity**

- **Multielectron coincidence study of the double Auger decay of 3d-ionized krypton**

- **Experimental and theoretical study of core-valence double photoionization of OCS**

- **Single and multiple photoionisations of H$_2$S by 40 - 250 eV photons**
  J.H.D. Eland, R.F. Fink, P. Linusson, L. Hedin, S. Plogmaker, and R. Feifel
• **Triple ionization of CO$_2$ by valence and inner shell photoionization**
  J.H.D. Eland, L. Andric, P. Linusson, L. Hedin, S. Plogmaker, F. Penent, P. Lablanquie, and R. Feifel

• **Symmetry breaking in core-valence double photoionization of SO$_2$**

• **Influence of double Auger decay on low-energy 3d photoelectrons of Krypton**

• **Homonuclear site-specific photochemistry by an ion-electron multi-coincidence spectroscopy technique**
  J.H.D. Eland, P. Linusson, M. Mucke, and R. Feifel

• **Formation and decay of core-orbital vacancies in the water molecule**
  M. Mucke, J.H.D. Eland, O. Takahashi, P. Linusson, D. Lebrun, K. Ueda, and R. Feifel
Author’s contribution

I have actively participated in all the experiments presented in this thesis, including their preparation, with the exception of the helium lamp experiments on cadmium reported in Paper III and the Laser pump x-ray probe measurements reported in Paper VII. Apart from the experimental work, my main contribution to Paper I was to the discussion. I analyzed the experimental data presented in papers II-III and participated in the writing of Paper II. For Paper III, V and VI S. Fritzsche carried out the calculations and wrote the corresponding sections in these papers. I had the main responsibility of writing the remaining parts in Papers III and VI. For Paper V I extended a previous draft with new analysis and text in order to finalize the work. I proposed to carry out the measurements presented in paper IV and wrote the first complete draft of this work. For Paper VII I analyzed the time-of-flight data and wrote the corresponding section in the paper.
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1. Introduction

This thesis concerns the broad field of photoionization, which implies the emission of charged particles, i.e. electrons, from matter upon irradiation by light. The first experiment revealing the existence of this phenomenon was done by H. Hertz in 1887 [1]. It was some twenty years (1905) later interpreted by Einstein as what we today call the photoelectric effect [2].

In the late 1950’s and 1960’s photoelectron spectroscopy, measuring the energies of the electrons emitted in the light-matter interaction, was developed into an analytical tool. This was mainly accomplished by the development of high-resolution electron spectrometers, in combination with X-rays from rotating anodes, for which the group of K. Siegbahn was chiefly responsible [3]. Another important instrumental improvement was the introduction of the helium lamp [4], a high-intensity source of monochromatic light from the Vacuum-Ultra-Violet (VUV) spectral region, where the energy is sufficient for valence ionization of atoms and molecules.

A typical photoelectron spectrum is a histogram of the kinetic energies of the electrons emitted from an atom or molecule following impact by monochromatic light in the VUV to X-ray spectral regions. The kinetic energy of a photoelectron is given by

\[ E_{\text{kin}} = h\nu - (E_f - E_i) \]

where \( E_i \) and \( E_f \) denote the energy of the sample in the initial and final state, respectively, and \( h\nu \) is the photon energy. As the total momentum must be conserved in the collision, and the departing electron has momentum, the ion in the final state will recoil. The kinetic energy of the ion due to the recoil is, however, often comparatively small and can often be neglected for low energies of the outgoing electron. The photoelectron spectrum therefore reflects the difference in internal energy between the ion and the neutral species, a quantity referred to as the binding or, alternatively, ionization energy [5].

A simple interpretation of a photoelectron spectrum is by a frozen orbital independent particle approximation. In the Hartree-Fock (HF) method the average electron-electron interaction is approximated by a mean field, and atomic and molecular electronic wavefunctions are obtained as a single Slater-
Determinant of one-electron spin-orbitals\textsuperscript{1}. If, following photoionization, it is assumed that the molecular orbitals are the same, i.e. "frozen", in the ion and the neutral species, the binding energy can according to Koopman’s theorem\textsuperscript{2} \cite{koopman1934} be approximated with the energy of the orbital from which an electron was removed. Moreover the photoelectron carries away spin and angular momentum, which implies the photoelectron spectrum is devoid of strict selection rules affecting fluorescence and photoabsorption processes. Therefore, in the independent particle picture, the photoelectron spectrum will also reflect the orbital occupancy in the neutral species, presenting a "snapshot" of the electron orbitals in atoms and molecules.

An important early application of photoelectron spectroscopy was ESCA \cite{esca}, electron spectroscopy for chemical analysis, developed in the 1960’s and onwards by K. Siegbahn and co-workers in Uppsala. In the X-ray spectral region the photons have enough energy to eject strongly bound core electrons occupying the innermost orbitals. Even in the case of solids and molecules core electron orbitals are mainly localized\textsuperscript{3} to their parent atoms. Moreover, their binding energy is characteristic of the atom, which means the X-ray photoelectron spectrum of a sample can probe its composition. The binding energy of a core electron is however affected by the surroundings, or the chemical environment, of the atom, i.e. it might be subject to a measurable chemical shift. The magnitude of the chemical shift in molecules was originally approximated in Ref. \cite{esca} using a ground state potential model

\begin{equation}
\Delta E_A = kq_A + \sum_{A \neq B} q_B \frac{1}{R_{AB}}
\end{equation}

where \( q_A \) and \( q_B \), respectively, are the effective charges on the core ionized atom A and the ligands, respectively, \( R_{AB} \) denotes the inter-nuclei distance and \( k \) is a parameter representing the interaction between a core and valence electron on A. Eq. 1.2 is quite instructive in that it gives a rationale for the chemical shift in terms of the oxidization state of the surroundings of the central atom A. However, only contributions to the chemical shift due to effects in the ground state of the neutral are considered in this ground state potential model, whereas possible contributions from final state effects, such as differences in orbital relaxation in the core-ionized atom, and charge flow from its surrounding, are not included. The respective importance of initial and final state effects to the

\textsuperscript{1}The Hartree-Fock method, and other independent particle approaches, is covered in many textbooks, see e.g. Ref. \cite{harter}, Chapter 3.

\textsuperscript{2}For a discussion on the applicability of Koopman’s theorem, see e.g. Ref. \cite{koopmanapp}.

\textsuperscript{3}Valence electrons, on the other hand, can sometimes be delocalized over the whole molecule or crystal.
chemical shift have been considered in numerous works following the introduction of ESCA, leading to more refined models. A more detailed discussion on initial and final state effects in ESCA-spectra can be found in e.g. Ref. [9].

Since the early days of photoelectron spectroscopy many new developments have taken place, both in terms of the techniques used and the physical phenomena studied. It was realized quite early on that although the frozen orbital independent particle approach could in many cases explain the main peaks in photoelectron spectra, side bands were also observed that could only be accounted for if electron-electron interactions were taken into account in the physical description in a more refined way than in the independent particle methods (see e.g. Ref. [10] and references therein). In some cases the frozen orbital approximation was in fact completely unsatisfactory [11; 12].

In this context the main topic of this thesis can be understood, which is single-photon multiple ionization. Excluding the well-known Auger effect the emission of two or more electrons induced by just one photon is an important manifestation of electron correlations. Unfortunately conventional photoelectron spectroscopy often does not probe these processes in a detailed and sensitive way, as the electron energies may be continuously distributed along the spectrum, and hence often completely lost in the background. It is therefore of great advantage to detect all the emitted electron and to have some means of differentiating the signal from photo multi-ionization processes from the (usually) much more probable single ionization processes. To accomplish the latter, the majority of photoelectron spectroscopy studies concerning multi-ionization processes have used so-called coincidence techniques (see Section 3.2). Pioneering work on electron-electron coincidences in connection with photoionization was carried out by Lablanquie et al. [13] and Price and Eland [14–16] in the late 1980’s and beginning of the 1990’s.

Subsequently, spectrometers and experimental techniques were developed which are more optimized for coincidence experiments, by emphasizing high collection efficiency. Such techniques can be broadly categorized into threshold photoelectrons coincidence (TPESCO) [17], time-of-flight photoelectron-photoelectron coincidence spectroscopy (TOF-PEPECO), cold target recoil ion momentum spectroscopy (COLTRIMS) and electron velocity map imaging (VMI) [18]. Reviews covering COLTRIMS and TPESCO can be found in Refs. [19] and [20], respectively. TOF-PEPECO in itself includes a wide range of instruments, differing conceptually mainly by the type of extraction field used for the electrons; electrostatic (see e.g. Ref. [21] and references therein), magnetic [22] or both, as in the "reaction microscope" [19].

This thesis is based on experimental results using the magnetic bottle TOF-PEPECO technique introduced in 2003 by John H.D. Eland of Oxford University, United Kingdom [22], which sacrifices angular information for a high
electron detection efficiency over a wide energy range and has good energy resolution.
2. Multiple ionization processes

In this chapter a brief description of the single photon multi-ionization processes that have been studied in this thesis work will be given. The discussion will be focused mainly on double photoionization (abbreviated DPI) because although higher charge states of some species have also been studied as a part of this thesis, they were formed through related processes.

