A space focused ion time of flight mass spectrometer, and spectroscopy of hydrogen chloride, deuterium chloride, and hydrogen sulfide at "hard" x-ray energies

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Physics

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December 1995
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Abstract

A space-focused ion time-of-flight mass spectrometer was used to study the relaxation dynamics of HCl, DCl, and H$_2$S following the excitation of a K-shell electron using synchrotron radiation. On resonance, fragmentation of the molecule involving neutral dissociation of hydrogen was found to be a significant decay channel, thus raising questions of how effectively dissociation competes with Auger decay in the relaxation process. In addition, a space-focused ion time-of-flight mass spectrometer was constructed to be optimized for use at the Advanced Light Source in Berkeley, California. Peaks with less than 1 ns full-width at half-maximum have been observed.
# Contents

Abstract iii

List of Figures v

Acknowledgements vii

Foreword viii

1 Intro 1
   1.1 Theory ................................................................. 5

2 Experimental Setup 11
   2.1 The Synchrotron-Radiation Source ................................. 12
   2.2 The Chamber .......................................................... 15
   2.3 The Analyzer and Detector .......................................... 16
   2.4 The Electronics ....................................................... 17
      2.4.1 The Constant Fraction Discriminator (CFD) ............ 17
      2.4.2 The Time to Amplitude Converter (TAC) ................. 17
      2.4.3 The Multi-Channel Analyzer ............................... 18
   2.5 Data Collection and Analysis ..................................... 19

3 The Time of Flight Mass Spectrometer 22
   3.1 Space Focusing ...................................................... 24
   3.2 Design ................................................................. 25
   3.3 Testing ............................................................... 29

4 Results and Discussion 36
   4.1 Total Ion and Total Coincidence Yield .......................... 36
   4.2 The Time of Flight Spectra ....................................... 40
   4.3 Conclusions ......................................................... 51

Appendix: Detector Efficiency 53

Bibliography 57
List of Figures

0.1 My first TOF spectrum, somewhere above threshold. ix
1.2 Decay pathways for atoms with a core shell vacancy. 7
2.3 Experimental setup 12
2.4 Schematic of a storage ring and beamline on a synchrotron-radiation source. 14
2.5 Graphic representation of 'jitter' introduced using a standard discriminator for timing. 18
2.6 Graphic representation of the operation of a CFD. 18
2.7 Schematic of how signal is measured in singles spectra. 20
3.8 The time of flight mass spectrometer 23
3.9 The effect of changing all analyzer dimensions on the voltages for the first acceleration region. 27
3.10 Time of flight spectra for $^{35}C{l}^+$ and $^{37}C{l}^+$ comparing an analyzer with all dimensions shortened, to an analyzer with all dimensions extended. 27
3.11 Time of flight spectra for $^{35}C{l}^+$ and $^{37}C{l}^+$ comparing an analyzer with the drift region only extended to an analyzer with the 2nd acceleration region only extended. 27
3.12 Time of flight spectra for $^{35}C{l}^+$ and $^{37}C{l}^+$ comparing an analyzer with all regions extended to an analyzer with the 2nd acceleration region only extended. 27
3.13 Spectrum collected at 3kV using the electron gun. 32
3.14 Spectrum collected at 3kV using the electron gun. The region around the Ar +3, +4, and +5 peaks is expanded. 32
3.15 Argon spectrum taken at a photon energy above the K-shell threshold (3205 eV) at beamline 9.3.1 during ALS two-bunch operation in August 1995. 35
4.16 Total ion yield spectra for DCI and HCl 37
4.17 Total coincidence yield spectra for H$_2$S 39
4.18 Spectrum taken on resonance for HCl. The prompt and H$^+$ peaks appear at the long time of flight end of the spectra due to an arbitrary choice of time delays in TOF measurement. Actual H$^+$ flight time is its distance from the prompt peak. 41
4.19 Spectrum taken on resonance for DCI. For an explanation of the prompt and H$^+$ peaks, see figure 4.18. 41
4.20 PIPICO spectrum taken on resonance for H\textsubscript{2}S. ............................................. 42
4.21 Ion fraction as a function of energy for HCl singles spectra. The Cl\textsuperscript{+6} peak was omitted for clarity ................................................................. 43
4.22 Ion fraction as a function of energy for HCl PIPICO spectra. The Cl\textsuperscript{+6} peak was omitted for clarity ................................................................. 43
4.23 Ion fraction as a function of energy for DCl. The Cl\textsuperscript{+6} peak was omitted for clarity ................................................................. 44
4.24 Ratio of hydrogen and deuterium ions to chlorine ions. ....................... 44
4.25 Ion fraction as a function of energy for H\textsubscript{2}S singles spectra. .................. 47
4.26 Ratio of hydrogen ions to sulphur ions in H\textsubscript{2}S singles spectra. .......... 47
4.27 Ion fraction as a function of energy for H\textsubscript{2}S PIPICO spectra. ........... 48
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Foreword

