FRAGMENTATION OF SMALL MOLECULES BY UV AND X-RAY IRRADIATION

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Abstract

Electron-ion coincidence spectroscopy has been used to study the fragmentation behaviour of small molecules in two distinct cases: to resolve the state specific fragmentation patterns of HgBr₂ and HgCl₂ subsequent to UV ionization, and to distinguish the dissociation behaviour of various chlorinated methanes (CH₃Cl, CH₂Cl₂, CHCl₃ and CCl₄) subsequent to X-ray irradiation. The mercury-compound work has revealed details on the electronic structure and dissociation dynamics of the valence states which were previously unknown. The study on the chlorinated methanes has found new details on the exact pathways of the appearance of a specific fragment and also investigates the speed of the dissociation in the four different chlorinated methane molecules. The results from the electron-ion coincidence spectroscopic experiments are presented and analysed together with theoretical and computational support.

Key words: Auger, electron, coincidence, chloride, halide, ion, mercury, photodissociation, photofragmentation, spectroscopy, valence, X-ray
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Oulu, July 2017   Esko Kokkonen
LIST OF ORIGINAL PAPERS

The present thesis contains an introductory part and the following papers which will be referred in the text by their Roman numbers.


The papers listed above are the result of teamwork. The author has performed the experiments, analysed the data, and been the main person responsible for writing the articles.

Original publications are not included in the electronic version of the thesis.
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Chapter 1

Introduction

Molecules along with atoms are the basic building blocks of all life and matter on earth. A fundamental way of getting information about them is to use spectroscopic methods, in particular electron and ion spectrosopies. With these methods, the electronic structure of atoms and molecules, the internuclear dynamics and binding processes within molecules, and the specific pathways that govern the dissociation of molecules can be resolved. An important feature in all of the experiments is the use of electromagnetic radiation which is used to perturb the atoms and molecules so that they reveal their properties.

The intrinsic interaction between light and matter was explained by Einstein in 1905 with the photoelectric effect [1] (originally observed by Hertz in 1887 [2]). This effect is the main principle behind photoelectron spectroscopy that was developed in the 1950s and 1960s [3–5]. Since its original invention, the technique has been used to investigate the valence levels of atoms and molecules using ultraviolet photoelectron spectroscopy (UPS) or the core-levels using X-ray photoelectron spectroscopy (XPS). In this thesis electron spectroscopy in the ultraviolet and X-ray ranges is used to study the electronic structure of various molecules.

On the other hand, Mass spectroscopy had been developed somewhat earlier than electron spectroscopy with the first developments by Thomson [6] in the early 20th century. Not long after the invention of photoelectron spectroscopy, the first coincidence experiments were conducted in conjunction with mass spectroscopy. The first experiments were done using photoelectrons and photoions [7]. Since then, the field has been used to investigate light-matter interactions including fragmentation processes in many molecular systems.

With the development of synchrotron radiation [8], both electron spectroscopy and coincidence studies could be done with a light source that provided much more intense light as well as being highly tunable to specific
requirements of the experiment. The trend continues even today with free electron lasers providing even higher photon intensities for electron, ion, and coincidence spectroscopies [9].

In the present work, coincidence spectroscopy has been utilized to measure the fragmentation behaviour of molecules when they interact with photons. Mercury containing compounds have been ionized using radiation in the UV range and the subsequent state selective fragmentation patterns were recorded. In a similar manner, some chlorohydrocarbon compounds were excited using X-rays and their fragmentation behaviour observed. The results from these experiments reveal the details of molecular photodissociation dynamics, which is important to fully understand within these molecules as they are subjected to light of varying energy.

This thesis is arranged into six chapters. Chapters 2 and 3 give the necessary physical and experimental background while Chapter 4 explains electron-ion coincidence spectroscopy in details. Chapter 5 contains the motivations and summaries of all the published papers. Conclusions from the studies are drawn in Chapter 6 with a brief look to future prospects. The author’s work has been mainly experimental in all the published papers and in all of the work during the thesis period. This is reflected in the contents of the introductory part of the thesis.
Chapter 2

Physical background

2.1 Atoms and molecules

Atoms consist of a positively charged nucleus and an electron cloud surrounding it. The electrons are distributed in the electron cloud on atomic orbitals, which are described as one electron wavefunctions characterized by their angular and spin momentum. Generally speaking, if the aim is to resolve the energies $E$ of the atomic orbitals, one seeks to solve the Schrödinger equation of the system:

$$\hat{H} \psi = E \psi,$$  \hspace{1cm} (2.1)

where $\hat{H}$ is the Hamiltonian operator which, when operating on the wavefunction, yields the eigenenergies of the system. [10, 11]

The solution of the Schrödinger equation also gives a set of quantum numbers for each electronic wavefunction which are conserved quantities in dynamical processes. Some of the most often used quantum numbers are: the principal quantum number $n$, orbital angular momentum quantum number $\ell$, the magnetic (projection of angular momentum) quantum number $m_\ell$, and the spin projection quantum number $m_s = \pm 1/2$. The principal quantum number takes integer values 1, 2, 3... and the quantum number $\ell$ can take values $0 \leq \ell \leq n - 1$, which is usually denoted with the letters $s, p, d$, etc. The magnetic quantum number $m_\ell$ takes values $-\ell \leq m_\ell \leq \ell$. [12]

To specify a quantum state belonging to a particular electron configuration (set of quantum numbers) the angular and spin momenta are usually coupled together using different coupling schemes. The states are given their own designations according to the coupling scheme and the quantum numbers of the electron configuration.

The non-relativistic Schrödinger equation does not take into account all aspects of the quantum mechanical systems which have to be considered.
One of them is the interaction between an electron’s spin and its angular momentum, known as the \textit{spin-orbit interaction}. With the spin-orbit interaction, the total angular momentum $j$ of an electron has two values: $\ell + 1/2$ or $\ell - 1/2$, which then causes two distinct states to appear with a specific energy difference.

Molecules are formed from individual atoms. When two or more atoms form a molecule, the potential energy of the complete system decreases until it reaches the minimum energy of the ground state of the molecular system. In the ground state, more energy is required to move the nuclei closer together due to the electrical repulsion induced by the Coulomb field of the nuclei and electrons. When atoms are bound, more energy is also required to overcome the bonding power of the electrons holding the atoms together. [10]

A useful model for the electronic wavefunctions in a molecule is that they are composed of several \textit{molecular orbitals} (MOs). An often used definition of a molecular orbital wavefunction ($\Phi$) is the linear combination of atomic orbital wavefunctions $\psi_k$, which are scaled with appropriate coefficients $a_k$:

$$\Phi = \sum_{k=1}^{K} a_k \psi_k. \quad (2.2)$$

This method is known as the linear combination of atomic orbitals, or LCAO, model. In this approximation, each atomic orbital is centered around the individual nuclei. With the LCAO method, each molecular orbital can be traced back to the individual atomic orbitals that contribute to the MO in question and thus one can deduce the bonding properties of the MO based on the atomic orbitals.

One of the most elementary examples of a MO is in the hydrogen molecule ($H_2$), where two H 1s atomic orbitals are brought together to form the corresponding molecular orbital. As the atomic orbitals form the MO, there are two linear combinations that can be constructed from the atomic orbitals:

$$\Phi_g = \frac{1}{\sqrt{2(1 + S_{12})}} (\phi_1 + \phi_2) \quad \text{or} \quad (2.3)$$

$$\Phi_u = \frac{1}{\sqrt{2(1 + S_{12})}} (\phi_1 - \phi_2), \quad (2.4)$$

where the subscript $g$ and $u$ denotes either even (\textit{gerade}) or odd (\textit{ungerade}) reflection in the midpoint of the molecule and $S_{12}$ is the overlap integral of the atomic wavefunctions. In this elementary molecule, the electronic states that are derived from the atomic orbitals cause two distinct states to appear. In the ground state of the molecule the two electrons create a molecular
orbital that has a density with a maximum at the midpoint between the two atoms. Thus, the MO $\Phi_g$ is a bonding orbital designated as $\sigma_g 1s$. By contrast, in the ungerade case the MO $\Phi_u$ has no density maximum between the nuclei and is therefore an antibonding orbital. The orbital is designated as $\sigma_u^* 1s$, where the superscript (*) indicates that the orbital is antibonding.

The electronic orbitals of a molecule can be roughly categorized as belonging to either the valence or core-shells. The valence orbitals are almost always delocalized throughout the molecule thereby participating in chemical bonding. The valence orbitals can be further classified into inner and outer valence, where outer valence is the first MOs. Inner valence constitutes as the rest of the MOs that are below the double ionization threshold. The core-shells, on the other hand, are localized on individual nuclei and have higher binding energy. This correspondence is schematically shown in Fig. 2.1a).

### 2.1.1 Potential energy curves

The total energy of a system consisting of numerous atoms always has a preferred geometry where the total energy reaches its minimum. In this geometry, the atoms are located at the equilibrium distance as more energy is required to bring the atoms closer to each other and also to move them further apart. The energy of the molecule as a function of internuclear distance is often plotted in potential energy curves, such as in Fig. 2.1b).

![Potential energy curves](image)

Figure 2.1: a) Schematic view of the electronic states in a diatomic $AB$ molecule. b) Potential energy curves showing the parabolic approximation (red dashed line) and the Morse potential (blue solid line).

There are several methods of approximating the shape of the potential energy curves for a specific molecule. In diatomic molecules, for example, a rough parabolic approximation gives somewhat realistic values for the energy at small distances around the equilibrium distance $R_e$. When the internuclear separation is larger, a more accurate potential shape is needed. An often used potential shape is the Morse potential as it takes into account
the effects of bond breaking. The potential energy function for a Morse potential is:

\[ V(r) = D_e \left( 1 - e^{-a(r-R_e)} \right)^2, \]  

(2.5)

where \( D_e \) is the depth of the potential well \( (D_e = V(\infty) - V(R_e)) \), \( R_e \) is the equilibrium distance, and \( a \) is a factor related to the force constant. [11]

The Morse potential is strictly valid only for a diatomic system, where there exists only one internuclear coordinate. However, some key factors can be pointed out from this model that are also applicable in more complex systems. First, there exists a point along the internuclear axis where a bound potential energy curve has a minimum energy. This is the point of equilibrium distance between the nuclei. Another key factor is the depth of the potential well, which is called the dissociation energy \( D_0 \). Dissociation energy is defined as the energy difference between the lowest possible energy state of the bound system (which turns out to be the zero-point energy) and the energy at an infinite internuclear distance. Commonly for diatomic molecules the internuclear distances are of the order 1–3 Å while the dissociation energies \( D_0 \) are of the order 4–6 eV [11].

The above expressions become slightly more complicated in a molecule with three or more atoms, or a polyatomic molecule. Already in a diatomic molecule we notice that even in the ground state there exists several substates along the ground state potential energy curve. These are known as vibrational states, which correspond to higher degrees of vibrational motion energy that the molecule can have. A diatomic molecule has only one vibrational degree of freedom, i.e. the molecule vibrates in only one dimension. Polyatomic molecules can contain several degrees of freedom and several vibrational modes. For example a water molecule (\( \text{H}_2\text{O} \)) contains an oxygen atom with two hydrogen atoms bound to it. It is therefore easy to imagine that the hydrogen bonds can bend and stretch in various ways. In general a non-linear molecule with \( N \) atoms will contain \( 3N - 6 \) vibrational modes and a linear one will contain \( 3N - 5 \). [10]

Additionally, the rotational motion of the molecules is quantized and contains energy. The rotational states are, however, less separated in energy and therefore beyond the measurements that are used throughout this thesis. They are thus not considered any further.