In the literature DPI is usually described as a result of two processes, a direct simultaneous release of two electrons from the system and an indirect process, where intermediate states are involved. In this thesis direct and indirect ionization are mostly considered as separate processes. However, as for autoionizing resonances in single ionization [23], interference between the direct and indirect process must be present to some extent, as they can lead to the same final state [24].

Regardless of the process leading to the doubly ionized state, it is, due to energy conservation, possible to write the following relation for double ionization of an atom or molecule A

\[ h\nu + E_A = E_{A^{2+}} + \varepsilon_1 + \varepsilon_2, \]  

(2.1)

where \( h\nu \) is the photon energy and \( E_A \) and \( E_{A^{2+}} \) is the energy of the neutral and double ionized system, respectively, and \( \varepsilon \) denotes the kinetic energy of the emitted electrons. The important, if perhaps obvious, conclusion to be drawn from Eq. 2.1 is that in general it is the sum of the kinetic energies of the two electrons released in DPI which is determined by the photon energy.

2.1 Direct double ionization

As mentioned above direct DPI refers to the simultaneous escape of two electrons; it can be written as:

\[ \gamma + A \rightarrow A^{2+} + e_1^- + e_2^-, \]  

(2.2)

where \( \gamma \) denotes a photon. Since no intermediate singly ionized states are involved the energy distribution of the two electrons is free of resonance structure. In other words the excess energy, the photon energy minus the energy
required for formation of the doubly ionized state, is shared between the electrons in a continuous fashion. Experimentally a continuous energy sharing is therefore an important indicator of the direct DPI process. As an example of purely direct DPI, energy distributions of the two electrons released in single photon double ionization of helium at photon energies of 87 and 200 eV, respectively, are given in Fig. 2.1.

![Figure 2.1](image)

**Figure 2.1:** Electron energy distributions of the two electrons ejected in double ionization of helium at two different photon energies; crosses mark results from measurements at 87 eV photon energy and triangles at 200 eV. To compare the two measurements with each other, and also with theory [25], the energy scale is divided by the excess energy and the intensities are normalized to each other for zero-energy electrons. The U-shaped appearance of the results from the 200 eV measurement is, within the knock-out/shake-off model interpreted as an increased contribution from shake-off at the higher photon energy. The intensity dip at the central energy results from a detection dead-time in our experiment which prevents registering of electrons of the same energy.

Direct DPI is sometimes modeled [25–28], and discussed, as a combination of two separate mechanisms; knock-out and shake-off. In Ref. [25] pure two-electron systems (He and He-like ions) were considered but it is anticipated [28] that DPI in the innermost (1s) shell is also well described by this model. It is not clear whether such a separation in terms of knock-out and

1\textsuperscript{1} In Ref. [26] a "half-collision" model was proposed but the physical motivation for both models is identical [25].
shake-off can be made for DPI in outer shells of systems with more than two electrons, which have been studied in this thesis. However, in a broader sense these models account for different interactions [27] and so still gives some intuition for double ionization processes.

2.1.1 Knock-out

As is implied by the name, in the knock-out model, double ionization is described as an internal collision where the electron which initially absorbs the photon "knocks out" a second electron from the ion, as illustrated in Fig. 2.2. Samson [29] proposed a conceptually very similar model of a direct proportionality between electron impact ionization and double ionization, after noticing that the cross section for helium double ionization at photon energies near the double ionization threshold resembles the cross section for electron-impact ionization. Samson also noted that there is no reason why the model cannot be used to describe cases where a second electron is excited instead of emitted.

![Figure 2.2: Schematic illustration of the knock-out DPI process where double ionization occurs as a result of an internal inelastic collision following photoionization.](image)

2.1.2 Shake-off

The shake-off model has a long history and was proposed, although not called as such, for the description of secondary ionization after $\beta$-decay of the nucleus [30–33]. It is based on the so called sudden approximation; the electron escapes from the nucleus on a much faster timescale than the motion of the bound atomic electrons, which means the Hamiltonian of that system has suddenly changed. Assuming $\beta^-$ decay and the sudden approximation, the system is then in a state $\psi_0$ that is not an eigenstate of the $Z+1$ Hamiltonian and should be projected onto the correct set of eigenstates $\psi$ of the $Z+1$ Hamiltonian. The probability $P_f$ to find the system in a final state $\psi_f$ is then given by
\[ P_f = |\langle \psi_f | \psi_0 \rangle|^2. \]  

Migdal [31] showed that the probability for a secondary ionization in $\beta$-decay decreases rapidly with the energy of the secondary electron. The most favorable case for shake-off is thus an unequal energy-sharing, with one fast electron and one slow electron.

The physical picture of shake-off in photoionization has some similarities to $\beta$-decay [10]. If a core electron is ionized the effective charge of the nucleus increases, which corresponds quite closely to the situation in $\beta$-decay. However, photoionization compared to $\beta$-decay implies that electron correlation in the many-electron system is changed as well [10]. As in the case of $\beta$-decay the primary electron must escape quickly, without time to interact with the bound electrons, which means that shake-off is mostly relevant at high photon energies. A detailed discussion on the role of shake-off and the extension of shake-off to finite photon energies can be found in Ref. [27].

2.2 Indirect ionization

Apart from the very special case where the atom (or molecule) is completely stripped from electrons, such as in double ionization of helium, triple ionization of lithium, and so on, there will exist an indirect path to multiple ionization. In the indirect process the doubly ionized state is reached via an intermediate state with some finite lifetime. There are in fact several conceivable indirect pathways, involving e.g. excited neutral states, but the most relevant to this thesis can be written as

\[ \gamma + A \rightarrow (A^+)^* + e_1 \rightarrow A^{2+} + e_1 + e_2, \]  

where in the first single photoionization step an excited singly ionized state is reached, which subsequently can decay by emission of a second electron. The second step of relation 2.4 is often called the Auger effect or, alternatively, Auger decay and $e_2$ is denoted as the Auger electron\(^1\). Autoionization is sometimes used instead of Auger decay, particularly when inner shell vacancies are not involved (see below). The dicaticionic state on the right hand side of relation 2.4 can also be excited, implying that subsequent triple (and further) ionization is possible, for instance in the form of a cascade of Auger decays.

This kind of indirect process is often initiated by photoionization of an electron from a (deep) inner shell, leading to the formation of a core hole. The core hole can be filled by an electron from an outer shell whereby the

\(^1\)This distinction is not clear if the energies of $e_1$ and $e_2$ are similar.
excess energy is transferred to another electron, which is emitted with a well-defined kinetic energy depending on the binding energy of the inner shell and the energy required for double ionization. In electron spectra this leads to the main, also called diagram [34], Auger lines.

The Auger decay of an inner-shell vacancy may, if energetically allowed, be accompanied by excitation of outer electrons, in addition to the main process. In the case of excitation to the continuum (i.e. ionization) one usually talks of Double Auger decay, which can be thought of as the Auger decay equivalent to direct DPI.

Even if a vacancy in an inner shell was not created, or if the binding energy of the inner shell is not sufficient, indirect DPI may still occur if additional electrons are excited in the initial photoionization step, as drawn schematically in Fig. 2.3. The "diagram" Auger effect tends to dominate in double ionization if it is energetically allowed, but indirect processes have also been shown to be important in valence-valence double ionization at photon energies below the deep inner shell thresholds [14; 16; 22].

Experimentally an indirect DPI process is, in principle, identifiable as it gives rise to two electrons of definite kinetic energies, if the two-step picture of photoionization and decay is valid. It is often useful to show how the emitted electrons share the excess energy in order to help identify the various ionization processes. In the previous example of DPI of helium, there is only one possible dicaticionic state, so a simple histogram shows all information of the energy sharing. Of course that is a special case, and in many-electron systems most often several states of the dication are reachable if the photon energy is
**Figure 2.4:** Map of measured electron-electron coincidences resulting from ionization of Kr by 88 eV photons. The size of each channel in the map is 50 meV × 50 meV (10 meV × 10 meV in the inset). The intensity (electron coincidence counts) of a channel is given on a grey scale and is scaled by the square root. Channels with intensity above 15 are drawn as pitch black in order to enhance the weaker features in the map. All DPI processes leading to a specific Kr\(^{2+}\) state leads to the release of two electrons whose kinetic energy sum is constant, which leads to stripes of increased intensity in the map. Indirect DPI processes are involved to a considerable extent in the formation of the Kr\(^{2+}\) states related to the 4\(p^4\) ground state configuration of the dication, and are visible in the map as dark islands of high intensity.