I’ve been told that frequently, students new to a research group, are introduced to the field of study by reading the thesis papers of students that have gone before them. So, it is to these students in particular, that I write this foreword. My desire in doing this is to put aside the technical detail for a moment, and give you anecdotally, some idea of what you’re getting into. But beside this, I remember as I was beginning my research career, there were numerous articles where the introductions were all that I understood. If this sort of experience is fresh in your memory, take heart, we’ve all been there. Learning can be quite an assault on your ego.

I think along the way, my impression of what “doing science” entails has changed. I was under the impression that scientists spent all their time at the “eureka, I’ve found it” moments of their research. After all, in the movies, the only work Dr. Frankenstein does is to flip the switch that brings his monster to life. Instead, I’ve found that there’s a tremendous amount of grunt work involved in reaching the point where you finally have something worth writing about. If this thesis were proportioned the same way that my time was, there would be pages and pages of accounts of stripping wires, tightening bolts, and doing other things which would make pretty dull reading. For example, I spent a long, frustrating semester doing nothing more than discovering that I had a few bad connections in the MCP assembly. The account would go something like this: “...check the signal, it doesn’t work. Vent the chamber and open it. Take everything apart, and break some stuff in the process. Fix what was broken, put everything back together, and pump down. Then check the signal,
it doesn't work..." I never expected that one of the lessons I would truly learn well in studying physics would be "righty tighty, lefty looisy". Thomas Edison spoke well when he said that genius was 99% perspiration. I must admit, though, I have enjoyed the fact that some of my grad school education has saved me money on plumbing repair.

Finally, for posterity, I'm going to record the story of my first time of flight spectra (figure 0.1). We had three weeks of beam time in May 1995 (part of it was during finals week, so that was hanging over my head too). When we arrived we discovered that ALS was down because the machine physicists had taken the storage ring for a joy ride and revved it up a little too much. The net result was that the beam was down for the first week and a half or so of our time. That wasn't so bad for me, at

Figure 0.1: My first TOF spectrum, somewhere above threshold.

1These are tightening instructions for bolts. From the front, look at the top of the bolt.
this point I was still wrestling with that MCP problem I mentioned earlier. Anyways, after some help from Jon Levin, and several calls to the manufacturers, the MCP assembly finally worked. We hooked up to the beamline and pumped down, only to discover that the MCA didn't want to cooperate. Things looked bleak, but with 15 minutes of beam left we fixed a bad cable to the MCA and took data. Just don't ask me to analyze this spectrum, the beam was hitting the needle and we collected a lot of garbage. But it worked! Eureka!
Chapter 1

Introduction

By studying atoms and molecules both before and after chemical reactions, chemists have, for centuries, been able to infer the processes involved in these reactions for atoms across the periodic table. However, these studies have been limited until recently by the fact that they involve only the ground state and valence orbitals of the systems. On the other hand, one of the triumphs of physics in the twentieth century has been the successful application of quantum mechanics to describe the electronic structure and relaxation processes of excited states. Unfortunately, for all but the most simple hydrogen-like systems, electron-correlation effects make analytic solutions impossible, and approximation techniques must be relied upon to obtain solutions. In the past century, a number of different probes have been developed which give insight into the quantum mechanical properties of the more complex systems. The insight into the physical principles governing molecules that these sources provide serves to blur the line between chemistry and physics[13].