### 2.2 Electronic transitions

Due to the wave-particle duality, light consists of discrete packets of energy known as photons. Each photon has an energy \( h\nu \), where \( h \) is Planck’s constant and \( \nu \) the frequency of the light. When photons of high enough energy interact with an atom or molecule, an electronic transition can occur.
2.2. Electronic transitions

In the transition, the system undergoes a change from one quantum state to another according to a specific set of rules.

2.2.1 Photoexcitation

Photoexcitation occurs when a photon with an energy \( h\nu \) is absorbed into an atom or a molecule. If the photon energy matches the energy difference of the electronic states in the system \( A \), and the lower electronic state is populated, an electron can be promoted from the lower state to the higher state:

\[
    h\nu + A \rightarrow A'.
\]

(2.6)

After absorbing the photon, the system is said to be in an excited state, \( A' \). Due to the finite lifetime of the excited state, it eventually decays to a state of lower internal energy of a specific electronic configuration.

Photoexcitation is governed by specific rules. The interaction between the electromagnetic radiation and the quantum mechanical system is considered to happen under the so-called electric dipole approximation. In the electric dipole approximation, the transition process is expressed only using the first terms of the series expansion of the electric dipole interaction operator, which is the dominant operator for the interaction between an electron in an atom and the electromagnetic field. The approximation works well for UV and soft X-ray regions, but in higher energies the contributions from different interactions contribute as well. A consequence of the electric dipole approximation are the electric dipole selection rules. These rules state the specific properties of the system have to be conserved in an electronic transition, which means that the change in quantum numbers may be restricted. In molecular systems also the quantum numbers between the vibrational and rotational states restrict the transitions. [11, 13]

2.2.2 Photoionization

If the incident photon energy is larger than the binding energy of an electron on a particular orbital of the atom or molecule, a photoionization may occur. In this case the photon can get absorbed by the system leading to the ejection of a photoelectron. The kinetic energy, \( E_k \), of the photoelectron is

\[
    E_k = h\nu - E_b - \Delta E_{\text{vib}},
\]

(2.7)

which depends on the binding energy \( E_b \) and the photon energy \( h\nu \). For molecular species, \( \Delta E_{\text{vib}} \) constitutes a vibrational band, which can be excited in the photoionization process\(^1\). Selection rules also govern the behaviour

\(^{1}\)The rotational states of the molecule can also be excited in the process, but these are rather small energies (in the order of meV)
of photoionization, but they do not restrict any processes. Instead, they provide a description between the molecule and the created ion and the photoelectron. [14, 15]

Whether photoionization happens when a photon interacts with an atom, depends on the photoionization cross section. The cross sections are different for each electronic orbital (and each element) while also changing as a function of photon energy. The cross section maxima are found near or at the photoionization thresholds and decrease gradually towards higher photon energies.

Depending on the incident photon energy, different set of orbitals become energetically possible to ionize. With ultraviolet (UV) photons, only the outermost orbitals, or valence orbitals, are accessible. As the photon energy is increased to the soft X-ray region, the inner valence orbitals are accessible and some core-levels as well. While it is also energetically possible to ionize valence levels with soft X-rays, their cross sections are lower compared to that of core-levels.

Experimental techniques used to study the electronic structure include ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). In these two techniques either UV light or X-rays are used to irradiate the sample and the kinetic energies of the emitted electrons are analysed. With UPS one gains direct information on the binding energies of the valence levels, while XPS is typically used to study the core-levels.

2.2.3 Auger processes

Normal Auger

If the core-level of an atom or a molecule is photoionized, the ionic state is highly unstable and will decay to a state of lower energy. In elements that are relatively light (atomic number $Z < 30$), it is highly probable that an Auger process occurs. In the Auger process, the core-hole is filled by an electron from a higher energy orbital. In the same instant, another electron is ejected from an outer orbital. This electron is called the Auger electron. The kinetic energy of the Auger electron is defined by the energy difference between the intermediate (core-ionized state) and final states. The normal Auger process is depicted on an energy level diagram in Fig. 2.2. All Auger processes are two electron transitions and therefore do not follow dipole selection rules. [16–18, 12]

After the Auger relaxation, the initial system has been left in a doubly charged state (i.e. the total charge is +2). In the case that the created vacancies are not on the outermost orbitals, the system is still left in a state of higher energy. This can further decay through a second Auger process emitting another Auger electron further increasing the total charge of the
2.2. Electronic transitions

A cascade process can therefore happen, where an initial ionization of a core-level initiates several Auger emissions sequentially. A radiative transition can also occur after the first Auger decay.

Because of the nature of the double hole final state and the fact that the final states can be the result of mixing of several single-electron orbitals, Auger spectra always contain several line components, even for the simplest systems such as closed-shell atoms. In comparison to photoelectron spectra, Auger spectra can contain several lines within a small energy range. High energy resolution is therefore required in the experimental setup.

The scheme in Fig. 2.2 can be further complicated by satellite transitions, where additional excitations or ionizations occur in the outer levels during transitions. These are also known as shake-transitions. The energies and intensities of the satellite transitions differ from the main lines making Auger spectra typically very rich in structure. [19]

**Resonant Auger**

If the core-level is photoexcited instead of photoionized, a resonant Auger decay can follow. In this case the core-level electron is first promoted to an unoccupied orbital through photoexcitation. The resulting core-hole is then filled by an electron similarly as in the normal Auger case. An Auger electron emission follows, which has an energy corresponding to the excess energy of the transition. The resonant Auger process is depicted on an energy level diagram in Fig. 2.3. [16, 19]
Chapter 2. Physical background

Figure 2.3: The resonant Auger process, which is initiated by an excitation of a core-level electron to an unoccupied level. The resulting Auger process can involve either the excited electron (participator Auger) or the other valence electrons (spectator Auger).

The resonant Auger process can be further classified into two categories depending on whether the initially excited electron on the outer orbital takes part in the relaxation. First, the excited electron may remain as a passive “observer” whilst the core-hole is filled. This process is known as spectator Auger process, and is depicted in Fig. 2.3. The second option is that the excited electron takes part in the Auger process, usually by being the electron that is emitted as an Auger electron. This is known as a participator Auger process, or an autoionization process, since the final state that is created is identical to outer-shell ionization processes. Spectator Auger final states are also accessible through a combined ionization and shake-up process, which ends up in the same final state. In the resonant Auger process the system is left with only one electron vacancy in it, so its total charge is therefore +1. [19]

While the normal Auger process can be initiated by any source of ionization, such as electron, ion, or photon bombardment, the resonant Auger process requires more sophisticated means. Often only the highly tunable synchrotron radiation is used to make the resonant excitations that are required to study the resonant Auger processes.

Measurements of Auger electrons in normal Auger processes or in resonant Auger processes are known as Auger electron spectroscopy (AES) or resonant Auger spectroscopy (RAS). Both of these methods give information on the levels that take part in the relaxation processes and therefore on the electronic structure of the system as a whole.
2.3 Molecular dissociation

An efficient method of reorganizing the internal energy of a molecular system after it has absorbed energy, is to dissociate, or break into smaller fragments. Photon-induced fragmentation reactions do not specifically require that the incident photon energy is larger than the ionization energy of the system [20]. In this thesis, only systems which have been created using incident energy that is larger than the ionization energy are studied. Hence, an electron is always emitted before, during or after the dissociation process. By carefully studying the properties of the electron emission, one can get quantitative and qualitative information on the dissociation process itself.

When considering the nuclear dynamics of a molecule, an often used approximation is the Born-Oppenheimer (BO) approximation. This approximation assumes that the movement of the electrons is much faster compared to the nuclear motion within a molecule so that the electronic and nuclear wavefunctions can be separated. The approximation originates from the fact that the mass of any nucleus is much greater than the mass of a single electron. [21]

With molecular potential energy surfaces, the Born-Oppenheimer approximation yields an important result. Electronic transitions within the so-called Franck-Condon region are assumed to happen instantaneously from one electronic state to another without any changes in nuclear geometry. The transitions are therefore drawn as straight vertical lines on the potential energy curve scheme. [11]

If the vibrational wavefunctions in the upper and lower electronic states are $\psi'_{\nu'}(R)$ and $\psi_{\nu}(R)$ and the transition takes place between a small interval of internuclear distances $dR$ around $R$, the probability can be expressed by the Franck-Condon factor:

$$f_{\nu'\nu} = \int \psi_{\nu'}^* \psi_{\nu} dR.$$  \hspace{1cm} (2.8)

The quantity $f_{\nu'\nu}$ is also known as the overlap integral between the vibrational wavefunctions in the upper and lower electronic states. The most intense transitions therefore occur between vibrational wavefunctions for which the overlap integral has the highest value (i.e. they are found within the same internuclear distance as the ground state).

Figure 2.4 shows an example of a dissociation scheme where the initial excitation in the Franck-Condon region can reach two different excited states. Potential energy curve (PEC) (a) represents an antibonding orbital. If the excitation is done onto this orbital, the resulting photoelectron spectrum contains an unresolved band with no vibrational features, since no bound structure is found. PEC (b), on the other hand can also lead to dissociation
Figure 2.4: Various electronic transitions leading to direct dissociation in a hypothetical $AB$ molecule. Excitation to a bound state with energy higher than the dissociation energy leads to increase in internuclear distance, as does promotion to a dissociative state.

of the molecule. In this case the dissociation can only happen if the electronic transition reaches a vibrational state that is higher in energy than the dissociation energy of the excited electronic state. Cases (a) and (b) in Fig. 2.4 are examples of direct dissociation. In these cases, the direct photoionization promotes the system to a state which rapidly decays in the form of fragmentation.

Other dissociation schemes exist as well, potentially violating the BO approximation. These are known as predissociation. For example in electronic predissociation, the system is first promoted to a higher lying vibrational state of a bound electronic state. Through rearrangement of electronic energy, there can be a non-radiative transition from the bound state to an unbound state [15]. This requires that the potential energy curve of the unbound state crosses the curve of the bound state at the higher lying vibrational state.

With polyatomic molecules containing several vibrational modes, an efficient method of predissociation exists. In this scheme the initial transition is to a vibrational mode that does not correspond to the reaction coordinate of the dissociation (the axis along which the dissociation occurs). Instead, the vibrational energy is rearranged and transferred to another vibrational mode which then can then lead to dissociation. [15, 20]

All photodissociation reactions obey the constraints of conservation of energy and angular momentum. By studying the vector correlations
between the electric field vector of the light, transition moment of the parent molecule, and the velocity and angular momenta of the photofragments, one is able characterize the photodissociation reaction itself. [20]

The research in this thesis is done in two different regimes. The first part deals with dissociation subsequent to UV photon absorption, which means that the processes that occur in the molecules deal with the dynamics of the valence orbitals. The second part deals with consequences of X-ray absorption. This involves the creation of a core-hole and the subsequent relaxation processes, such as Auger decay. These relaxation processes are often followed by dissociation.