sufficiently high. In those cases the data is often better displayed as a "map", or other 3-D plot, of the electron-electron correlations. In the works which this thesis is based on such maps are referred to as *coincidence maps*, due to the experimental technique used. As an example of a case where indirect DPI processes play an important role data from the double ionization of krypton by 88 eV photons (see Paper VI) is shown in Fig. 2.4 in the form of a coincidence map (see caption for details). At that photon energy is not yet possible to open a 3\(d\) core hole, instead indirect double ionization occurs via singly ionized two-hole one particle states. In the inset of Fig. 2.4 a series of strong islands of intensity is seen, which arise due to the decay of a Rydberg series of the cation which converges on the \(^1D\) threshold of Kr\(^{2+}\).
It can be noted that the above description of indirect double ionization as a sequence of two distinct steps is again an approximation, which is often justified if the lifetime of the intermediate state is long, but which in some cases is not valid. A well-known example is post-collision interact (PCI) which can in the case of photoionization from inner shells be qualitatively understood by a classical consideration: After photoionization a photoelectron is overtaken by the Auger electron from a subsequent decay, if the latter has higher kinetic energy. For the slow electron it then appears as if the charge of the ion has increased and thus it gets slowed down, whereas the opposite is true for the fast electron. This classical picture is of course oversimplified, and PCI in connection with Auger decay requires at least a semi-classical treatment for reliable predictions [35]. In electron spectra PCI causes a shift of the photoelectron and Auger lines and may even lead to electron recapture if the photon energy is close to the inner shell threshold. Returning briefly to the discussion of direct processes in section 2.1 the cross section for DPI involving inner shells must also be modified by PCI, as the electron energy distribution span the whole available excess energy range. Moreover, in view of the preferred unequal energy sharing for shake-off, one could assume PCI to be mostly relevant for that process. This aspect has (as far as the author of this thesis is aware) not been investigated so far, but may be an interesting question for future studies of DPI.

The two-step picture also fails in a dramatic way for the $4p$ ionization of elements around $Z = 54$ [36]. In these cases very rapid $4p^5 \rightarrow 4d^8 e f$ super-Koster-Cronig transitions are possible and the notion of an intermediate well-defined $4p^5$ 'hole' state is not appropriate. Some authors refer to such in-between cases of direct and indirect DPI as "resonance-affected" double ionization [34].

### 2.3 Multiple ionization of molecules

The multiple ionization of molecules is more complex than for atoms, because of the added degrees of freedom of the nuclei. For instance in the case of the indirect processes, the intermediate state may be of dissociative character. If the lifetime is long enough the ion partially fragments, in some cases to considerable extent, before a second electron is released [37]. The competition with dissociation implies that indirect DPI at photon energies below the binding energies of core levels is less pronounced, which in turn means DPI in small molecules can be mainly direct [38]. In the works this thesis is based it is mainly DPI in the (atomic-like) core of molecules (see papers I and II) which is considered. To a first approximation, the DPI processes are considered being atomic-like.
3. Experimental technique

3.1 Time of Flight spectroscopy

The principle of Time-Of-Flight (TOF) spectroscopy is to measure the time required for a particle to travel a known distance. The TOF can then, at least in the context of this thesis, be related to the kinetic energy of the particle simply by classical mechanics. A requirement for measuring the TOF is to know when to "start the clock", i.e. there must exist a time reference for the experiment that marks when the particle started to travel. In photoion spectrometry this can, for example, be obtained by applying a strong electric field across the interaction region and putting two detectors on either side, one for electrons and one for ions. The electrons, being much lighter than any ion, will arrive very quickly at the detector because of the accelerating field and therefore the signal can be used as a trigger for the ion TOF-measurement. For such experiments a continuous light source can in principle be used. Obtaining a time reference in electron TOF spectroscopy is more demanding. The most common and straightforward way is to use a pulsed light source and utilize a signal taken from the light source itself as the time reference. Pulsed light sources (described in section 3.3) are the only kind used in the experiments presented in this thesis.

3.2 Coincidence measurements

The basic aim of coincidence spectroscopy is to determine whether different events, such as detector signals, are correlated. A coincidence event is established within a period of time in which any detected signal is regarded as coming from the same source. The extent of the time window is determined by the actual boundary conditions. In electron TOF spectroscopy a natural time window is defined by the time it takes for near-zero energy electrons to reach the detector.

In order for a coincidence experiment to produce reliable data the conditions must be such that random coincidences, arising from uncorrelated events, do not dominate in comparison with the signals due to inherently correlated events of interest. In the experiments which this thesis is based on this implies...
that the probability for a second atom or molecule to be ionized within the time window of the coincidence event should be lower than the probability for multiple ionization. The probability that \( n \) photoionization processes occur per coincidence event can be described by a Poisson distribution

\[
P(n) = \frac{\lambda^n e^{-\lambda}}{n!}
\]  

(3.1)

where \( \lambda \) is the average number of ionized atoms per coincidence event. \( \lambda \) depends on several factors, most notably the intensity of the ionizing light and the number of target atoms, either of which can usually be controlled (within limits) to reduce the chance of ionizing several atoms by the same light pulse. In the experiments presented in this thesis the situation is actually more complicated because what is detected is the number of electrons, which is not the number of atoms that were ionized. Moreover, random coincidences will be distributed according to the shape of the total photoelectron spectrum.

An alternative approach to extracting information on the correlation of events is afforded by the method of covariance mapping \([39; 40]\), which in the context of this thesis offers a way of subtracting random coincidences from the raw data. According to that method, by performing a statistical analysis on the recorded data it is possible to conduct experiments with much higher average hit rate, which is in principle advantageous as data is gathered more quickly. A drawback of a high hit rate is that limitations, if they exist, in the experimental setup, such as dead-time of electronic equipment and saturation of detectors, become more significant.

Other sources of background which have not yet been discussed are "non-statistical" background events, i.e. artefacts introduced by the experiment, the most important of which is emission of electrons following collision by a primary photoelectron (or ion) with a surface or molecule. Such secondary processes can in principle be reduced by removing potential targets for the primary electrons (reducing gas pressure and making sure that metal surfaces are far removed from the expected electron flight paths) but are in practice not always easy to avoid.

In the experiments presented in this thesis background of a statistical nature (originating from e.g. two single ionization events from two different atoms) tends to arise from random coincidences between at least two electrons of high kinetic energy. Often a large portion of these coincidences can immediately be discarded as they violate energy conservation if assumed to originate from a single photon. Non-statistical background on the other hand is much harder to treat in the analysis. Experience has shown that such background is mainly formed by at least one low-energy electron in coincidence with another electron that has an energy which coincides with a strong line in the photo-,
Auger-electron spectrum. If possible and practical, experiments are planned such that the major part of the signal we want to study is not described by this scenario.

3.3 Light sources

The results presented in this thesis are based on measurements carried out using two different pulsed light sources, a discharge lamp [41] and synchrotron light from an electron storage ring operated in single bunch mode. The lamp is also often used for preparatory experiments.

3.3.1 Discharge lamp

A schematic figure of the discharge lamp is shown in Fig. 3.1. The operation of the lamp can be described as follows: A small capacitor connected to a hollow cathode is charged by a high-voltage source, typically applying 8-10 kV. An externally controlled hydrogen Thyratron firing at a repetition rate of several kHz rapidly connects one side of the capacitor to earth. This causes the cathode potential to quickly rise and a discharge through a gas-filled capillary occurs. The discharge causes excitation and ionization of the gas in the capillary, which can deexcite by the emission of photons.

A turnable toroidal grating is used in our home laboratory setup to select single wavelengths of interest. The discharge gas most often used is helium. To start up the lamp a mix of a few percent of e.g. air can be used to facilitate the discharge. A gas mixture may also help to collisionally deexcite metastable

\[ \text{Figure 3.1: Schematic drawing of the discharge lamp. In reality the diodes in the chain are connected in parallel with resistors to prevent them from breaking down due to the high voltage applied.} \]

\[ \text{see e.g. www.tesla-coil.com/thyratron.htm} \]
states that otherwise contribute to afterglow of the lamp. Typically the lamp produces light pulses of approximately 10 ns duration. The pulse shape depends on several factors, notably gas pressure, Thyratron repetition rate and the voltage supplied. How these factors relate to each other in determining the actual pulse shape is not fully explored yet and some manner of user optimization starting from typical values is nearly always required. The light pulses due to emission from HeII, for example, often have pre-pulses which can be tuned while monitoring the effective light pulse shape, which is reflected in an electron TOF spectrum.

3.3.2 Synchrotron radiation

For photoionization involving inner shells and multiple ionization of higher order it is necessary to have access to photons in the soft X-ray spectral region, which ranges from about 100 eV up to 10 keV. For this purpose the discharge lamp is insufficient. A tunable source of soft X-rays is provided by monochromatized synchrotron light from electron storage rings such as the synchrotron radiation facility BESSY II [42] in Berlin, Germany.

In the BESSY II storage ring electrons are accelerated up to relativistic speeds (1.7 GeV) and forced to travel in an approximately circular trajectory (∼240 m circumference) by bending magnets placed around the ring. There are 16 straight sections in total around this ring, 11 of which are equipped with undulator insertion devices. An undulator is an array of magnets which produce a varying magnetic field so that electrons passing the undulator will start to "wiggle" and electromagnetic radiation is emitted at each turning point. In our experiments carried out at BESSY II light was provided by the U49/2 undulator. The electron beam wiggles in the floor plane, and linearly polarized light is emitted by this undulator.