There are three primary probes of the electronic structure of a system: ions, elec-
trons, and photons. When using charged particle probes, valence shell electrons in
the sample have the highest interaction cross sections across the energy spectrum. In
addition, processes in which the incident charged particles lose energy over a contin­
uum of values serve to degrade the information and complicate interpretation of the
experiment. On the other hand, light, when used as a probe of matter, has the ad­
vantage of being massless, and is therefore unable to carry away kinetic energy from
the interaction. But perhaps the most attractive property of photons as a probe of
matter is that they excite specific resonances between electronic energy states much
more selectively than charged-particle probes[8].

Of the light sources available, lasers can only operate at relatively long wave­
lengths. In contrast Röntgen-tube x-ray sources, which have remained essentially
unchanged since 1913, operate at shorter wavelengths. Unfortunately, their intensity
is sufficient at only a few fixed frequencies $^2$ which are too widely spaced in energy to
provide the selective excitation required for detailed studies of the energy dependence
of different processes. Thus the dynamical properties of atoms and molecules remain
essentially unprobed by these sources[9].

Synchrotron radiation has grown to become a useful counterpart to these sources.
Predicted in the late 1800’s, and first observed in the 1940’s by nuclear physicists who
considered it a technical nuisance in the operation of particle accelerators, synchrotron
radiation is emitted across a wide band of energies which stretches from the far infrared
to the x-ray region of the spectrum. This radiation is emitted over a continuous

\[ \text{for example, } \epsilon_I = 21.22\text{eV}, \epsilon_{II} = 40.8\text{eV}, \text{ the } \text{M} \text{ lines of } Y \text{ to } Mo = 132-192\text{eV}, \text{ and the } \text{K} \text{ lines } F = 676\text{eV}, Mg = 1.25\text{keV}, \text{ and } Al = 1.49\text{keV} \]
spectrum of wavelengths, and through the use of monochromators is highly tuneable. In addition, with the advent of insertion devices in modern storage rings, synchrotron radiation provides a beam which may be as much as $10^6$ times brighter (photons cm$^{-2}$ s$^{-1}$ eV$^{-1}$ steradian$^{-1}$) than conventional x-ray machines[8].

Except in the simplest cases, calculation of the material properties of matter from first principles is still not possible. Instead, a number of different approximation methods are used. Synchrotron radiation experiments provide a means by which the accuracy of these approximation methods can be checked, thus helping to increase the level of sophistication of the theory. As an example, if we look back to the 1950's, we find that atomic theory had not advanced much beyond the level of the single particle hydrogenic approximation[9]. In the early 1960's, work done at the National Bureau of Standards revealed a number of discreet autoionizing resonances in the photoionization spectrum for helium[10]. Because it involves the simplest example of multi-electron correlation effects, this result is of great significance in understanding multi-electron systems. Thus, at the fundamental level, these studies provide a means for testing modern theories of atomic structure and processes, and in addition, the insights gained by these experiments are often illuminating in other disciplines, such as nuclear physics, where the many-body problem is central in understanding physical phenomena[12].

It has also become clear that understanding the atom in the free state is a prerequisite to understanding the complex structures involved in the solid state[11]. Thus beside their usefulness in illuminating electron correlation, synchrotron radiation ex-
periments are useful in such fields as surface physics, condensed matter, and atmospheric science where atomic interactions in solids or molecules can have important implications in the properties of the system under study.