2.3.1 Valence region

In this thesis the experiments dealing with valence dissociation study the relative differences in the fragmentation behaviour of the valence orbitals upon ionization. The fragmentation processes were studied in molecules using ultraviolet light (often using photon energy of approximately 40 eV) which is enough to ionize most of the outer and inner valence orbitals.

After an ionization according to Eq. 2.7 the molecule is left with a hole in one of the valence orbitals:

\[ h\nu + M \rightarrow M^{+(*)} + e^- \]  

where \( M^{+(*)} \) is the ionized (and potentially excited) parent molecule. Depending on the nature of the molecular orbital from which the electron was ejected, the parent can fragment in different ways. Single ionization of the highest occupied molecular orbitals (HOMOs) often does not induce any fragmentation and the parent molecule remains singly charged. In this case the electronic state of the singly ionized molecule \( M^+ \) is still bound in the potential energy scheme, but the equilibrium internuclear distance may differ from the neutral molecule. [22–26]

Ionization from the other valence orbitals almost always leads to fragmentation in all molecules. In these cases the molecule \( M^+ \) fragments into several daughter ions:

\[ M^+ \rightarrow \begin{cases} A^+ + B \\ A + B^+ \end{cases} \]  

where \( A \) or \( B \) can be also excited. Which one of the two fragmentation pathways actually occurs depends on the nature of the valence orbital that was ionized.

Experimental electron spectra also contain information on the dissociation dynamics. The vibrational bands can be altered specifically by a
dissociation process. By studying these alterations in the electron spectra, one can gain information on the type of the dissociation (direct or predissociation) and on the energetics.

A more straightforward method is to utilize coincidence methods, such as photoelectron-photoion coincidence (PEPICO) spectroscopy. In PEPICO one measures photoelectrons and photoions created from the same photoionization events, which contain clear signatures of the fragmentation behaviour of the molecular orbital that has been ionized. This methodology is explained in more detail in Chapter 4. [27, 26]

2.3.2 Core excitation and subsequent processes

Excitation of core-levels and subsequent effects on molecular fragmentation are also studied in this thesis. Core-level photoexcitation (and photoionization) of a molecule inevitably promotes the system to a higher energy state, which decays to an electronic state that is likely to be dissociative. Moreover, the fact that core-levels are unique for each element can be exploited when studying the fragmentation behaviour of molecules. By tuning the photon energy to target core-levels in a specific element in the molecule, one can achieve so-called site selectivity in the fragmentation. This makes it possible to investigate many different phenomena in molecular dissociation processes, including charge transfer or specific bond cleavage mechanisms. [28, 29]

As mentioned earlier, the creation of the core-hole by photoionization or photoexcitation is followed by a relaxation process, such as Auger decay. The final states reached by Auger decay are often rather unstable and prone to fragmentation. Especially the double-hole final states subsequent to normal Auger decay dissociate easily due to Coulomb explosion, i.e. rapid bond breaking due to strong Coulombic repulsion of the nuclei. In the same manner as with final states that are reached through direct ionization, the exact fragmentation pathway that Auger decay initiates depends on the molecular orbitals that are involved in the transition processes. [30]

Figure 2.5 depicts the dissociation subsequent to resonant Auger relaxation. The first process (a) is the core-excitation using photons with energy equal to the energy difference of the ground and core-excited states in the same manner as in the left picture of Fig. 2.3. The resonant Auger relaxation that follows (b) then decays the system into a singly ionized state in the same way as in the right panel of Fig. 2.3. In this case the final state is repulsive, which causes the dissociation.

Depending also on the nature of the repulsive final state that is reached, it is probable that the fragments will gain kinetic energy. This kinetic energy release (KER) often carries valuable information on the dynamics and energetics of the dissociation process, and gives information on the
2.3. *Molecular dissociation*

![Diagram of molecular dissociation](image)

Figure 2.5: Core excitation and subsequent dissociation as depicted on potential energy curves in the case of a diatomic $AB$ molecule. In (a) the molecule is first promoted to the core-excited state and in (b) it relaxes into the final state by emission of an Auger electron. The fragments may also gain kinetic energy (KER).

shapes of the potential energy surfaces [31]. In Fig. 2.5, KER is depicted to appear subsequent to an Auger relaxation, but strictly speaking its origin is independent of how the final state is reached. KER can also manifest in direct dissociation, such as depicted in Fig. 2.4, depending on the repulsive nature of the potential energy curve, and on the internuclear distance. [30]

Experimentally, fragmentation processes after core-level excitations are often studied using electron-ion coincidence methods. When used in conjunction with resonant Auger emission the method is known as Auger-electron photo-ion coincidence spectroscopy, and it can be used to determine the fragmentation pathways and relaxation dynamics that core-excitation facilitates. Often systems where core electrons are excited to unoccupied orbitals, can experience strong geometrical changes and, through the core-excited state, can reach potential energy surfaces that are not reachable otherwise. [29, 32]

### 2.3.3 Ultrafast dissociation

Core ionization of a molecule and the subsequent electron relaxation takes place on time scales of a few femtoseconds. In the context of ultrafast dissociation, this may also be the time scale for any significant nuclear motion within the molecule. Nuclear motion and electronic decay in the
form of Auger decay can compete with one another and cause varying effects to the Auger electron emission. [33]

Ultrafast dissociation (UFD) is defined as the molecular dissociation that occurs before any core-hole decay has taken place. This means that the molecular system has been promoted to an antibonding orbital which causes fast nuclear motion where the initial core-hole is left in one of the fragments. The core-hole relaxation then proceeds in the fragment, which experiences a slightly different chemical environment and thus different energies of the levels between which the process occurs.

![Diagram of potential energy curves of the CH₃Cl molecule. The red spectrum indicates transitions that occur within the molecule, which has not dissociated yet while the green is the resonant Auger spectrum from a dissociated Cl fragment.](image)

**Figure 2.6:** UFD in potential energy curves of the CH₃Cl molecule. The red spectrum indicates transitions that occur within the molecule, which has not dissociated yet while the green is the resonant Auger spectrum from a dissociated Cl fragment.

UFD can be studied using modern light sources, such as free electron lasers. These types of light sources with very short pulse lengths can be used to investigate the nuclear dynamics in the femtosecond regime, which is the same timescale as the electron dynamics. However, another approach is also possible which does not utilize any femtosecond timing of light sources, whereby the internal “core-hole clock” [34–38] inherent to the molecular system is exploited to gain information about the timescales. The ion fragmentation patterns alone do not help with resolving the timing of the fragmentation, but often the electrons escaping the dissociated system contain the necessary information to reconstruct the nature of the system from which they were emitted. In this case it is enough to simply record a high energy resolution Auger electron spectrum to study UFD. Complex
2.3. **Molecular dissociation**

molecules, however, contain several electronic states with very small energy intervals. Since the various electronic states might dissociate differently, they can be distinguished using coincidence spectroscopy. By identifying and filtering the fragments, one can focus on final states that are of interest, thereby decreasing the amount of structure seen in the spectra.

Since the first discovery of UFD in the 1980s [39], it has been experimentally observed in several different halogenated systems [40–45], as well as in other molecules such as water and ammonia [46, 47].

Figure 2.6 demonstrates how UFD could be seen on a resonant Auger spectrum, in the CH₃Cl molecule, as an example. If there is not much nuclear movement during the lifetime of the core-excited state, the following Auger decay takes place in a molecule that is almost intact. The resulting Auger spectrum therefore contains peaks, which are quite broad due to the slope of the potential energy curve in the final state (peaks and transitions in red in Fig. 2.6). If, however, the nuclear dynamics are fast and UFD occurs, then the CH₃Cl molecule has time to dissociate and the Auger relaxation takes place in the ejected Cl atom. In this case the transition occurs at a larger internuclear distance and the potential energy curves of the core-excited and final states are much more parallel. This has the consequence that the Auger electron spectrum will contain peaks with much smaller linewidth. The kinetic energies of the emitted Auger electrons will also be slightly higher. In fact, the kinetic energies will be similar to atomic chlorine case as if the system from which the electron is ejected is purely atomic chlorine. These states are depicted as green peaks in Fig. 2.6.
Chapter 2. Physical background
Chapter 3

Experimental background

3.1 Synchrotron radiation

Synchrotron radiation is emitted by charged particles in accelerating motion with relativistic velocities \( v \approx c \). To achieve the emission of the radiation, a beam of charged particles (almost always electrons) is created and guided into a storage ring. The ring is designed to maintain the beam of particles as long as possible with minimal losses due to collisions with residual gas or the walls of the ring. Special magnetic arrays, undulators, are fitted into straight sections of the ring to create a periodic magnetic field with alternating polarity. As the electron beam passes through the undulator, the electrons are forced into an undulating motion and emit dipole radiation with very high brilliance. Because the electrons are travelling with relativistic speeds, the Lorentz transformation of the dipole emission from the electron’s frame of reference to the laboratory frame causes the emission to be very sharply directed towards the direction of propagation. [48, 49]

Other devices used for generating radiation in a synchrotron are bending magnets and wigglers, which produce a different emission spectrum than an undulator. These are not considered further in this thesis.

Undulator radiation is characterized using the undulator parameter

\[
K_u = \frac{eB_0 \lambda_u}{m_ec 2\pi},
\]

where \( B_0 \) is the magnetic field strength and \( \lambda_u \) the length of one magnet period [49]. The parameter \( K_u \), among other things, defines the energy of the emitted radiation. It is therefore easy to tune the energy of the emitted radiation by changing one of the variables, such as the magnetic field strength \( B_0 \). In practice with permanent magnet undulators this is done by varying the gap between the two magnetic arrays. A schematic view of an undulator is shown in Fig. 3.1. [48]
Figure 3.1: Schematic view of an undulator.

The spectrum emitted from the undulator contains several peaks of very high brilliance. A monochromator is used to choose a specific part of a single peak, or harmonic, from the undulator emission spectrum. The monochromator houses one or more gratings that are used to perform very accurate energy selection on the undulator radiation. Often, a slit placed after the monochromator improves the energy resolution of the light, making the photon energy band, which is directed to the sample even narrower. The beamline includes the necessary optics to focus, collimate, and direct the light to the experimental chamber at the end of the beamline.

### 3.1.1 Beamline I411

All experiments in the thesis were conducted on the Finnish-Swedish soft X-ray beamline I411 of the 1.5 GeV MAX-II storage ring of the MAX IV synchrotron radiation facility in Lund, Sweden. The beamline was capable of producing photons in the energy range of approximately 40 to 1500 eV and it was designed for electron spectroscopy with samples in gas, liquid or solid phases. I411 had a 2.65 m long undulator with 88 poles and a period length of 58.85 mm. The radiation from the undulator was monochromatized using a modified Zeiss SX700 plane grating monochromator. A variable exit slit in the range 5-20 μm was also used followed by refocusing optics. To facilitate the high pressure required for gas phase experiments and ensure an ultra high vacuum environment for beamline optics, a differential pumping unit was fitted before the experimental chambers. [50–52]

The permanent end-station of the beamline housed a Scienta R4000 type Hemispherical Deflection Analyzer (HDA). The vacuum chamber of the end-station enabled users to use many different sample environments in solid, liquid, or gas phase [53]. The beamline also had a section designed
for user equipment, which was known as the “one-meter section”, where all of the experimental electron-ion coincidence equipment in this thesis were placed.