The synchrotron light is conveyed to users in so-called beamlines that extend tangentially from the ring. We have carried out our experiments at the two neighboring beamlines U49/2-PGM-1 and U49/2-PGM-2 [43], which provide photons in the energy range of 80-1900 eV. The optical layout of U49/2-PGM-1 is shown in Fig. 3.2, where also the most important parts of our experimental setup are schematically presented. Descriptions of the chopper and the spectrometer are given in section 3.3.3 and section 3.4.2, respectively. The most important part of the beamline optics is the plane grating [44], which is designed to work with collimated light, hence the collimating mirror close to the undulator. U49/2-PGM-2 has today a similar layout as that of the PGM-1 line, shown in Fig. 3.2, with four optical elements. However, when the measurements were carried out for Papers I-III, V and VII, the refocusing mirror was not yet installed.
Figure 3.2: Schematic of the setup for the experiments most recently carried out at the U49/2-PGM-1 beamline of BESSY-II. The optical layout is drawn after the beamline documentation, but the size of the equipment and the angles are exaggerated for clarity. The indicated optical elements are (from the left to the right): $M_1$ (collimating toroidal mirror), $M_2$ (plane vertically deflecting mirror), $G$ (spherical grating, 600/1200 lines per mm), $M_3$ (cylindrical mirror focusing on the exit slit), $M_4$ (refocusing toroidal mirror with a divergence of 2 mrad full-width; $F$ marks the focal spot of the mirror).
The electrons circulating in the storage ring are not homogeneously distributed but travel together in short bunches, which ultimately means that the emitted light will arrive in pulse rather than be continuous. A single light pulse from the undulator U49/2 is approximately 30 ps, which is very short for our purposes and the time-broadening of the pulse will have little to no influence on our results. BESSY II offers several different modes of operation, which differ in the bunch pattern and the number of electrons in each bunch. The two basic modes of operation are called multi-bunch and single bunch, respectively. In multi-bunch mode the total beam current is divided into electron packets, 400 being the maximum number of "slots" available, separated in time by approximately 2 ns. In single bunch mode, only a single electron packet circulates the ring, taking approximately 800.5 ns to complete a revolution. The single bunch mode has a price in terms of a reduced total beam current, by approximately an order of magnitude, compared to multi-bunch mode. Variations on these two themes also exist at BESSY II, in form of a so-called hybrid bunch-mode where a part of the 800.5 ns is filled with multibunched electron packets, which is followed by a time gap (typically ~100 ns) in which there is only a single bunch. At the time of writing of this thesis the hybrid mode is the standard mode of operation of BESSY-II. Our experimental results have exclusively been obtained when the storage ring was operated in single bunch mode.

3.3.3 A mechanical chopper

The high repetition rate of synchrotron light from electron storage rings, even when operated in single bunch mode, is in some ways disadvantageous to our experiments (c.f. section 3.4). Furthermore, also for many other experiments it may be beneficial to reduce the number of light pulses received at the experimental station. A device which can be used for this purpose is sometimes called a chopper. A mechanical chopper was recently modified for use with our experiments carried out at BESSY-II, where a fellow doctoral student at Uppsala University, S. Plogmaker, played a key role\(^1\). A more thorough description of the chopper can be found in Paper VII, while a summary of the most important features for our experiments is given here.

The chopper consists of two 104 mm circular discs fixed onto the axis of a small DC electric motor (see Fig. 3.3). Around the discs 110 µm wide apertures are milled at regular intervals. The discs can be rotated with respect to each other to determine the final aperture size. Different discs with varying number apertures can be cut according to the demands of the experiment. Our most recently used setup has one ring with 120 slits on the outer edge of the

\(^1\)S. Plogmaker succesfully defended his thesis in March 2012, see Ref. [45]
Figure 3.3: (a) Explosion drawing of the chopper. (b) Photograph of the chopper showing the discs.

disc and one ring with 15 slits closer to the center. The discs and motor are mounted inside a vacuum chamber with standard flanges for connection to the beamline and experiment. A small rectangular disc facing the rotating circular discs is attached to the motor housing holds a 40 µm wide slit and a 2 mm aperture. The aperture can be used to bypass the chopper if desired and the fixed slit partly determines the opening time (see below). The entire setup rests on a movable stage so that the chopper can easily be aligned to intersect the light beam. Under operation the motor typically rotates at a speed of approximately 650 revolutions per second (settable), and only those light pulses which arrive in front of a slit on the discs are let through. For a frequency of the discs \( f \), disc aperture size \( d_{\text{disc}} \), fixed slit width \( d_{\text{slit}} \) and distance \( r \) of the slit from the motor axis the opening time of a slit is approximately

\[
t_{\text{open}} = \frac{(d_{\text{disc}} + d_{\text{slit}})}{2\pi rf}.
\] (3.2)

An important property of this chopper is that the disc rotation can be phase-locked to the storage ring cycle. For a non-phase-locked chopper the number of light pulses let through on average is determined not only by the number of slits but also by the ratio of the opening time to the inter-light pulse period. In addition only a fraction of some light pulses are let through, as the slits are not always central with respect to the light beam when a pulse arrives. The combination of these effects can lead to a considerable loss in average light intensity.
3.4 Magnetic bottle spectrometers

3.4.1 Operating principle

Fig. 3.4 depicts a magnetic bottle field configuration where the magnetic flux density is increased at opposing ends of a region of lower flux density, forming what are called magnetic mirrors or magnetic bottlenecks [46]. An electron traveling at a point where the magnetic flux density is $B_w$ with velocity $v$, which has components $v_{w||}$ and $v_{w\perp}$ parallel and perpendicular to the magnetic field, respectively, has a magnetic moment\(^1\) $\mu = \frac{m_e}{2} v_{w\perp}^2 / |B_w|$ due to its gyromotion [47]. If the change of the magnetic flux density is small over the distance traveled by an electron during one rotation, the magnetic moment is invariant [46].

As the electron transitions to a point in the strong field region where the magnetic flux density is $B_s$, the invariance of $\mu$ implies

$$\frac{m_e v_{w\perp}^2}{2|B_w|} = \frac{m_e v_{s\perp}^2}{2|B_s|},$$

(3.3)

where $v_{s\perp}$ is the electron’s velocity component perpendicular to the magnetic field in the region of high flux density. As the kinetic energy of the electron is conserved in the magnetic field the magnitude of its total velocity is unchanged, which means its velocity component parallel to the magnetic field must be reduced for Eq. 3.3 to hold. The electron may be forced to travel in the opposite direction depending on the field configuration and initial conditions. At the turning point $v_{s||} = 0$, which implies that $v_{s\perp} = |v|$. Eq. 3.3 then simplifies to

$$\sin \theta = \sqrt{\frac{|B_w|}{|B_s|}},$$

(3.4)

where $\theta$ is the angle of the helical motion with respect to the magnetic field at the starting point, and is usually called the pitch angle. For given initial and maximum magnetic flux densities, $B_i$ and $B_{\max}$, respectively, Eq. 3.4 defines the critical pitch angle $\theta_c$. Electrons with smaller initial pitch angles than $\theta_c$ will not be trapped in the bottle.

Eq. 3.3 implies that a magnetic bottle field configuration can be used to parallelize electron trajectories, as the velocity component perpendicular to the magnetic field lines must reduce when the electron travels from the strong field region to the weak field region. This property makes such a device suitable as a TOF-spectrometer, as one magnetic mirror can be replaced with a

\(^1\) not to be confused with its intrinsic magnetic moment.
Figure 3.4: Example of an electron trapped on a helical trajectory in a magnetic bottle.

detector. The velocities of electrons emitted in the strong field region, or in a region of intermediate field intensity, can be made near-parallel to the magnetic field in the weak-field region over a small distance of space. The weak-field region can be extended into a uniform magnetic field over a long distance, making the time required for parallelization small compared to the time later spent traversing the weak-field region to the detector. Kruit and Read [48] thoroughly investigated the potential use of a magnetic bottle field configuration as a TOF-spectrometer and electron imaging device.

3.4.2 Spectrometer

The concept of using magnetic bottle spectrometers for the coincidence experiments presented in this thesis was originally developed by J.H.D. Eland at Oxford University, England [22]. Two of the original Oxford instruments [22; 49], as well as a new instrument dedicated to Free Electron Laser experiments, are available in our laboratories and differ mainly in length of the flight tube and some minor details of design. As they operate in essentially the same way only the one used at BESSY-II will be described here, which is also primarily the one used by the author of this thesis. An overview of the instrument is shown in Fig. 3.5. Essentially it is half of a magnetic bottle, where at one end a magnetic mirror is replaced by an electron detector consisting of three microchannel plates (MCP), with an open-area ratio of 60%, arranged in a Z-stack configuration with a potential difference of $\sim 850$ V per plate and simple metal plate anode for charge collection. The front MCP plate is kept at $\sim 300$ V relative to earth to ensure detection of electrons.