The advent of synchrotron radiation has allowed the study of the interaction of photons and matter at higher energies. However, most of these studies have concentrated in the soft x-ray region (approximately $10eV \leq h\nu \leq 1keV$, or $1000\AA \geq \lambda \geq 10\AA$). In the hard x-ray region ($\lambda \leq 10\AA$), only a few gases have been studied beyond photoabsorption measurements, and most of this work has been done on atoms. In the hard x-ray region, x-rays can interact with the K-shell (1s) electrons in argon, chlorine, and sulphur, as opposed to soft x-rays, which typically interact with the L-shell (2s, 2p) electrons.

The research for this thesis was done in two parts. In the first, an ion time-of-flight mass spectrometer was used at the National Synchrotron Light Source (NSLS) in Brookhaven, New York to study the fragmentation dynamics of $H_2S$, HCl, and DCl following the excitation of a K-shell electron by x-ray synchrotron radiation. In the second part of the research, completed after the data was collected at NSLS, an ion time-of-flight analyzer was constructed. This device was modeled on the one used at NSLS, however, it was optimized for use at the Advanced Light Source (ALS) in Berkeley, California. This thesis is organized to give a complete picture of the design, construction, testing, and experiments done using an ion time of flight mass spectrometer. However because of opportunities arising from collaboration with researchers outside of UNLV, the experimentation was done first.
In addition to the information gained by ion time of flight spectroscopy, this research also serves as a first step toward even more detailed measurements of de-excitation dynamics. While the data collected in this thesis was obtained by ion spectroscopy, with some modification, the equipment used will be able to take electron-ion, or electron-ion-ion, coincidence measurements, thus further clarifying the decay pathways.

1.1 Theory

When a photon interacts with matter to ionize an electron, the fundamental relation governing the photoionization process is the Einstein equation[16],

\[ E_k = h\nu - \Phi \]  \hspace{1cm} (1.1)

where \( E_k \) is the kinetic energy of the electron, \( h\nu \) is the energy of the incident photon, and \( \Phi \) is the binding energy of the electron. Closely related to photoionization are resonance processes where the photon is not energetic enough to remove an electron from its orbital, but is sufficient to excite the electron to one of the unoccupied orbitals

\[ h\nu = \Delta\Phi \]  \hspace{1cm} (1.2)

where \( \Delta\Phi \) is the energy difference between the two states of the system.

The cross section for interaction of a system in state \( i \) with an unpolarized photon beam leaving the system in a state \( f \) with electrons of energy \( \epsilon \) and ions in state \( j \) is given by[16]

\[ \sigma_{ij}(\epsilon) = \frac{4\pi^2\alpha^2}{3g_i}(\epsilon + I_{ij})|M_{ij}|^2 \]  \hspace{1cm} (1.3)
where \( \alpha \) is the fine structure constant \((1/137)\), \( a_0 \) is the Bohr radius, \( g_i \) is the number of degenerate sublevels at the energy of the initial state, \( I_{ij} \) is the ionization energy, and the matrix element \( |M_{ij}| \) is given by

\[
|M_{ij}|^2 = \frac{4}{(I_{ij} + \epsilon)^2} \sum_{i,j} |<f| \sum_{\mu} \exp(-i k_\nu \cdot r_\mu) \nabla_\mu |i>|^2
\]  

(1.4)

Where \( r_\mu \) is the position coordinate of the \( \mu \)th electron, and \( k_\nu \) is the propagation vector for the photon[16]. Since \( k = 2\pi/\lambda \) and \( \lambda \approx 5\AA \), and because of the high nuclear charge, \( r_\mu \) is less than the Bohr radius \((a_0)\) for the 1s shell, so that \( k \cdot r \ll 1 \).