3.2 The electron spectrometer

The electron energy resolved electron-ion coincidence technique was used in almost all of the experiments conducted in this thesis. The technique crucially relies on an instrument that is capable of measuring the kinetic energies of the emitted electrons. Here, an HDA was utilized for this purpose. In papers I and II, a Scienta SES-100 type HDA with a 100 mm mean radius hemisphere was used, while in papers III and IV, a Scienta SES-200 [54] type HDA with a mean radius of 200 mm was used instead.

The operation of these spectrometers is very similar – they both house a pre-retardation/acceleration lens system that is used to ensure a somewhat larger collection angle and some energy modification to the electrons before they enter the hemispherical analyser section. [55, 56]

The main part of an HDA consists of the hemispherical section, where electrons with different energies are deflected by a different amount. Due to the Lorentz force, the electrons are forced on a curved trajectory. Electrons with smaller energies are deflected more than electrons with higher energies, and they will therefore hit different positions on the end of the trajectory where the detector is located. The kinetic energy of the electron’s trajectory along the centerline of the HDA is known as the pass energy, which is often kept constant using the lens system when measuring larger kinetic energy ranges.

Originally both spectrometers had a detector system that consisted of a fluorescent screen and a charge-coupled device (CCD) camera for resolving the hit position of the electrons. The system, however, suffers from rather slow detection timing (the time the electron signal is output is in the range of milliseconds), which is unacceptable for electron-ion coincidence experiments due to the movement of the ions in this time range. The detectors in both spectrometers were therefore replaced with a detector that consists of multichannel plates (MCP) and a resistive anode [56]. With this detector, the electron output signal has a much shorter delay with respect to the actual electron arrival time. The time delay of the resistive anode is on the order of microseconds.

The MCPs are placed on top of the resistive anode. Their role is to enhance the electron signal by multiplying each electron hit. This happens through an avalanche effect inside the channels of the plate. The micrometer sized holes of the plate are coated with a material which easily releases secondary electrons when it is hit with primary electrons of high enough
energy. With three consecutive plates, a single electron on the input side corresponds to a bunch of electrons on the output side, which yields a detectable signal on the anode. On the resistive anode, the signal propagates to each of the corners of the anode. By measuring how much the signal has attenuated in each corner, one is able to calculate the hit position within the anode plate.

In the current experimental setup, all coincidence measurements are conducted using fixed voltages on the electron spectrometers. Therefore only electrons from a fixed kinetic energy range are collected. In the SES-100 and SES-200 type spectrometers, the gross etendue – the size of the kinetic energy range – is approximately 10% of the selected pass energy e.g., a 100 eV pass energy gives an energy window of about 10 eV. Currently in coincidence operation, the measurement software is unable to directly measure the energies of the electrons. Instead, the coincidence computer receives the hit position of the electron in the direction of electron energy dispersion. The transformation from hit position to energy always has to be done by offline analysis, since the measurement software has no information on the correspondence between hit position and energy.

When using the electron spectrometer in coincidence mode, the conversion from detector hit coordinates to kinetic energy is done with the help of an additional sample. The requirements of this sample are that it has to have a rather narrow photoelectron line, thus usually noble gases are used. By changing the voltages of the spectrometer, the photoelectron line from the sample is moved across the detector in step. At each step the hit location in the energy dispersive direction of the spectrometer is extracted. By fitting a second order polynomial to the measured points, one gets a good correspondence between the detector hit position and kinetic energy. Due to the operational differences of the spectrometer for each pass energy, the conversion has to be performed individually for each pass energy.

Two crucial parameters of the HDA are its resolution and transmission. Resolution refers to the spectrometer’s ability to separate electrons with different energies from each other. In both SES-100 and SES-200 type electron spectrometers, the resolution is closely related to the pass energy and entrance slit width. Generally, the resolution of the electron spectrum can be improved by choosing smaller entrance slit or a smaller pass energy [55]. Decreasing these parameters unfortunately also decreases the transmission of the spectrometer. Transmission is defined as the ratio between all the electrons created in the ionization to those that make their way to the detector and is geometrically defined by the solid angle of acceptance of the spectrometer. Since the lens system of the hemispherical analysers has only a relatively small acceptance angle, the transmissions of these types of spectrometers is often less than one percent.
3.3 The ion mass spectrometer

The ion mass spectrometer used in this thesis is a Wiley-McLaren type two field time-of-flight mass spectrometer (TOFMS) [57]. A two-field TOFMS consists of separate extraction and acceleration regions, which provide good spatial focusing of ions, when operated in the so-called Wiley-McLaren conditions. Under these conditions the effect of the ion’s initial position on its flight time is minimized. In paper I, a ∼300 mm TOFMS [58] was used while experiments in papers II–IV used a ∼600 mm TOFMS. Although the geometries and detector systems of the two spectrometers are slightly different, the operating principle remains the same. The schematic view of the new TOFMS tested in the thesis work and used in the experiments of papers II–IV is in Fig. 3.2.

Successful ion time-of-flight analysis relies on two signals: the start and the stop signals. The start signal can be produced in different ways depending on how the spectrometer is operated. One option, which has been predominantly used in the experiments here, is to operate the spectrometer using pulsed extraction\footnote{Another option is to use a constant field in the extraction region in which case the start pulse must originate from some other source, such as the light pulse.}. In this mode, the ion extraction field is not on at all times, but is instead pulsed with a fixed frequency and pulse length. The start signal is therefore the same as the rising edge of the extraction pulse, which gives the ions their initial push towards the detector. The timestamp of this signal is then used as the first reference to which it is possible to compare the subsequent stop signal(s). The stop signal(s) can be taken also from multiple sources, but if only the timing of the ions is of interest, a simple metal anode is sufficient, or even the pure MCP signal. The stop signal is then fed into the appropriate signal handling electronics, which deduces the time difference between the start and the stop signals which ultimately is the time-of-flight of that ion. In the current spectrometer, the stop signals are first preamplified (RoentDek FAMP8 preamplifier) and digitized using an oscilloscope capture card. The card is integrated in a PC system, which controls the whole measurement process.

If additional information on the ions is needed, the detector system of the spectrometer can be amended with, for example, a position sensitive detector. With a position sensitive detector both the timing information and the hit position \((t, x, y)\) of each ion can be measured. Recording the full \((t, x, y)\) information of the ions at the detector makes it possible to deduce the momenta the ions have gained in all three directions \((p_z, p_x, p_y)\) in the ionization or fragmentation process. This is useful when it is desirable to study momentum and KER distributions of a particular fragmentation reaction. In this thesis, however, the position information on the detector
Figure 3.2: A schematic view of a time-of-flight mass spectrometer with different regions highlighted

was omitted while only focusing on the time-of-flight aspects of the ions and therefore the mass spectroscopic information. [59, 60]

The motion of an ion with mass $m$ and charge $q$ can be modelled using Newtonian equations of motions and charged particle equations. The time-of-flight of an ion in all three regions of the spectrometer can thus be deduced, and the variables that the flight time depends on can be calculated. The ion is created with initial kinetic energy $E_{k0}$ and with an initial velocity vector $v_0$ pointing in an arbitrary direction with an angle $\theta_0$ with respect to the axis of the spectrometer (see Fig. 3.2 for a schematic view of the TOFMS). The ion is created at the center of the extraction region (ER), at a distance $s_0$ from the grid towards the acceleration region (AR). The extraction and acceleration regions have electric fields of $\varepsilon_{ER}$ and $\varepsilon_{AR}$ and total lengths $s$ and $d$, respectively. This gives the flight times in the ER, AR and the field-free drift region (DR) as

$$T_{\text{ER}} = \frac{\sqrt{2m}}{q\varepsilon_{\text{ER}}} \left( \sqrt{E_{k0} \cos^2 \theta_0 + q \varepsilon_{\text{ER}} s_0} \pm \sqrt{E_{k0} \cos^2 \theta_0} \right)$$

$$T_{\text{AR}} = \frac{\sqrt{2m}}{q\varepsilon_{\text{AR}}} \left( \sqrt{E_k} - \sqrt{E_{k0} \cos^2 \theta_0 + q \varepsilon_{\text{ER}} s_0} \right)$$

$$T_{\text{DR}} = \sqrt{\frac{m}{2E_k} D}$$

where $D$ is the length of the drift region. The total energy that the ion gains after the extraction and acceleration region is $E_k = E_{k0} + q s_0 \varepsilon_{\text{ER}} + q d \varepsilon_{\text{AR}}$. 

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3.3. The ion mass spectrometer

The total flight time of any ion is then

\[ T = T_{\text{ER}} + T_{\text{AR}} + T_{\text{DR}}. \]  \hspace{1cm} (3.5)

According to the above equations, the time-of-flight of an ion with mass-to-charge ratio \( m/q \) depends primarily on the lengths of the various regions and the electric fields within them. The dependence of the initial position \( s \) to the time-of-flight can be minimized by setting the derivative of \( T \) with respect to \( s \) to zero:

\[ \frac{dT}{ds} \bigg|_{s=s_0} = 0, \]  \hspace{1cm} (3.6)

where \( s_0 \) is the exact midpoint of the extraction region. One of the variables from the partial differential equation can then be then solved. For example, the length of the drift region would depend on the electric fields and lengths of the other regions according to the condition as:

\[ D = 2s_0(k_0)^{\frac{3}{2}} \left( 1 - \frac{1}{k_0 + \sqrt{k_0 s_0}} \right), \]  \hspace{1cm} (3.7)

where \( s_0, \varepsilon_{\text{ER}}, d \) and \( \varepsilon_{\text{AR}} \) are contained in \( k_0 \) as

\[ k_0 = \frac{s_0\varepsilon_{\text{ER}} + d\varepsilon_{\text{AR}}}{s_0\varepsilon_{\text{ER}}}. \]  \hspace{1cm} (3.8)

If condition 3.7 is fulfilled, then in theory the initial position of an ion has no effect on its flight time. The system is then said to be space focused. Eq. 3.7 is also known as the Wiley-McLaren condition. [57]

If the time-of-flight spectrometer is operated in the Wiley-McLaren conditions, the broadening of the peaks is independent of the ions’ initial locations in the ER. The broadening, however, does reflect the initial kinetic energies of the ions. Since the velocities perpendicular to the axis of the spectrometer do not contribute to the time-of-flight, only the velocities parallel increase the broadening. If an ion has an initial velocity vector towards the detector of the TOFMS, then the flight time of the ion will be decreased somewhat. Vice versa, the ions with initial velocities away from the detector will have slightly longer time-of-flight. The combination of these effects is a peak shape that is broadened and the size of the linewidth is a measure of the kinetic energy distribution of the ions.

3.3.1 Operation of the current TOFMS detector system

Here a short description of the current operation of the TOFMS system and the measurement process is given. In all of the measurements, the
electron-ion coincidence measurement software that was used was set to capture the energies and flight times of up to four ions in a coincidence event. The software was originally designed [61, 62] based on similar coincidence logic that is used in Ref. 63. Currently, the detector system in the TOFMS is produced by RoentDek Handels GmbH [64], and the software for measuring time-of-flight spectra together with detector hit positions has been developed during the thesis work by the author.