A weak (a few mT) homogeneous magnetic field is created by a solenoid wound around an approximately 2.2 m long stainless steel tube, usually called the flight tube, and is protected from external magnetic fields by a $\mu$-metal shield. At the other end of the flight tube a chamber is attached in which a per-
manent magnet with a conically shaped pole-piece (∼ 0.8 T at the pole face) is located that contracts the magnetic field lines to create a magnetic mirror. The whole system is kept under high-vacuum, typically 5 × 10⁻⁷ Torr. Sample gas is typically let into the system as an effusive jet through a thin needle. For the experiments presented in paper III, in which cadmium was studied, the needle was replaced with by small, resistively heated, furnace. The intersection of the light beam with the gas jet defines the interaction region where photoionization takes place. The permanent magnet and gas needle are mounted on motion manipulators movable in all three spatial directions. The permanent magnet position, and hence the field in the interaction region, is critical to ensure electrons ejected from the interaction region are imaged onto the detector at the other end of the flight tube. A properly optimized spectrometer has a collection efficiency approaching the full solid angle for electrons with energies ranging from 0 to several hundred eV. The resolution of the instrument depends on the kinetic energy of the electrons and can be expressed as a fixed ratio $\frac{E}{\Delta E} \sim 50$ (FWHM). However, the maximum resolution obtained has been around 20 meV, for low (< 1 eV) energy electrons. Inside the flight tube a second metal tube is inserted, which is electrically insulated from the rest of the instrument. In this way a small (typically <1 V) electric field across the interaction region can be applied to help electrons with near-zero energy to be collected and arrive at the detector within a reasonable (3-6 µs) time frame.

![Figure 3.5: Schematic of the magnetic bottle TOF electron spectrometer used for this thesis work.](http://www.roentdek.com/)

The electron detector signals are recorded, after discrimination, relative to a trigger signal obtained from the ionizing light pulses. Expect for the experiments presented in Paper IV, an 8-channel time-to-digital (TDC) card was used. The TDC accepts logic signals (NIM-standard), has 0.5 ns time resolution and a multi-hit dead-time of detection of approximately 10 ns. A recent improvement to the timing electronics of our setup is the use of an analog-to-digital converter (ADC¹), which digitizes the detector signal and thus allows further post-processing of the data.

¹http://www.roentdek.com/
In the experiments where light pulses are provided by the helium discharge lamp or by synchrotron radiation at a frequency reduced by the chopper a trigger obtained from a light pulse provides an absolute time reference, as the inter light pulse period is longer than the TOF of electrons that have any initial kinetic energy, because of the small accelerating field applied. In the experiments carried out at BESSY-II when a chopper was not used, the inter light pulse period (800.5 ns) is less the TOF of electrons with low (∼ 21 eV or lower) kinetic energy. Special consideration then has to be taken to obtain the electron TOF for low energy electrons, as the fastest electron of any ionization event can only be recorded modulo 800.5 ns if light pulses are used as a trigger. Over the years various strategies have been developed to overcome the timing problem in TOF spectroscopy carried out using synchrotron radiation.

1. If at least one electron in the coincidence events of interest has a high kinetic energy, then slower electrons from the same event are guaranteed to be referenced to the correct light pulse, assuming all electrons are detected. This strategy is particularly useful in studies of atoms and molecules where the creation of a core vacancy, as the emission of a high kinetic energy Auger electron is very likely. A drawback of this approach is that in those cases where the fast electron is not detected, the TOF of slow electrons is registered in error, distorting the shape of the total electron TOF spectrum.

2. If one particle from a coincidence event has a known TOF, it can be used as a time reference. In one of the first magnetic bottle experiments carried out using synchrotron radiation [50] the double Auger decays of a xenon 4d core vacancy could be mapped by using the TOF of photoelectrons from 4d photoionization, whose kinetic energy and flight time were known, as a time reference. Other conceptually related schemes for obtaining an absolute time reference for slow electrons include the coincident detection of ions [51] or energy-selected electrons [52].

Even if an absolute time reference cannot be obtained for slow electrons, it can still be possible to correct the TOF (recorded in error by at least one inter-light pulse period) of some coincidence events from the possible kinetic energies of the electrons. However, a correction is never possible for all electron energies and the corrected data has to be examined very carefully for appearance of artifacts introduced by the procedure (see Paper VII).
3.4.3 Time-to-energy conversion and calibration

Electron flight times are converted to kinetic energy using the formula

\[ E_{\text{kin}} = \frac{D^2}{(t-t_0)^2} + E_0 \]  

(3.5)

where \( E_{\text{kin}} \) is the kinetic energy of the electron in eV and \( t \) the measured flight time in ns. \( D, t_0 \) and \( E_0 \) are essentially fitting parameters but nevertheless are related to physical properties of the spectrometer. \( D \) is related to the length of the electron flight path, \( t_0 \) to time delays between the start of the measurement and the time of impact of the light pulse and \( E_0 \) to electric fields in the interaction region, introduced in part deliberately as described above. \( D \) and \( t_0 \) are essentially constant unless the experimental setup is changed in some way whereas \( E_0 \) can vary also depending on the sample species, probably because of changes of surface potentials of the vacuum system. In practice all parameters are optimized, mainly to ensure against a drift of the timing reference pulse. The calibration parameters \( D, t_0 \) and \( E_0 \) are optimized by record-

![](image)

**Figure 3.6:** Time-of-Flight spectra of electrons ejected in the Auger decay of Xe 4d vacancies. On the top axis some selected electron energies are given for comparison with the TOF-scale. The stepsize is 0.5 ns for the TOF-scale.

ing spectra with lines of well-known energy and fitting to equation 3.5. One such spectrum is the photoelectron spectrum of the oxygen molecule [53] at a photon energy of 21.22 eV (which corresponds to the \( 2p \rightarrow 1s \) fluorescence transition in neutral helium). This has for example been used for the calibration of the cadmium spectrum in Paper III recorded with the helium discharge.
lamp. For the experiments carried out at the BESSY-II storage ring the primary calibration source used was the xenon and krypton photoelectron spectrum recorded at suitable photon energies above the 3\textit{d} ionization energies for Kr, or the 4\textit{d} ionization energies for Xe, when the creation of a core vacancy is likely. The Auger decay of the core hole states leads to well-known electron spectra [54; 55] which can be used for calibration. For both Kr and Xe the \( nd_{5/2} \) and \( nd_{3/2} \) (\( n = 3 \) for Kr and \( n = 4 \) for Xe) thresholds are well separated in energy which leads to well-resolved peaks in the photoelectron spectrum. Since we can detect both the photo- and Auger electrons in coincidence means the Auger lines from each of the two levels can be selected separately, which can help to resolve the lines. As an example the N\textsubscript{5}OO and N\textsubscript{4}OO Auger electron TOF spectra recorded with our 2.2 m instrument are shown in Fig. 3.6.

For reference identification of the peaks in the TOF spectra with Auger lines reported in the work of Carroll et al. [54] are given in table 3.1. Electrons with low (<5 eV) kinetic energies are emitted in cascade Double Auger decay, and their energies are reported for Kr in Ref. [56] and for Xe in Ref. [50]. Observing these low-energy Double Auger lines in the electron spectrum is also useful for ensuring the spectrometer collects low-energy electrons correctly. As they arise from triple ionization they are most clearly observed in coincidence events where three electrons were detected.
Table 3.1: Auger lines (cf. Fig 3.6) often used for calibration and optimization of the synchrotron experiments. The energies are taken from Ref. [54] where they are given with an absolute uncertainty of 11 meV and a relative uncertainty better than 5 meV. $^a$ This peak hides a doublet resolved in the high-resolution work of Ref. [54]. The listed value is an average.

<table>
<thead>
<tr>
<th>Peak no.</th>
<th>Energy (eV)</th>
</tr>
</thead>
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<tr>
<td>1</td>
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</tr>
<tr>
<td>2</td>
<td>33.33$^a$</td>
</tr>
<tr>
<td>3</td>
<td>32.323</td>
</tr>
<tr>
<td>4</td>
<td>29.967</td>
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<tr>
<td>5</td>
<td>19.686</td>
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<td>6</td>
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<tr>
<td>13</td>
<td>31.946</td>
</tr>
<tr>
<td>14</td>
<td>21.665</td>
</tr>
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<td>15</td>
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<td>18</td>
<td>10.279</td>
</tr>
</tbody>
</table>
4. Results

4.1 Double Core Holes in molecules

The first two papers included in the thesis concern the creation of a double core hole (DCH) in molecules. A DCH is a highly excited state of a molecule which has two vacancies in an inner shell. Atoms which have two vacancies in the 1s shell are sometimes called hollow atoms [57], and have mainly been investigated by the observation of hypersatellites (K$^{-2} \rightarrow K^{-1}L^{-1}$) in X-ray emission [58] and Auger electron spectra [59].

Experimental results on DCHs in free molecules utilizing electron detection\(^1\) where the vacancies are situated in the 1s shell of a heavy atom did not exist in the literature prior to this thesis work. Almost simultaneously to our publication, however, at least two more papers showing experimental results on molecules with vacancies in the 1s shell were published- on by the group of P. Lablanquie and F. Penent, who use an experimental technique similar to ours [61], and another by Fang et al. [62]. While our results, and those of Lablanquie et al., mainly rely upon electron-electron interactions for the formation of DCHs by single-photon double ionization, the work of Fang et al. was carried out at a X-ray Free Electron Laser (XFEL). The very short and intense light pulses available at XFELs allow for the absorption of more than one photon by the same target species, thus enabling DCH formation in a two-step process, prior to the decay of a single core hole.