We can then apply the series expansion

\[
e^{-i k \cdot r} = 1 - i k \cdot r + \frac{(-i k \cdot r)^2}{2!} + \ldots
\]  

(1.5)

and neglect all but the first term so that we approximate the exponential with

\[
e^{-i k \cdot r} \rightarrow 1
\]  

(1.6)

then by substituting

\[
[\hat{H}_0, \hat{x}_i] = \left[ \frac{\hat{p}^2}{2\mu}, \hat{x}_i \right] = -\frac{i}{\mu} \hat{p}_i
\]  

(1.7)

it can be shown that[17]

\[
|M_{ij}|^2 = \frac{4}{(I_{ij} + \epsilon)^2} \sum_{i,j} |<f| \sum_{\mu} |\nabla_\mu |i>|^2 = \sum_{i,j} |<f| \sum_{\mu} r_\mu |i>|^2.
\]  

(1.8)

This substitution is the dipole approximation. From this it can be seen from where the dipole selection rule is derived. Since the position operator can be expressed as a sum of the creation and annihilation operators, the inner product shown in equation 1.8 is zero except in the situation where for the initial and final states \( \Delta \ell = \pm 1 \).
Following the initial interaction with an x-ray photon, there are a number of pathways by which an atom or molecule may decay from the excited state created by core ionization[15]. These processes are shown schematically in figure 1.2.

![Diagram showing decay pathways for atoms with a core shell vacancy.](image)

Figure 1.2: Decay pathways for atoms with a core shell vacancy.

Radiative transitions (fluorescence) occur when the inner core hole is filled by an electron from a higher shell, and a photon is emitted following the transition. For argon, this can be written

\[ \text{Ar} + h\nu \rightarrow \text{Ar}(1s^{-1}, 4p^1) \rightarrow \text{Ar}(3p^{-1}, 4p^1) + h\nu', \]  

(1.9)

where \(1s^{-1}\), and \(3p^{-1}\) indicate shells with missing electrons, \(\nu\) is the frequency of the incident photon, and \(\nu'\) is the frequency of the radiated photon. Because the process is very close to the initial interaction of the photon and the atom (only in reverse,
and with less probability), the matrix elements governing this process are similar to those governing the initial interaction.

Auger decay occurs when, following the creation of a core hole, one higher shell electron makes a transition into the empty orbital, and another electron is ejected. For example

\[ \text{Ar} + h\nu \rightarrow \text{Ar}^+(1s^{-1}) + e_p^- \rightarrow \text{Ar}^{2+}(2p^{-2}) + e_p^- + e_a^- \]  

where \( \text{Ar}^+(1s^{-1}) \) represents a positive argon ion with a K-shell hole, and the subscripts a, p, indicate whether the electron was ejected by photoionization or Auger decay. In this example, the two L-shell holes may further Auger decay.

Auger decay involves two-electron transition matrix elements. The probability of making a transition can be expressed by Møller’s formula \[15\],

\[
< f | H_{\text{interaction}} | i > = e^2 \int \int \psi_f^*(2) \psi_i^*(1) (1 - \vec{a}_1 \cdot \vec{a}_2) \frac{e^{ikr_{12}}}{4\pi r_{12}} \psi_i(2) \psi_i(1) d^3r_1 d^3r_2
\]

where \( \vec{a} \) is the Dirac velocity, \( \psi \) represents the initial and final wave function, and \( r_{12} \) is the inter-electron distance. For the interaction operator:

\[
\hat{I} = e^2(1 - \vec{a}_1 \cdot \vec{a}_2) \frac{e^{ikr_{12}}}{4\pi r_{12}}
\]

The first term may be regarded as arising from the Coulomb repulsion, and the second from the relativistic current-current interaction. Because equation 1.12 does not have the same \( r \) dependence as equation 1.8, dipole selection rules do not apply to Auger decay, instead, the selection rules governing these transitions in the L-S coupling representation are \[15\]

\[
\Delta S = \Delta L = \Delta M_S = \Delta M_L = \Delta J = 0
\]  

(1.13)
\[ \pi_i = \pi_f \quad (1.14) \]

where equation 1.13 states that the projection quantum numbers for the whole state (ion and continuum electron) are unchanged and equation 1.14 represents conservation of parity. For jj coupling, \( \Delta M = \Delta J = 0 \), and parity is conserved. These selection rules arise from the fact that in the non-relativistic limit, Auger processes are essentially a Coulombic interaction between the electrons, and \( e^2/|r_1 - r_2| \) is the operator governing the processes.