The detector of the TOFMS consists of three multichannel plates with a delay line anode with three wires in a hexagonal configuration. Therefore, seven different signals from the detector (two ends of three delay lines and the MCP signal) need to be processed. With the addition of the \textit{start} signal, the measurement electronics has to be able to receive at least eight different signal simultaneously. In the new coincidence measurement process, a time-to-digital card (TDC) is used for this purpose. One of the signals can be treated as the trigger signal, to which all the others are compared to. In the current setup, the \textit{start} signal is considered as the trigger, so that the timestamps on all other channels are automatically calculated with respect to the trigger. It also means that data from the trigger channel does not usually need to be saved.

The three wires that make up the anode are wrapped around the anode helically, with a 60° angle between them. Each wire is denoted with a different letter, \(x\), \(y\), and \(z\). The ends of the three wires that exit the detector through a vacuum feedthrough are preamplified and enter the TDC. Within the software the six different signals are labelled \(x_1\), \(x_2\), \(y_1\), \(y_2\), \(z_1\) and \(z_2\). Each wire loop has its own intrinsic pitch propagation speed, which determines the speed at which the signals propagate along the wire. Taking this into account, the hit position of the ion along each of the wires can be calculated as:

\[
\begin{align*}
    u &= (x_1 - x_2)d_1 \quad (3.9) \\
    v &= (y_1 - y_2)d_2 \quad (3.10) \\
    w &= (z_1 - z_2)d_3 + O, \quad (3.11)
\end{align*}
\]

where \(d_1\), \(d_2\) and \(d_3\) are the conversions from time to position along the wire and \(O\) is an offset value ensuring all three wires have common crossing point. Since the wires are placed at an angle with respect to each other, the conversion to \((X, Y)\) in laboratory coordinates is done by:

\[
\begin{align*}
    X_{uv} &= u + O_x \quad (3.12) \\
    Y_{uv} &= \frac{1}{\sqrt{3}} (u - 2v) + O_y \quad (3.13) \\
    X_{uw} &= X_{uv} \quad (3.14) \\
    Y_{uw} &= \frac{1}{\sqrt{3}} (2w - u) + O_y \quad (3.15)
\end{align*}
\]
3.4 Sample preparation

\[
X_{vw} = w + v + O_x \tag{3.16}
\]

\[
Y_{vw} = \frac{1}{\sqrt{3}} (w - v) + O_y. \tag{3.17}
\]

Arbitrary offsets \(O_x\) and \(O_y\) are added to compensate for mechanical imperfections and misalignment of the detector. From the above equations it is also clear that only two wires are required to get a full \((X, Y)\) coordinate for a hit. The third wire is a redundant backup that can be used in situations where one signal is not registered. The third wire is also useful in cases where multi-hit capabilities are needed. \([65, 66]\)

As the software begins to record data from the detector, it saves all the events in a matrix where the rows are the individual trigger events. Each event consists of any number of hits. Often however, there has to be some maximum number of hits per trigger, but the user can choose this number. Each hit consists of timestamps from the MCP and six delay line signals.

During measurement the program calculates the time-of-flight spectrum continuously and updates it. Also the detector image is calculated from the delay line signals using equations 3.17 and updated.

When the TOFMS is measured in the coincidence mode together with the electron spectrometer, more information needs to be recorded. The same data format is used, with the exception that also information on the electron hit position and event status is recorded. The electron-ion coincidence event types are explained further in Chapter 4.

3.4 Sample preparation

In the experiments in this thesis, the studied samples were either solid, liquid, or gas in normal room temperature and pressure. In order to study these molecules as individual particles, they need to be appropriately introduced to the interaction region of the the vacuum chamber.

For samples that are solid at room temperature, effusive evaporation ovens are commonly used \([67, 68]\). In papers I and II, the mercury bromide and mercury chloride samples were heated in the vacuum to temperatures of approximately 60°C so that the sample vapor pressure \(i.e.\) the sample density in the interaction region was high enough to record an intensity of good statistical quality with the electron and ion spectrometers.

For samples that are in gas phase at room temperature (such as \(\text{CH}_3\text{Cl}\) used in papers III and IV), only a gas line is required with the appropriate pumping so that the sample can be transferred to the vacuum as clean as possible. Within the vacuum chamber the gas is let in through a hypodermic needle, which is positioned as close to the interaction region as possible.

For liquid samples, such as \(\text{CH}_2\text{Cl}_2\) which was used in paper IV, the same gas line system is used as with gas phase samples. The sample is
placed in a liquid container into the gas line system, which is then pumped to remove air. To ensure that the sample does not boil away during pumping, it is first frozen. Once the sample is solid, the container can be pumped. After this the sample is thawed and warmed up so that the vapor pressure in the gas line is high enough, and the sample molecules can be released into the vacuum system. This process is known as a freeze-pump-thaw cycle and it can be performed multiple times to ensure minimal contamination of the sample with air. It also ensures that any air that is mixed in with the liquid is removed.
Electron-ion coincidence spectroscopy

In general, coincidence techniques are employed when it is desirable to investigate processes in atomic or molecules systems that involve emission of one or more particles from a single photoionization event. If the measurement involves the detections of a photoelectron and \( n \) ions, the scheme is often called photoelectron-photoion coincidence (PEPICO) spectroscopy. The same technique can, however, be utilized for detections of other electrons as well, such as Auger electrons. In these situations we call the method Auger-electron fragment-ion coincidence spectroscopy. Regardless of the actual nature of the electrons, the measurement method is identical. [59, 69–71]

4.1 Measurement process

All photoelectron-photoion coincidence measurements consist of individual events, which begin with the detection of an electron. Before the measurement begins, the electron spectrometer has to be set up in such a way that the electrons of the desired energy range are analysed. The electrons are then detected on the detector of the electron spectrometer with a probability \( P_e \), which is the fraction of electrons originating from the interaction region.

As the electron is detected, a signal goes from the detection electronics to a high voltage pulser, which raises the voltages in the TOFMS extraction region forcing the created positive ions towards the ion detector. The high voltage is kept for a specified time interval, which typically is a longer than the flight time of the heaviest ion that is measured. For every start signal (every electron detection), up to \( n \) ions are measured by the TOFMS. The ions are detected with a probability \( P_i \). Figure 4.1 shows the current electron-
ion setup which consists of the electron analyzer and the time-of-flight spectrometer. Because $P_e$ is much lower than $P_i$ ($P_i \gg 100 P_e$) due to the differences in transmissions of the electron and ion spectrometers, there is a rather large chance that multiple molecules are ionized before any electrons are detected. When eventually one electron from one of the ionizations is detected, it is very likely that more than one ions are measured by the TOFMS. In such a case, an accidental coincidence event might be recorded between an electron and ion which in reality have no correlation because they originate from different ionization events. This type of scenario is represented in Fig. 4.2 in the case of just two molecules in the interaction region. In Fig. 4.2a) the ideal situation is depicted where the “correct” electron and ion pair are detected while in b) the accidental, or “false”, coincidence case is shown. In c), a situation where ions originate from different ionization events is shown. In this case the event will consist of both true and false coincidences. In reality the situation can be more complicated than what is depicted in Fig. 4.2 since there may be several molecules ionized at the same time, depending heavily on the used photon flux and molecular number density (pressure) in the interaction region. The coincidence data that is saved thus consist of events which are of type a), b) or c).

False coincidences can be removed from the analysis using statistical methods. If the TOFMS measurement is initiated using an external pulse, which is not correlated with any electron detections, one is able to mimic the false coincidence event. The ions which are gathered using the external pulse must be measured in exactly the same experimental conditions as the ones with electron coincidences. To do this, the external pulse triggered events (often called random coincidences) are interjected between the electron triggered events using an external pulse generator set to output start pulses with a fixed frequency. This type of event is shown in Fig. 4.2d).

Figure 4.1: The current electron-ion coincidence measurement setup.
4.1. Measurement process

Since the electron triggers arrive at random intervals, the time delay between two triggers, whatever its source, is always unknown. [72]

Data for each coincidence event contains the energy of the electron (or its hit position, which is later converted to energy) and the flight times of up to \(n\) ions. Furthermore, the coincidence event that is saved on disk might also include information on whether the event is randomly triggered or electron triggered. While this information can be deduced later on, for example from the electron energy as the randomly triggered events have no energy, it can be useful to also record it while measuring.

During the measurement process, two types of events are thus continuously encountered: those triggered by an electron detection, \(P_{\text{electron}}\), and those triggered externally, \(P_{\text{random}}\). \(P_{\text{electron}}\) contains events which are true and events which are in coincidence by accident, or false. \(P_{\text{random}}\), however, always only contains false events. One can then find out the true coincidences by:

\[
P_{\text{true}} = P_{\text{electron}} - P_{\text{random}}. \tag{4.1}
\]

Often \(P_{\text{electron}}\) and \(P_{\text{random}}\) are not collected at exactly the same rate, so they have to be scaled properly so that the subtraction is achievable. The scaling parameters can be, for example, the trigger rates for the two types of events. [72]

In the current set up, the electron signal and the trigger signal from the random pulse generator are first connected to a Stanford model DG535 pulse generator via an OR connection, which picks either of the pulses. The pulse generator sends another signal to the high voltage pulser (Directed Energy Inc. model PVX-4450), which initiates the extraction pulse, while also sending appropriate signals to the ZTEC oscilloscope card (model

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**Figure 4.2:** Schematic representation of the origin of true and false coincidences in the case of two molecules being ionized. Particles shown with green color are detected while red ones are not.
which serves as the start signal for the ion time-of-flight analysis. A third signal from the pulse generator goes to a National Instruments data acquisition card (NI-DAQ) (model NI-PCI6251). The NI-DAQ card is used as the trigger to start reading the y-pulse signal containing the electron hit coordinate. In the case of a electron triggered event, the y-pulse signal will contain a pulse with a voltage that is proportional to its y-position on the detector, while in the case of randomly triggered event, the y-pulse provides 0 V. Thus the logic is also used as a way to distinguish the two event types from each other. Simultaneously, as the electronics deduces the event type and measures the voltage of the y-pulse, the time-of-flight spectrometer is continuously accepting stop signals from the ion detector. The programming logic then combines these two sources of detections and stores the measurement on an event-by-event basis, where each event consist of information denoting whether the source of the event was from an electron or random source, the voltage of the y-pulse, and up to four ion flight times. The limitation of accepting only up to four ions per event is arbitrary, it could be increased if the experiment requires it.

The random pulsing is realized through the same NI-DAQ card that reads the y-pulse signal. Another channel on the card is created for the sole purpose of generating digital signals with a known frequency and width. The random pulse is connected to the other input of the OR connector, which also accepts the electron signals.

The coincidence apparatus and measurement logic was explained originally by Kukk et al. [63]. The same method has been used in multiple electron-ion coincidence measurements of the Nano and molecular systems research unit [73–80].

4.2 Performance of the coincidence setups

4.2.1 TOF spectrometers

The two TOF spectrometers used in this thesis are different in their size and ion detection mechanism. The original TOFMS was used in paper I, while the current spectrometer, which was developed and constructed during the early parts of this thesis work, was used in papers II–IV. The current spectrometer has a drift tube length of 660 mm, which is approximately twice the length of the original. This increases the flight distance and therefore the flight time of the ions i.e. the maximum achievable resolution.