If a molecule contains more than one heavy atom, such as in CO\(_2\), O\(_2\) or N\(_2\), there are two types of possible DCH states, depending on which of the atoms the two core-holes are located. If they are situated on the same atom the DCH is usually called a single-site DCH, while if they are located on different atoms it’s called a two-site DCH.

In paper I it is demonstrated that single-site 1s DCHs created by the absorption of a single photon can be probed using the experimental technique described in this thesis. Two molecules were investigated in this way, CH\(_4\) and NH\(_3\). The main result in this paper, besides the proof-of-principle, are

\(^1\)Double excitations in lithium compounds have been studied using the alternative technique of Resonant Inelastic X-ray Scattering (RIXS) by M. Agåker an coworkers, see e.g. the PhD thesis of M. Agåker [60].
the ionization energies of the DCH states, found to be $651.5 \pm 0.5$ eV and $892 \pm 0.5$ eV for CH$_4$ and NH$_3$, respectively. The approximate energy of the DCH "preedge resonances", states where one of the core electrons is excited not to the continuum but to an unoccupied molecular orbital, is also reported.

Paper II is a follow-up work to paper I in which the chemical shifts of single-site DCH states are investigated more closely. In electron spectroscopy for chemical analysis (ESCA [5]) core electrons ionization energies are measured. The core level ionization energy can be shifted depending on the chemical environment, i.e. the local charge distribution around the atom in the initial state. However, the ionization energy shift depends not only on initial-state but also on the response of the electron charge distribution to the core vacancy, i.e. relaxation. In other words; single core hole ionization energies are not always a satisfactory tool to investigate the chemical environment of a specific atom, as relaxation can "hide" the chemical information of the initial state [63]. In single-site DCHs the relaxation effects are greater, which allows an estimate of the relaxation energy by measuring both the single and double core hole energies, as described below.

The S2$p^{-2}$ DCH states of three sulfur-containing molecules, H$_2$S, CS$_2$ and SO$_2$, were investigated, and the S2$p^{-2}$ DCH spectra of all three molecules are

Figure 4.1: Double core-hole spectra (a) for CH$_4$ at $h\nu = 750$ eV and (b) for NH$_3$ at $h\nu = 950$ eV, respectively (cf. Paper I).
shown in Fig. 4.2. The S2$p^{-2}$ double hole states can also be reached by Auger decay of a vacancy in the innermost shell, although the relative intensities of the final states will be different than those observed in Paper II. The chemical shifts observed in Auger electron spectra of molecules and solids have, like the binding energies of core levels, been the subject of much research; particularly when the final states involve two vacancies in core levels [64–67], for the reasons given in the last paragraph.

The S2$p^{-2}$ DCH ionization energies for the three systems studied are given in Table 4.1, where also the S2$p^{-1}$ single core hole ionization energies and results from Multi-Configurational Self Consistent Field (MCSCF) quantum-chemical calculations are included. The DCH ionization energies and associated chemical shifts of these three molecules were analyzed in Paper II using the following model:

$$\text{DIP}(S2p^{-2}) = 2\text{IP}(S2p^{-1}) - \text{ERC}(S2p^{-2}) + V_{abab},$$  \hspace{1cm} (4.1)

where IP and DIP are the single and double core ionization energies, respectively, and ERC is the generalized relaxation energy which includes non-additive correlation and relaxation effects [68] to the double core hole creation. The term $V_{abab}$ needs some further explanation; according to both the theory
Table 4.1: Experimental (E) and calculated (T) single (IP) and double (DIP) core ionization energies for the $2p^{-1}$ and $2p^{-2}$ states of H$_2$S, SO$_2$, and CS$_2$. $\epsilon$ denotes Hartree-Fock orbital energies. All energies are given in eV.

<table>
<thead>
<tr>
<th></th>
<th>DIP ($2p^{-2}$)</th>
<th>IP ($2p^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
<td>T</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$^3P$</td>
<td>373.5 (0.2)</td>
</tr>
<tr>
<td></td>
<td>$^1D$</td>
<td>380.0 (0.2)</td>
</tr>
<tr>
<td></td>
<td>$^1S$</td>
<td>388.4 (0.2)</td>
</tr>
<tr>
<td>Ave.</td>
<td></td>
<td>376.7</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td></td>
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</tr>
<tr>
<td>SO$_2$</td>
<td>$^3P$</td>
<td>382.1 (0.2)</td>
</tr>
<tr>
<td></td>
<td>$^1D$</td>
<td>388.4 (0.2)</td>
</tr>
<tr>
<td></td>
<td>$^1S$</td>
<td>396.1 (0.4)</td>
</tr>
<tr>
<td>Ave.</td>
<td></td>
<td>385.1</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS$_2$</td>
<td>$^3P$</td>
<td>370.0 (0.2)</td>
</tr>
<tr>
<td></td>
<td>$^1D$</td>
<td>376.9 (0.2)</td>
</tr>
<tr>
<td></td>
<td>$^1S$</td>
<td>384.7 (0.4)</td>
</tr>
<tr>
<td>Ave.</td>
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<td>373.3</td>
</tr>
<tr>
<td>$\epsilon$</td>
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and the experiment the energy spacing of the $^3P$, $^1D$ and $^1S$ states is not constant for all the molecules, and therefore state averaged energies were calculated according to the statistical weights, with ratios 9:5:1 for the $^3P$, $^1D$ and $^1S$ states, respectively. In that way an averaged two-hole repulsion integral $V_{abab}$ for a single-site DCH could be calculated and was found to be 54.5 eV for all three investigated molecules.

Eq. 4.1 can be used to analyze the shift in DCH energy between two different molecules, or relative to a reference atom $^1$. Assuming a constant hole-hole repulsion for different molecules, the difference $\Delta$DIP in the DCH ionization energy between two molecules can be written as

$$\Delta \text{DIP} = 2 \Delta \text{IP} + \Delta \text{ERC},$$

(4.2)

where $\Delta \text{IP}$ and $\Delta \text{ERC}$ are the differences in single core hole ionization energy and generalized relaxation energy, respectively. According to Eq. 4.2 the difference in generalized relaxation energy of a DCH between two molecules can be determined from experimental values only. The question remains as to what

### Table 4.2:

Experimental (E) and theoretical (T) differences for CS$_2$ and SO$_2$ relative to H$_2$S in terms of the generalized relaxation energy ERC and the relaxation $R$ of a single S 2$p$ core hole as determined by Eq. 4.2.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta \text{ERC}/2$ (E)</th>
<th>$\Delta \text{ERC}/2$ (T)</th>
<th>$\Delta R$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>0.4(4)</td>
<td>0.2</td>
<td>-0.3</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>1.3(4)</td>
<td>1.3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

is measured by a difference in ERC, i.e. what information about the chemical environment is gained. At the level of second-order perturbation theory [68], ERC/2 is approximately equal to $R$, the strict relaxation energy (without correlation) of a single core hole. Determining the shift in $R$ then allows an estimate of to what extent the ground state potential (here reflected by the SCF orbital energies) influences the shift in the ionization energy. The quantity $\Delta \text{DIP} - 2 \Delta \text{IP}$ can also be viewed as a final state Auger parameter [67], which is usually determined by the difference in chemical shift of a strong Auger electron line (when the final state is a double core hole) and the chemical shift of the ionization energy. The results of Paper I thus suggest that an extension of a "Auger" parameter is, at least in principle, possible to single-site DCHs in light

$^1$This is a slightly different presentation, for illustrative purposes, compared to that given in Paper II, where the experimental and theoretically derived quantities were more directly compared.
elements such as O, C and N where, in fact, a proper Auger parameter is not available as the Auger decay of the 1s single core holes involves delocalized valence electrons.

Using the results for H$_2$S as a reference, the difference in ERC/2 determined by Eq. 4.2 using the (averaged) experimental values for the S$2p^{-2}$ doubly ionized states and the S$2p^{-1}$ singly ionized states is shown in Table 4.2, where also the difference in ERC/2 calculated with the MCSCF method and the difference in strict relaxation determined by a separate SCF calculation is presented. The results for SO$_2$ are not conclusive, as a systematic deviation of the relaxation energy is observed, which may be due to correlation effects. For CS$_2$ the experimental and theoretical differences in relaxation (ERC/2) to H$_2$S are in good agreement, and the higher relaxation in CS$_2$ is can be explained as charge flow from the CS moiety to the core ionized S atom.