The total resolving power of the two spectrometers is non-trivial to compare, since also the used voltages influence it. However, the current spectrometer with its longer flight tube allows for a greater mass range to be
measured with better resolution than what was possible with the original TOFMS.

The current spectrometer is equipped with a position sensitive detector (see section 3.3.1). It enables the determination of kinetic energies and full three dimensional momenta of the ions.

The sizes of the spectrometers affect the ion collection efficiencies. The smaller TOF has an entrance diameter of \(\sim 25\) mm for the ions, while in the current instrument it is \(\sim 44\) mm. Thus the collection efficiency of the current TOFMS is improved, especially for ions that have considerable kinetic energy. The current spectrometer is designed on the same principles as previously reported cases \[81, 82\]. In the literature and for simulations performed for this spectrometer, it is estimated that, for example, singly ionized carbon ion can be captured up to initial kinetic energy of 12 eV. Kinetic energies larger than this are lost due to collision with the walls of the acceleration and drift tubes.

### 4.2.2 Coincidence performance

The resolution of the obtained electron spectrum depends on the used pass energy and slits in the electron spectrometer. In coincidence mode the pass energy has to be quite large in order to get a good transmission of electrons and to be able to record the whole energy region of interest at the same time. The presence of the TOFMS also contributes to the obtained resolution with penetrating electric fields to the interaction and residual fields.

In experiments that led to the results in papers I and II, the total electron detection rate was set to about 20-30 counts/second. It is customary to set the random trigger rate to approximately match the electron rate, which means that the total trigger rate for these experiments was around 60 Hz. With this trigger rate, the total ion detection rate was less than 0.1 ions/trigger, meaning that most of the events contained only the trigger signal (either electron or random trigger) and no ions.

By contrast, in the experiments on the chlorinated methanes in papers III and IV, the electron trigger rate was chosen by adjusting the photon flux and sample gas pressure so that the rate was about 100 Hz and the total trigger rate thus approximately 200 Hz. The total ion detection rate in these experiments was somewhat higher at about 0.8 ions/trigger. Higher ion collection rate was because the experiments were done in the X-ray regime. At the higher photon energies, the probability of double (or higher order) ionization is much higher and therefore there are several ions left from a single ionization due to fragmentation. The higher electron countrate was achieved in these experiments with the improved transmission of the electron spectrometer operated with a larger pass energy. The combined effect is that \(P_e\) was essentially brought a bit closer to \(P_i\) in the case of the

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chloromethane experiments. The difference in the true ion collection rates was about one order of magnitude, with the higher countrate observed in the chloromethane work.

4.3 Coincidence data handling

Electron-ion coincidence data can be presented in various ways. For example, TOF spectra can be plotted in three different ways: with only the electron triggered events, random triggered events, or with only true coincidences. The true coincidence TOF spectra show the preferred fragmentations in coincidence with the electrons that were recorded since all false coincidences are removed. This is exemplified in Fig. 4.3 where the CH$_3$Cl molecule was measured in a coincidence experiment with a focus on the resonant Auger final states. The three spectra are plotted from only $P_{\text{electron}}$ or $P_{\text{random}}$ events. The true coincidence TOF spectrum is then calculated according to Eq. 4.1. The spectra show how, for instance, the relative intensities of the CH$_n$ group ($n = \{3, 2, 1, 0\}$) change in the true coincidence spectrum with respect to the ones that contain false coincidences. The mass spectra in the region with the CH$_n$ peaks indicate that CH$_2$ is a preferred fragment to be released in the Auger final states that were studied.

Another way to plot the coincidence data while also showing the fragmentation differences in the measured electronic states is to show the data in a two-dimensional map, where the x-axis shows the energy of the coincident electron and the y-axis shows the ion time-of-flight. The
4.3. Coincidence data handling

Figure 4.4: A 2D map from the coincidence measurement of the fragmentation of HgCl$_2$ molecule in the Hg 5$d$ orbital (figure from paper II).

Coincidence events are then shown as a 2D histogram with the intensity as the color of the pixel. An example of this is in Fig. 4.4, where the fragmentation of the HgCl$_2$ molecule is found to be very different in the two spin-orbit components of the Hg 5$d$ orbital. From the 2D map, it is clear that the chlorine fragment only appears significantly in coincidence with the $^2$D$_{3/2}$ band. The other fragments, Hg$^+$ and HgCl$^+$ are in coincidence with the $^2$D$_{5/2}$ spin-orbit band.

The 2D maps are, however, difficult to use when quantitative analysis is required. The data is therefore often displayed in a coincident ion yield (CIY) format. In a CIY spectrum, a region around each ion on the time-of-flight axis is chosen and all the hits in this region are counted for each electron energy value. The CIY spectrum for each cation is therefore composed by summing all the coincident ions in each photoelectron energy channel for all fragment ions separately.

Often the CIY spectra need to be compared to each other and their relative differences are of interest. Relative CIY spectra can be composed for ion $i$ at energy $E$ as:

$$I_{i}^{rel}(E) = \frac{I_{i}(E)}{\sum_{j} I_{j}(E)}$$

(4.2)
where \( I_i(E) \) is the ion \( i \) CIY at energy \( E \) and the index \( j \) includes all ions.

CIY and relative CIY spectra present changes individual fragments experience in the measured electron energy region. When overlayed with the electron spectrum, it is easy to see the fragmentation behaviour of each electronic state.

### 4.4 Coincident constant final state spectroscopy

Coincidence measurements are often performed using constant photon energies. Since the experiment requires a rather low ionization rate, the measurement times can be long (up to \( \sim 12 \) h for a single measurement). This means that during a typical beamtime at a synchrotron radiation facility one cannot always perform multiple measurements using different photon energies due to time limitations. However, in the experiments that led to the results in paper III, the two spectrometers could be operated with higher ionization rates than before due to a higher transmission in the electron spectrometer. This allowed us to gather decent coincidence data in a shorter time period than what has been possible before without sacrificing statistical quality.

With the higher ionization rates coincidence experiments in which also the photon energy is scanned are possible. Scanned photon energy coincidence measurements reveal detailed information on the dissociation behaviour of molecules. In comparison to fixed photon energy coincidence experiments, the method gives a broader view of the changes in fragmentation processes when different orbitals are excited or ionized. Scanned photon energy experiments are especially useful in situations where the interest is on dynamical changes close to the ionization threshold of a particular orbital, or across several resonances.

Two dimensional electron spectroscopy (i.e. electron spectroscopy as a function of incident photon energy) is a completely new approach. Previously, it has been utilized by simply fixing either the kinetic energy range, or the binding energy range and scanning the photon energy. These measurements are known as constant final state (CFS) or constant initial state (CIS) spectroscopy\(^1\) [83, 84]. Previously, the methodology had not been extended to electron-ion coincidence studies\(^2\), which opens up a whole new avenue of research in the same way typical electron spectroscopy is extended using photon energy scanned measurements. While focusing only on the final states and keeping the kinetic energy window of the measured

\(^1\)CIS is also known as constant ionic state.

\(^2\)An exception is a method known as threshold photoelectron-photoion coincidence spectroscopy, TPEPICO, where the incident photon energy is scanned while measuring the threshold photoelectrons and photoions.
4.4. Coincident constant final state spectroscopy

electrons constant, we have named this method *coincident constant final state spectroscopy* (CO-CFS).

The CO-CFS data is essentially electron-ion coincidence data (which records data in the dimensions of electron energy and ion time-of-flight) that is extended to the photon energy dimension. It is therefore three dimensional data as depicted in Fig. 4.5. To display information from the data in a useful manner, the 3D data has to be sliced or filtered in some manner. One option is to pick a small time-of-flight region around each ion and make a two dimensional CIY map. These 2D-CIY maps contain information on the fragmentation dependencies of a particular ion as a function of electron and photon energies.

![3D representation of the coincidence data with a potential slice forming one 2D-CIY map indicated by the red plane intersecting the cube.](image)

Figure 4.5: 3D representation of the coincidence data with a potential slice forming one 2D-CIY map indicated by the red plane intersecting the cube. Figure from paper III.

Fig. 4.6 shows schematically how a 2D-CIY map could represent different kinds of features. If the kinetic energy range of the measured window is fixed, direct photoionization and (direct) photodissociation will produce diagonal lines, due to the correspondence between photon and electron energies: \( E_k = h\nu - E_b \). This is shown with label (a) in Fig. 4.6.

When the incident photon energy matches the energy difference of a core-level and an unoccupied outer orbital, a resonant Auger emission process is possible. These are seen as separate “islands” on the 2D-CIY map if the potential energy surface that the system is promoted to causes a fragmentation process producing the ion that is used to make the 2D-CIY map (labels (b) and (c) in Fig. 4.6). It is also possible that the resonant Auger process populates the same single hole state that is created through direct photoionization. With a fixed photon energy measurement, these processes are indistinguishable, but when a photon energy scanned measurement
Figure 4.6: Schematic representation of a 2D-CIY and how it can represent different aspects of the data. (a) show the direct photodissociation, (b) and (c) resonance excitation processes and (d) shows normal Auger states.

... is conducted, the direct photoionization is clearly seen as a diagonal line. The resonant Auger states that are energetically possible and populate the same final states as the direct photoionization will therefore be seen as an enhancement of the intensity at the photon energy of the resonance. This is depicted with the label (b) in Fig. 4.6. In some cases, sharp lines are seen on the 2D-CIY map such as those depicted with label (c) in Fig. 4.6, which might originate from atomic fragments due to UFD.

Once the photon energy is high enough to ionize a core-level of the system, the normal Auger process becomes dominant. The final states of the normal Auger process are often lower in kinetic energies than final states of resonant Auger and their dissociation products can also vary greatly with respect to resonant Auger. In a 2D-CIY the normal Auger final states are straight lines as the kinetic energies of the emitted electrons do not depend on the used photon energy. These states are depicted with the label (d) in Fig. 4.6.

In a complex molecule, several final states are often populated due to resonant and normal Auger decay. The fragmentation behaviour of these final states can be also rather complicated, which is the reason why CO-CFS method is an elegant tool to disentangle these overlapping structures and processes. By choosing a specific fragment one can remove all the final states that do not fragment by releasing the chosen ion. The formed 2D-CIY from the chosen fragment can then be used to study the photon and electron energy dependent features.

Creation of 2D-CIYs from the CO-CFS data is only one potential way of slicing 3D data. The slicing could be done in some other axis as well. For example, by choosing a specific electronic state and investigating the changes in ion contributions would be another possibility.
4.4. Coincident constant final state spectroscopy

The above mentioned CO-CFS data only contain energetic information on the electrons and time-of-flight information on the ions. In the case that more information is gathered, the data processing becomes more complex. If information on the emission angle is also measured from the electrons and ions, the “data cube” in Fig. 4.5 gains several additional dimensions. Slicing and filtering is therefore required for readable presentation, but the possibilities of extracting useful data are countless. For example, Sann et al. [85] have measured the fragmentation of HCl$^+$ in the vicinity of the Cl 2$p$ ionization energy in a photon energy scanned electron-ion coincidence measurement, and demonstrate filtering of the data in an intriguing manner. They have filtered the data so that they can differentiate the respective final ionic states into the resonant Auger states and the direct photoemission states. Additionally, they have been able to measure the electron angular distributions in coincidence with the Cl$^+$ ion at different photon energies, which demonstrates the change in the shape of the orbital from which the electron is ejected. All of the results they have observed are due to the UFD effect subsequent to the $\sigma^*$ type excitation in the HCl molecule.
Chapter 4. Electron-ion coincidence spectroscopy
Results and discussion

In this chapter some main motivations and a summary of the results contained in the accompanying publications are presented. The research consists of a study into the fragmentation of mercury-containing compounds under ultraviolet light ionization and the study into X-ray induced processes in chlorinated hydrocarbons (CHC).