### 4.2 Multiple ionization of atoms

#### 4.2.1 Double ionization of cadmium

Paper III reports results from single-photon double ionization of cadmium at selected photon energies of 40.814, 48.37, 85.1 and 200 eV. The experiments that used the two lower photon energies were carried out using the discharge lamp described in Section 3.3.1, while experiments based on the higher photon energies were carried out at BESSY-II using synchrotron radiation. The valence-valence double photoionization spectra of cadmium recorded at 40.814 and 48.37 eV photon energy are shown in Fig. 4.3 from which the lowest double ionization energy of the $[Kr]4d^{10}1S_0$ Cd dication ground state is found to be $25.91 \pm 0.04$ eV. An interesting feature of the cadmium double ionization spectrum is that the peak related to the dication ground state is by far the strongest in the spectrum. This is in clear contrast to the single ionization spectrum recorded at UV photon energies, where the corresponding peak related to the ground state is quite weak. It was found that the reason for this is that the dication ground state is almost exclusively formed in an indirect ionization process, mediated by $4d^{-1}$ singly ionized satellite states. The binding energy of the $4d$ shell is not high enough to undergo Auger decay, but this process becomes possible if in addition to $4d^{-1}$ ionization an electron from the $5s$ shell is excited. Multi-Configurational Dirac Fock (MCDF) calculations were performed to identify the most prominent intermediate states involved in the formation of the dication ground state. The excited doubly ionized states with leading configurations $4d^95s$ and $4d^95s$ are also mainly formed indirectly, but Auger decay from the most intense $4d^{-1}nl$ singly ionized satellite states is not energetically allowed.
Figure 4.3: Single photon double ionization spectra of cadmium recorded at the photon energies 40.814 (upper panel) and 48.37 (lower panel) eV. Some artificial peaks related to the shape of the light pulse from the helium lamp are visible in the spectra, which are indicated by single and double asterisks.

At the two higher photon energies electrons from the $4p$ and $4s$ inner shells of cadmium can be ionized. $4p$ and $4s$ hole states in cadmium, in contrast to a $4d$ hole, can decay via Auger processes. When it is energetically possible for the Auger decay to only involve orbitals within the same atomic shell, such as $4p^{-1} \rightarrow 4d^{-2}\epsilon l$, the interaction between the initial and final states can become very strong, which is the case in cadmium. This type of Auger process is usually referred to as Coster-Kronig decay. In cadmium the interaction between the $4p$ hole states and continuum and bound states based on a $4d^{-2}$ core becomes so strong that it represents a complete breakdown of the quasi-particle approximation for the $4p$ hole states[69]. This implies that it is not long-lived enough to produce a spectral line with some narrow width. The conventional photoelectron spectra of cadmium $4p^{-1}$ ionization no longer exhibits a doublet corresponding to spin-orbit split components of the $4p$ hole states, but rather a very broad asymmetric single peak is observed [12]. The ionization of $4p$ and $4s$ electrons greatly affect the cadmium double ionization spectrum. At the higher photon energies the dominant peak is related to $4d^{-2}$ ionization, formed mainly by Coster-Kronig decay of $4p^{-1}$ hole states and at 200 eV photon energy also the $4s^1$ hole state. The formation of the dication ground state appears to be relatively unaffected by Coster-Kronig processes, instead the same intermediate singly ionized states appear to be involved at all the photon energies investigated in this work.
4.2.2 Double and triple ionization of krypton

Paper IV concerns DPI of krypton by 88 eV photons, which is not sufficient to create a 3d vacancy; some of the results (cf. Fig. 2.4) have already been shown in Section 2.2, in connection with the discussion concerning indirect double ionization processes.

Figure 4.4: Double ionization spectrum of Kr by 88 eV photons. The dashed line indicates a contribution to the spectrum from triple ionization (cf. Paper VI).

The spectrum of valence doubly ionized krypton is shown in Fig. 4.4. The most intense group of peaks at around 40 eV double ionization energy are related to the 4p⁴ (⁵P, ¹D and ¹S) states. The next two peaks at ~ 53 and ~ 56 eV are fairly easily assigned to ³P and ¹P states with leading configurations 4s4p⁵ but at higher energies the spectrum becomes quite complex, with many overlapping peaks. Strong correlation in the dication, which in configuration interaction methods is described by states with a high degree of mixing of the 4s4p⁵ and 4s²4p³4d configurations [55], distributes the spectral intensity of the 4s4p⁵ states over a large part of the double ionization satellite spectrum.

The formation of the lowest-lying 4p⁴ ³P, ¹D and ¹S states of the dication is investigated in detail in the work presented in Paper IV. From the electron energy distributions for each final state it is found that continuum parts of the distributions, indicating contribution from direct double ionization processes, amount to about half the total intensity of the peaks associated with the states related to the 4p⁴ configuration. The remaining intensity derives from indirect ionization processes via intermediate singly ionized states. A series of strong peaks, which can be related to a 4p⁴(¹D)nd ²S Rydberg series of Kr⁺,
is observed in the electron energy distribution related to the $4p^4 \, ^3P$ final state. Autoionization of the $^1D \, nd^2S$ states to a $^3P$ state of the dication is not allowed in the LS coupling scheme, but becomes possible when departure from LS coupling is considered. A branching ratio of approximately $2.2 : 1 : \sim 0$ could be determined for autoionization to the $J = 2, 1, 0$ levels, respectively, for the intermediate states energetically allowed in all exit channels. For higher excited intermediate states (above $\sim 45$ eV binding energy) the character of a Rydberg series is mostly lost. Excited configurations of the $4s^2p^5nl$ and $4s^2p^3nl'nl'$ type gives rise to many possible states, and few of them are expected to have dominant weights for single configurations [70]. Detailed assignment of these intermediate states would require support from extensive calculations. Nevertheless it was possible from the experimental data to, at least, estimate the branching in autoionization of the strongest features in the electron energy distributions related to the $4p^4 \, ^3P$, $^1D$ and $^1S$ states.

If photons of energies above $\sim 100$ eV interact with krypton atoms, photoionization from the 3$d$ sub-shell becomes a very important process. The most probable photoionization process is single 3$d$ ionization, followed by Auger decay to the various states of Kr$^{2+}$, which leads to well-known Auger electron spectra [55; 71]. Triple ionization by direct or cascade Double Auger decay processes [56; 72] is also possible, as the binding energies of the 3$d$ core levels, $\sim 93.8$ and $\sim 95.0$ eV [73], lie above the Kr$^{3+}$ ionization potential ($\sim 74$ eV [56; 72]).

In addition to emission of a 3$d$ electron, the photoionization process may result in emission of a second electron from the outer $n = 4$ shell, i.e. core-valence ionization, if the photon energy is sufficiently high. In paper V we focused on the formation and decay $3d^{-1}4p^{-1}$ doubly ionized states resulting from the interaction of krypton atoms with photons of 150 eV energy. An energy level diagram of the first three charge states of Kr which illustrates the relevant processes is shown in Fig. 4.5. It is noteworthy that the $3d^{-1}4p^{-1}$ states lie below the quadruple ionization threshold [74], so that their decay necessarily leads to triply ionized states of Kr, neglecting decay by emissions of X-ray photons.

The experimental results are visualized in Fig. 4.6 by a 3D-plot, where the sum of the kinetic energy of two electrons, reflecting intermediate doubly ionized states, is plotted against triple ionization energy, i.e. the photon energy minus the energy sum of all three electrons.

If the intensity in Fig. 4.6 is projected onto the y-axis (sum of the kinetic energy of two electrons) the spectrum of intermediate doubly charged states involving core and valence shells is obtained, which is shown in the lower panel of Fig. 4.7. The experimental results are compared with simulated spectra (Fig. 4.7, upper panel) based on Multi-Configuration Dirac-Fock (MCDF)
**Figure 4.5:** Schematic energy level diagram of Krypton in various charge states.

**Figure 4.6:** Triple electron coincidence map recorded at a photon energy of 150 eV, which shows the formation of Kr\(^{3+}\) states by single Auger decay from Kr\(^{2+}\) core-valence intermediate states. The y-axis represents the kinetic energy sum of two electrons which reflects core-valence intermediate states. The x-axis represents the photon energy minus the total kinetic energy sum of all three detected electrons, and the z-axis represents coincidence counts per channel.
calculations, and a general good agreement between theory and experiment is observed for the relative intensities. From Fig. 4.6 it is also possible to reveal how the intermediate core-valence ionized states contributes to the triple ionization, by selecting an energy region on the y-axis corresponding to the one of the peaks \(a-e\) in Fig. 4.7 and projecting the intensity onto the x-axis. The decays of the different intermediate states are investigated in detail in Paper V.

![Figure 4.7](image.png)

**Figure 4.7:** Lower panel: Single photon core-valence double ionization spectra of Kr. Upper panel: Simulated spectrum using Kr\(^{2+}\) state energies and photoionization amplitudes obtained from MCDF calculations, convoluted with the estimated experimental resolution and calculated lifetime widths. The calculated levels and relative intensities are indicated by bars, together with \(LS\) term symbols.