5.1 Mercury-containing compounds

5.1.1 Motivation

Mercury (Hg) is a heavy metal element that is known to produce harmful effects in the environment. It is used commonly in many consumer applications making the probability for its release into the environment and atmosphere rather high [86]. Elemental mercury, Hg(0), has a residence time of about a year in the atmosphere [87, 88]. It is therefore susceptible to global transport. A particular interest lately has been the contamination of Arctic and Antarctic regions with mercury and its compounds [89, 90]. Reactive gaseous mercury, Hg(II) and particulate bound ionic mercury have a much shorter atmospheric residence time in the order of days or weeks, which results in local deposition. Mercury is released into the ecosystem largely as Hg(II) [91, 86].

While in the atmosphere elemental mercury undergoes redox chemistry, transforming between the Hg(0) and Hg(II) states. There still remains some uncertainty on the complete chemical reaction pathways, but regardless, it is known that photochemistry is a large contribution to the oxidation pathway that forms Hg(II) [91]. Evidence also suggests that halogen atoms oxidise Hg(0), turning it into a more reactive species which is deposited to the ground [92]. These events, which occur during the polar sunrise, are often called mercury depletion events (MDEs). There currently also
exists uncertainty about the role of photoreduction of Hg(II) species back to Hg(0).

In this thesis, we have focused on studying the fragmentation reactions of mercury-containing heavy metal compounds. We study the fragmentation in the outer and inner valence levels of the molecules. The energies required to reach these levels are below 20 eV, which makes them accessible by the solar UV irradiation.

Coincidence methods were used to study mercury(II) bromide ($\text{HgBr}_2$) and mercury(II) chloride ($\text{HgCl}_2$) to obtain fundamental information on these compounds under UV light irradiation. The results were compared to previously published work by Kettunen et al. [77] who investigated the fragmentation of a very similar molecule, cadmium chloride ($\text{CdCl}_2$) in the same inner valence region using vacuum ultraviolet (VUV) radiation.

Quantum chemical computations of excited systems with many electrons are also notoriously difficult to simulate dynamically. Therefore this study provides reference data for the purposes of improving the computation programs and codes so that they would be more capable of handling complex systems such as the ones we have studied here. One such difficulty is the inclusion of proper spin-orbit interaction in electronic structure calculations together with nuclear dynamics.

Studies of electronic structure and fragmentation of mercury compounds have gained interest in the past as well. The pure photoelectron spectra in the valence region for $\text{HgCl}_2$ and $\text{HgBr}_2$ have been recorded already in the 1970s by Eland [93] and Berkowitz [94]. In these studies, the detailed valence energies were reported as well as the observation of the curious broadening of the Hg $5d$ levels. These first photoelectron measurements were done with He I $\alpha$ and He II $\alpha$ radiation excitation. Photofragmentation and dissociation have been studied by Linn et al. using photoionization efficiency measurements [95, 96]. The photoefficiency measurements were well suited for measuring the appearance energies (minimum energies required for the creation of a specific fragment ions) and some fragmentation pathways, but in these works the authors were unable to see the detailed electronic state dependent fragmentation patterns that can be investigated using electron-ion coincidence methods.

5.1.2 Results

The coincidence experiments conducted in the valence and in the Hg $5d$ region of $\text{HgBr}_2$ and $\text{HgCl}_2$ reveal state specific fragmentation behaviour. Both $\text{HgBr}_2$ and $\text{HgCl}_2$ share similar electronic structure in the valence orbitals, which consist of six bands formed out of the hybridized molecular orbitals of atomic Br $4p$ or Cl $3p$ orbitals and a Hg $6s$ orbital (see Fig. 5.1). The six bands that are formed in the photoionization are then given state
5.1. Mercury-containing compounds

Figure 5.1: Valence and Hg 5d region photoelectron spectrum of HgBr$_2$ and HgCl$_2$ measured with $\nu = 40.2$ eV.

designations $^2\Pi_{3/2g}, \ ^2\Pi_{1/2g}, \ ^2\Pi_{3/2u}, \ ^2\Pi_{1/2u}, \ \Sigma_u$ and $\Sigma_g$. Vibrational motion gives each band a slight broadening.

After the valence levels, the atomic-mercury-like 5$d$ orbitals form the next bands. Spin-orbit interaction causes splitting of the 5$d$ level, and the bands are given state designations $^2\!D_{5/2}$ and $^2\!D_{3/2}$, which are also present in a purely atomic mercury spectrum. Since the mercury compounds have a strong intramolecular electric field, both of these spin-orbit states are further split by it. The phenomenon is essentially a Stark shift (splitting), which removes the degeneracy of each spin-orbit state. Thus, the $^2\!D_{5/2}$ band is split into three components, differentiated by the projection quantum number of the total angular momentum onto the molecular axis, ±3/2, ±1/2 and ±1/2. The $^2\!D_{3/2}$ band experiences the same, being split into two levels with quantum numbers ±3/2 and ±1/2.

The first peak in the 5$d$ region (peak $^2\!D_{5/2} \pm 5/2$) is observed to have a very narrow linewidth in all mercury compounds [93]. This is due to the fact that the orbital lies in a plane, which is perpendicular to the molecular axis. Since the orbital does not actively contribute to the bonding process, the photoelectron peak on the spectrum has a very small full-width at half-maximum (FWHM).

Effect of spin-orbit interaction on the fragmentation of HgBr$_2$ (Paper I)

In paper I the focus was on the fragmentation behaviour of the HgBr$_2$ molecule in the atomic-mercury-like 5$d$ region. It was observed that photoionization from the two different spin-orbit components cause the molecule to fragment in quite different ways. The band in the higher binding energy ($^2\!D_{3/2}$) fragments predominantly by only releasing the halogen fragment and leaving behind a neutral mercury and bromine part.
where the atoms may be bonded or not. In the other spin-orbit state the observed behaviour is different. The fragmentation reaction in the state $^2D_{3/2}$ is

$$\text{HgBr}_2 + h\nu \rightarrow \text{Br}^+ + \text{HgBr}$$  \hspace{1cm} (5.1)$$

and in the $^2D_{5/2}$ band the two possible fragmentation reactions are

$$\text{HgBr}_2 + h\nu \rightarrow \begin{cases} 
\text{Br}^+ + \text{HgBr} \\
\text{Hg}^+ + \text{Br}_2.
\end{cases}$$  \hspace{1cm} (5.2)$$

In these situations it is also possible for the neutral fragmentation products HgBr and Br$_2$ to be released as atomic Hg + Br and Br + Br, respectively.

When considering the fragmentation of a molecule subsequent to ionization of a particular molecular orbital, it is often assumed that the spin-orbit interaction has no effect on the dissociation. Here, we have shown that this is not always the case. If the spin-orbit components induce different fragmentation, even small changes in incident photon energy can cause the fragmentation of a molecule to change considerably. For example, in the case of HgBr$_2$, one could imagine that by choosing the incident photon energy to be exactly between the two spin-orbit bands, the relative amount of mercury cation is drastically different than if the energy is only a couple of eVs lower.

Fragmentation of HgBr$_2$, HgCl$_2$, and CdCl$_2$ (Paper II)

In paper II the focus was on the differences in fragmentation of the molecule subsequent to ionization of the 5$d$ states in mercury compounds and in the atomic-cadmium-like 4$d$ orbital in the CdCl$_2$ molecule. The CIY spectra of the three different molecules (HgBr$_2$, HgCl$_2$ and CdCl$_2$) are shown in Fig. 5.2. The data for the CdCl$_2$ spectrum is from Ref. 77. Already in the mercury compounds we see a clear difference in fragmentation between the two molecules. In HgBr$_2$ the ionic halogen fragment has a rather high probability of being emitted in coincidence with the photoelectron from the spin-orbit component in lower binding energy. In HgCl$_2$, however, there is almost no signal from the halogen component in the corresponding electronic states. The behaviour is again different in CdCl$_2$, where no big differences are seen in the two spin-orbit states of the 4$d$ orbital, as they both fragment by producing the halogen cation almost exclusively.

The fragmentation behaviour was tentatively explained using the internal fragment energies, which were computed by subtracting the total energy of the possible fragments from the total energy of the parent. All total energies were obtained by optimizing their ground state geometries. If we focus only on the the fragmentation of HgCl$_2$ (since HgBr$_2$ and CdCl$_2$...
5.1. Mercury-containing compounds

Figure 5.2: CIY spectra of the halogen and mercury components in HgBr$_2$ and HgCl$_2$ as measured in the 5d region. As a comparison, the cadmium 4d region CIY of Cd$^+$ and Cl$^+$ from CdCl$_2$ is shown as the top curves. The bars for HgCl$_2$ correspond to calculated fragment energies according to Eqs. 5.3 and 5.4. The CdCl$_2$ data is from Ref. 77. Figure adapted from paper II.

follow the same logic) and note that the chlorine fragment can, in principle, only appear through the following reactions:

\[
\text{HgCl}_2 + h\nu \rightarrow \text{HgCl}_2^+ + e^- \rightarrow \text{HgCl} + \text{Cl}^+ \quad (5.3)
\]

\[
\text{HgCl}_2 + h\nu \rightarrow \text{HgCl}_2^+ + e^- \rightarrow \text{Hg} + \text{Cl} + \text{Cl}^+. \quad (5.4)
\]

The fragmentation energies for these two reactions are calculated as 16.26 and 17.21 eV. Chlorine cation hardly appears at all in coincidence with the 5d$_{5/2}$ spin-orbit band even though the fragmentation producing Cl$^+$ is calculated to be energetically allowed through reaction 5.3. We therefore conclude that reaction 5.3 is a very low yield reaction, and most of the chlorine originates from reaction 5.4. The exact relative reaction yields for the two reactions remain unknown due to the differences in transmission and detection efficiencies for the Cl$^+$ and Hg$^+$ fragments.

For CdCl$_2$, the calculated reaction energies for the reactions corresponding to Eqs. 5.3 and 5.4 are both below the 4d bands. It is likely that the chlorine seen in coincidence with ionization of both the 4d spin-orbit components is through the high-yield reaction, but the CIY gives no evidence
either way, since the components are higher in energy than the reaction energies.

For the case of \( \text{HgBr}_2 \) the reaction energies for the two types of fragmentations that could produce \( \text{Br}^+ \) are also below the spin-orbit bands. The experimental results seem to agree with the fragment energies quite well with the exception of the first peak in the \( ^2\text{D}_{5/2} \) band. Here, other competing factors must dominate so that the \( \text{Cl}^+ \) fragment production is suppressed and only \( \text{Hg}^+ \) fragment is seen.

### 5.2 Chlorohydrocarbon compounds

#### 5.2.1 Motivation

In this thesis, the investigation into chlorinated hydrocarbons (CHC) has focused on four different chlorinated methanes: chloromethane (\( \text{CH}_3\text{Cl} \)), dichloromethane (\( \text{CH}_2\text{Cl}_2 \)), trichloromethane (\( \text{CHCl}_3 \)) and carbon tetrachloride (\( \text{CCl}_4 \)). Structures of these molecules are seen in Fig. 5.3. All of the mentioned molecules play a role in industrial applications of modern society. They are also commonly found in the atmosphere where they take part in various processes which can have negative impact on the global climate as a whole.

![Chemical structure of the various chlorinated methanes: a) chloromethane, b) dichloromethane, c) chloroform, d) carbon tetrachloride.](image)

Figure 5.3: Chemical structure of the various chlorinated methanes: a) chloromethane, b) dichloromethane, c) chloroform, d) carbon tetrachloride.

Chloromethane is the most abundant volatile halocarbon in the atmosphere despite the fact that vast amounts of chlorofluorocarbon (CFC) compounds are released to the atmosphere from anthropogenic sources [97]. CFC compounds were originally designed to work as aerosol propellants, blowing agents, solvents and as refrigerants due to their chemical inertness and were given trade names such as ‘Freon’ and ‘Arcton’ [98, 97]. CFC compounds were later found to have a rather large ozone-depletion potential (ODP), which is caused by their strong reaction with sunlight which causes photolysis and a release of atomic chlorine free radicals. Chlorine atoms that collide with ozone molecules are highly efficient at producing chlorine monoxide and oxygen. Since chlorine monoxide can further react in a
way that atomic chlorine is produced, a ozone depletion cycle is created where ozone is destroyed into molecular oxygen but chlorine atoms are not consumed [98]. Since it was discovered that CFC compounds have a large ODP, their usage has been restricted by various treaties, such as the Montreal Protocol and its amendments.

This thesis aims to produce information on ionic chemistry. Since CHC compounds are heavily used in various areas of modern society, it is important to know their effect in different environments. In this work, we have measured the fragmentation behaviour of chlorinated methanes and determined their relative probabilities of producing certain fragments such as ionic chlorine.

5.2.2 Results

The coincidence experiments with CHC compounds were similar to the experiments detailed in section 5.1 with the exception that they were performed with X-rays and not with UV radiation. The X-ray induced processes can, however, in some cases result in final ionic states that are similar as with UV radiation induced processes. The most probable reactions with X-rays, however, deal with perturbations to the inner shells of the molecules, which can induce Auger processes since the atoms that are involved have a relatively low atomic number $Z$.

In all experiments, photon energy of approximately in the 200 eV range was used. This energy is roughly in the binding energy of the chlorine $2p$ orbital. When the photon energy is few eVs below the binding energy, it is likely that a $2p$ electron is promoted to an unoccupied orbital close to the ionization continuum threshold. This excitation decays primarily by spectator Auger emission, resulting in a two-hole, one-electron final state, where the two holes are localized in valence orbitals while the electron is excited into an antibonding orbital.

**Formation of HCl$^+$ from CH$_3$Cl (Paper III)**

The lowest unoccupied molecular orbital (LUMO) is strongly antibonding in most molecules. Therefore, a promotion of an electron to this orbital causes strong fragmentation behaviour. In paper III we have found that in CH$_3$Cl the electronic transition Cl $2p \rightarrow \sigma^*$ causes a reaction in the molecule which follows a fragmentation pathway that can lead to a production of the HCl ion. The appearance of HCl$^+$ from CH$_3$Cl subsequent to the X-ray resonance excitation was already reported earlier by Miron et al. [99] We expanded on that measurement by conducting the coincidence measurement by also scanning the photon energy, i.e. with a CO-CFS experiment. We were thus
able to confirm that the appearance of HCl\(^+\) happens only at the Cl \(2p \rightarrow \sigma^*\) excitation using photon energy of approximately 201 eV.

The computational work done in paper III suggests also a potential pathway for the production of HCl\(^+\). Using equation

\[
E(M) + h\nu = E_{\text{kin}}(e_{\text{Auger}}^-) + E(M^{++})
\]

we were able to calculate the kinetic energies of the Auger electrons, \(E_{\text{kin}}(e_{\text{Auger}}^-)\). In this equation \(E(M)\) corresponds to the ground state energy of CH\(_3\)Cl molecule and \(E(M^{++})\) the different final states. All quantum chemical calculations, such as the energies of the ground and final states were calculated using the DALTON chemistry code package [100]. Further details about the computational parameters can be found in paper III.

Using Eq. 5.5, four final states were found with Auger electron kinetic energies that matched the experimental values very well. In these states the \(\sigma^*\) orbital is occupied and there are two holes in the inner valence. Configurations in which the holes are in the outer valence were calculated to be much lower in energy than the energy range which we studied experimentally and thus they were ignored.

The four states that were found to agree with experimental energies were then subjected to a geometry optimization routine. In the geometry optimization, the initial positions of the nuclei were taken as the ground state values. According to the internal forces of the system in these four final states, only one of them optimizes the nuclei in such a way that a rotation of the methyl group brings one proton to a closer proximity to the chlorine nucleus. As the kinetic energy of the resonant Auger final state corresponds well to the electron kinetic energy range where most of the HCl\(^+\) cation is seen, we believe this to be a good indication of actual nuclear dynamics subsequent to the Auger decay.

**Role of UFD in the fragmentation of some CHCs (Paper IV)**

In paper IV the focus was shifted to more general fragmentation differences in the four different chlorinated methanes. The coincidence results indicate that ultrafast dissociation is a prominent fragmentation method for two of the lighter methanes (CH\(_3\)Cl and CH\(_2\)Cl\(_2\)) but not for the two heavier ones (CHCl\(_3\) and CCl\(_4\)). The dissociation is initiated with a resonance excitation of a chlorine 2p electron to the \(\sigma^*\) orbital.

CH\(_3\)Cl is a well known species where UFD is clear [101, 99]. Our results also indicate this, for example, in the CIY spectrum of the chlorine cation. In the CIY spectrum three clear peaks are seen, which match the energies of atomic chlorine final states \(^1S, ^1D\) and \(^3P\). This is due to the fact that the chlorine nucleus has had significant time to distance itself from the rest.
of the molecule before the Auger decay has taken place. Therefore, as the Auger electron is emitted, it is actually released from the chlorine atom. Since the atom no longer experiences the full molecular field of the rest of the methyl group, the energy of the Auger electron is correspondingly changed to match the atomic value. Since the transition also happens between two potential energy curves that are quite parallel, the width of the peaks in the CIY spectrum is also narrower than if the transition would happen while the chlorine nucleus was still part of the molecule.

![Figure 5.4: Cl+ CIY spectra from the four different chlorinated methanes with the HCl resonant Auger electron spectrum at the top. The dashed lines correspond to the three atomic chlorine states.](image)

The CIY of Cl+ from CH₂Cl₂ shows very similar structure as CH₃Cl: three peaks with energies close to the atomic energies and small widths, as indicated in Fig. 5.4. UFD has been seen in this species as well previously [102, 103], where the reason for UFD was explained using the repulsive nature of the potential energy curves.

The two heaviest chlorinated methanes (CH₃Cl and CCl₄) in contrast show no sign of an UFD process that would yield chlorine cations. The Cl+ CIY signal is the weakest signal out of all the observed cations in these two molecules, which is why the CIY is lower than in the other cases.

Our preliminary conclusion is that as more chlorine atoms are added to the methane molecules, more preferable dissociation pathways are created. The timescale of the dissociation along these preferred pathways...
is unknown at this time, but it seems to be evident that emitting a single chlorine with the created core-excitation (which could later decay as atomic Auger) seems to be inefficient in chloroform and carbon tetrachloride. Due to the difficulty modelling these systems using quantum chemical codes, and especially the nuclear dynamics, more work is needed to fully visualize and conclude what are the pathways along which the dissociation proceeds in the heavier molecules.
Chapter 6

Summary and outlook

Synchrotron radiation has been used to study the fragmentation behaviour of mercury-containing molecules in the valence electronic levels and chlorinated methanes in the core-levels. The well-established methodology of electron-ion coincidence using a hemispherical deflection analyzer and a time-of-flight mass spectrometer has been used in all experiments in the included papers. Work has been made in further developing the method so that in the future information from the position sensitive detector on the TOFMS could be added to the coincidence experiments.

The experimental results in the study of dissociation behaviour of mercury compounds revealed state specific fragmentation patterns that had not been fully explored previously. The atomic-mercury-like 5d state with moderately high spin-orbit splitting was found to exhibit major differences in the fragmentation in the two spin-orbit bands. Further, by employing fragment energy calculations in two different fragmentation pathways and comparing the results to the experimental spectra, we were able to estimate the yields of the fragmentation processes.

The fragmentation of chlorinated methanes was also investigated by using X-rays to either excite or ionize the electrons from the Cl 2p orbital, which is the lowest lying core-level accessible in these molecules. In CH$_3$Cl molecule it was confirmed that a specific excitation of the Cl 2p electron to the unoccupied $\sigma^*$ type orbital causes significant hydrogen movement within the molecule which causes HCl$^+$ fragments to be released. The photon energy dependent features (i.e. HCl$^+$ only appears in specific resonances) was confirmed by performing a photon energy scanned coincidence experiment, which we have named CO-CFS. The computational work also verified a rotation of the methyl group which causes one hydrogen to move closer to the chlorine atom. The rotation only happens in one Auger final state corresponding exactly to the experimental value of the final state energy where HCl$^+$ was found.
Chlorinated methanes are also good systems to probe nuclear dynamics that occurs faster than electronic relaxation — a phenomenon known as ultrafast dissociation. The experimental results indicate that out of the four studied chlorinated methanes, two lighter ones (\(\text{CH}_3\text{Cl}\) and \(\text{CH}_2\text{Cl}_2\)) have a tendency to fragment via UFD while the two heavier ones (\(\text{CHCl}_3\) and \(\text{CCl}_4\)) do not. This indicates that as more chlorine is added to the molecule, more fragmentation pathways are created that are more efficient at redistributing the excess energy from the photoexcitation.

Some unresolved questions still remain, especially in the chlorinated methane work. For example, the details of the nuclear motion for the heavier molecules and especially its timescale with respect to the Auger decay is not resolved completely. Further experiments may shed more light on the situation, especially if one is capable of resolving the ionic fragment energies, which would give more details on the dissociation pathways. With the addition of the position sensitive detector to the coincidence measurements I expect the results to be much more revealing. Theoretical work also has the potential of explaining the details in a much more thorough manner in the form of potential energy surfaces, for example. Such details are, however, very demanding on several levels.

The research in this thesis has continued the fundamental atomic and molecular research that has long been part of the Nanomo group. I expect that in the future, the experiments that were initiated here will be further explored. Coincidence experiments with the current instrument are expected to give a whole plethora of additional information on the dissociation dynamics. Additionally, the capabilities of the MAX IV Laboratory and the FinEstBeAMS beamline (Finnish Estonian Beamline for Atmospheric and Materials Science) [104], which houses a similar electron-ion coincidence spectrometer setup, are going to make new kinds of experiments possible in the field of coincidence spectroscopy.
Bibliography


Bibliography