### 4.2.3 Multiple ionization of argon

In the interaction of argon atoms with single photons the \(3\)P, \(1\)D and \(1\)S doubly ionized states of \(2p^{-2}\) character can be formed in different ways. If the photon energy is sufficiently high (\(\sim 3200\) eV) ionization of a \(1s\) electron is possible, which may be followed by Auger decay leading to the \(2p^{-2}\) states. At photon energies well below the binding energy of the \(1s\) shell, which was the case for the measurements presented in Paper VI, the double hole states may be formed.
in direct double ionization processes or via intermediate resonance states derived from excited configurations of type $2s^{-1}2p-1nl$ or $2p^{-2}nl$. Interference between the two pathways is also possible. In order to study the formation of the $2p^{-2} \, 3P, \, 1D$ and $1S$ states quadruple electron coincidence data from photoionization of Ar at the photon energy of 670 eV was analyzed according to the scheme

$$Ar^{2+}(2p^{-2}) \rightarrow Ar^{3+}(2p^{-1}) + e_{A1}^- \rightarrow Ar^{4+} + e_{A1}^- + e_{A2}^-,$$

i.e. the decay of the double hole states was assumed to be a sequence of two distinct steps, emitting electrons with well-defined kinetic energies in each step, leading to quadruply ionized states. From that scheme two-electron data mainly related to the formation of the $2p^{-2}$ states could be extracted. The experimental spectrum is shown in Fig. 4.8 and reflects peaks related to the $3P$, $1D$ and $1S$ states with relative intensities of 2:2:5:2:1, respectively. The electron energy distributions related to the $1D$ state were also extracted. No clear peaks related to intermediate states, which must be involved in the formation of the double hole states to some extent (even if very little), could be identified. In Paper VI the experimental results are compared to Multi-Configuration Dirac-Fock (MCDF) calculations of direct double ionization cross sections, which were based on the same scheme as that used for the results presented in Paper VI. This comparison is shown in Fig. 4.9. For the calculated results

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**Figure 4.8:** Experimental electron coincidence spectrum of doubly ionized argon of $2p^{-2}$ character.
Figure 4.9: (a) Calculated spectra for different sharing of the excess energy (1 a.u. ≈ 27.21 eV) between the two photoelectrons. (b) Calculated spectra for different sizes of the Configuration State Function (CSF) basis used in the representation of the dicaticonic states in the MCDF calculations. (1) $2p^43s^23p^6$ single-configuration representation of the bound state of the remaining photoion; (2) including, in addition, $2p^2 \rightarrow 3d^2$ excitations but by restricting the scattering states to $d$ electrons in the continuum; (3) the same as (2) for $\varepsilon s + \varepsilon p + \varepsilon d + \varepsilon f$ continua of the outgoing electrons.

shown in (a) the sensitivity of the MCDF calculation to the energy sharing of the two electrons was tested since it was not possible in the calculations to perform a complete summation over all possible energy sharings of the two electrons. See the caption of Fig. 4.9 for details concerning the calculations. The conclusions were that at least the most important double excitations had to be included in the wavefunction expansion of the final states for a reasonable prediction of the final state intensities. It was, however, not clear if a convergence of the intensities had been reached at that point. As the experimental results were not conclusive on the importance of intermediate resonances a further comparison beyond this reasonable agreement did not appear meaningful. Paper VI thus reports preliminary findings on the DCH formation but also shows that further effort is required both on the experimental side and theoretical side. In particular, refined experiments should aim at showing more clearly what role intermediate resonance state might have in DCH formation.
5. Outlook

The multi-ionization studies of atoms and molecules in the gas phase using the TOF-PEPECO technique together with soft X-rays from synchrotron radiation on which this thesis is based, continue to be carried in my group and at other places in the world. Some of the questions which may be addressed in future work in this direction have already been mentioned. For instance, how shall post-collision interaction be considered in connection with "direct" double ionization processes involving two vacancies inner shells? From the perspective of a "complete" description of multiple ionization this question would perhaps not arise, but in practice approximate model calculations appear necessary, treating the formation of the double hole states as a separate process.

The Auger decay of a double core hole state is often considered as a step-wise process of two-electron transitions, where in the first step an outer electron "fills" the hole and another is excited. However, similar to the case of single-step double excitations, three-electron transition are possible, with two vacancies being filled simultaneously and another electron carrying the energy of both transitions. The TOF-PEPECO coincidence technique should be well suited to study such phenomena, as the signal for the double hole states can be singled out in the coincidence data.

On the experimental side more information about multi-ionization processes is obtained if the ions are detected in coincidence with electrons, as the dissociation dynamics of selected states can be studied. Different schemes of electron-ion detection can be envisaged, e.g. extracting the ions to a detector in the opposite direction of electrons. This necessarily involves making a path for the ions to travel (and suitable electrodes for the extraction field), which in the current setup implies having a hole in the permanent magnet, which is not optimal for the magnetic field strength. The permanent magnet setup could, however, be abandoned in favour of an electro-magnet solution where a suitable ion flight path is incorporated in the design. In my research group simulations are currently in progress for a magnetic bottle set-up of this kind.

By the advent of the new "fourth generation" X-ray free electron lasers it is now possible to study non-linear dynamics in the X-ray region of the spectrum. I have been part of very recent experiments carried out at the Linear Coherent Light Source at Stanford, USA aiming to detect double core holes at different atomic sites in molecules on which the data analysis is still on-going.
The very intense light pulses provided by LCLS means the probability for ionizing samples in the focus region of focus is high. Moreover, the repetition rate of LCLS is quite low, 60-120 Hz. Pure coincidence measurements under such conditions has obvious limitations, hence multi-dimensional covariance mapping appears to be a very suitable method for extracting the correlations of the detector signals. If both ions and electrons are detected with high efficiency this would entail the possibility of very detailed studies of the formation and dissociation dynamics of molecules under intense X-ray field conditions. Single-site and two-site double core hole states in molecules are predicted to show very different dissociation dynamics, but this has not yet been verified experimentally.
Avhandlingen bygger på studier av atomer och molekyler genom fotojonisation, som innebär att elektroner (negativa laddningar) slås ut från atomerna och lämnar kvar positivt laddade joner. Albert Einstein förklarade fenomenet i början av nittonhundratalet med hjälp av den fotoelektriska lagen, som säger att energi enbart överförs av ljus till materia i diskreta energipaket, fotoner, och att den (foto)elektron som slås ut får en bestämdd rörelseenergi beroende av den energi som tillförts av fotonen och det arbete (bindningsenergi) som krävs för att avlägsna elektronen. I atomer ockuperar elektronerna orbitaler i olika skalen \( n \) \((n = 1, 2, 3, \ldots)\) där det krävs mer energi för att avlägsna en elektron från en orbital i ett inre skal med lägre \( n \), som kallas huvudkvantalet. I molekyler kan motsvarande orbitaler formas utav kombinationer av atomära orbitaler.


De hårdast bundna elektronerna i de inre skalen har bindningsenergier som motsvarar röntgenstrålning och är specifika för atomen, även om den ingår i en molekyl eller ett fast ämne. Därför ger de en signatur för en viss atom, en topp, i ett spektrum av elektron energier som mäts up om ett ämne bestrålas med ljus av känd energi. Toppens exakta läge i ett spektrum kan vara något skiftat beroende på den specifika omgivning atomen befinner sig i, vilket kallas ett kemiskt skift. Det kan också inträffa att fler än en elektron slås ut efter att en foton inverkat på en atom eller molekyl. I så fall delar de på den tillgängliga energi som tillförts och det kan vara nödvändigt att mäta alla de emitterade elektronernas energier på samma gång, det vill säga i koincidens. Då krävs att elektronerna detekteras med stor sannolikhet. Ett sätt att åstadkomma detta är att fanga elektronerna i en magnetisk flaska, och sedan styr dem mot en detektor, som ligger någon till några meter bort. I den typen av elektronspektro-


Molekyler med två vakanser, hål, i det innersta skalet undersökes i molekylerna metan och ammoniak. Sådana ihåliga molekyler är exempel på extremt högt exciterade tillstånd, och det är väldigt osannolikt att de bildas när bara en foton verkar på molekylen. De är också intressanta för att deras kemiska shift förväntas vara större än det när bara ett hål bildats i en fotojonisationprocess, vilket är betydligt mer sannolikt. De kemiska shiften för dubbla hål i det näst innersta skalet uppmättes och analyserades för molekylerna i divätesulfid, kol-disulfid och svaveldioxid.
Acknowledgements

I would first like to thank my supervisors Mats Larsson and Raimund Feifel for the opportunity to do my PhD within the Stockholm-Uppsala collaboration. Special thanks also goes to Prof. John H.D. Eland for sharing his considerable insight into coincidence spectroscopy and for all the help along the way. Experimental work is rarely done alone and I want to mention the BESSY-II U49/2 "staff", former and present; Melanie, Stefan, Lage, Sergei, Richard and Egil. I leave the nightshifts to the new generation now, have fun! Thanks to Tomasz for putting up with me as a roommate, it can’t have been easy. I wish you and your family all the best. And to Peter, for all the tennis distractions of various kind (and sorry about the elbow!). To Leif Karlsson and Svante Svensson for the physics discussions and encouraging words to a stressed-out student. It has helped. And to my cat, for her helpful input to the text.

Sist men absolut viktigast vill jag tacka min familj, vänner och speciellt min Loretto. För allt, egentligen.


References