A process related to Auger decay is autoionization of core-hole excited states. This occurs when, rather than being removed as in photoionization, a core electron is resonantly excited to an empty orbital. This is followed by the decay of the excited states, for example in argon, the process goes as follows:

\[
Ar + h\nu \rightarrow Ar^* (1s^{-1}, 4p^1) \rightarrow Ar^{+1} (1s^2, 2p^{-1}, 4p^1) + e^{-\text{Auger}}. \quad (1.15)
\]

Such processes are energetically allowed only when

\[
E_f - E_i \geq E_{\text{ionization}} \quad (1.16)
\]

where the left side of the equation refers to the energy of the resonant transition, and the right side of the equation refers to the binding energy of the electron ejected. Core-hole autoionization is often referred to as a resonant-Auger process, because of the similarity of the resonant photoelectron spectra to auger spectra resulting from core ionization.
Coster-Kronig transitions are a subset of Auger transitions, and involve the filling of a core-shell hole by another electron from the same shell, accompanied by ionization of a valence-shell electron. For example:

\[
Ar^+(1s^22s^12p^63s^23p^6) \rightarrow Ar^{++}(1s^22s^22p^53s^23p^5) + e^- \quad (1.17)
\]

It should be noted that because of the lack of electrons in the K shell which can participate, Coster-Kronig transitions occur only for holes in the L and higher core shells.

Finally, the yields for these decay processes are given in table 1.1[14] for each of the atoms studied in this thesis.

Table 1.1: Sulphur, chlorine, and argon radiative and radiationless pathway yields. Coster-Kronig yields are given for L\(_1\) shell to be filled by an electron making the transition from an L\(_2\) or L\(_3\) shell. It should be noted that L\(_2\) and L\(_3\) shell fluorescence yields are identical as are L\(_2\) and L\(_3\) shell yields for Auger decay. Yields are listed as the fraction of all processes which occur.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Process</th>
<th>Fluorescence</th>
<th>Coster-Kronig</th>
<th>Auger</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>L(_1)</td>
<td>L(_2),L(_3)</td>
<td>L(_1)-L(_2)</td>
</tr>
<tr>
<td>S</td>
<td>0.078</td>
<td>7.4\times10^{-5}</td>
<td>2.6\times10^{-4}</td>
<td>0.32</td>
</tr>
<tr>
<td>Cl</td>
<td>0.097</td>
<td>1.2\times10^{-4}</td>
<td>2.4\times10^{-4}</td>
<td>0.32</td>
</tr>
<tr>
<td>Ar</td>
<td>0.118</td>
<td>1.8\times10^{-4}</td>
<td>2.2\times10^{-4}</td>
<td>0.31</td>
</tr>
</tbody>
</table>
Chapter 2

Experimental Setup

While each component will be further described later in this section, for the sake of clarity, it is useful to first describe the experiment as a whole (figure 2.3). The processes under study are initiated when a photon, emitted through synchrotron radiation, interacts with an atom or molecule of the gas being studied. The multitude of decay paths available to the atom produce ions of different charge states (for example, between +1 and +7 in argon). An ion formed in the extraction region of the Time of Flight (TOF) analyzer is accelerated toward a micro-channel plate assembly which detects the ion by providing an electron cascade with a gain of about $10^8$. The signal is then further amplified, and timing information is extracted using a series of electronic components which include a constant fraction discriminator, a time-to-amplitude convertor and an analog to digital convertor (ADC). The ADC outputs a digital signal to a PC-based multi-channel analyzer which allows the data to be saved and analyzed.
2.1 The Synchrotron-Radiation Source

Charged particles give off electromagnetic radiation when they are accelerated. When electrons are constrained to a circular path, the acceleration which causes the change in direction of motion also causes them to emit radiation. At relativistic velocities, electrons emit light radiation in a narrow cone tangential to the electron’s orbit. This radiation, which extends from the far infrared to the x-ray region of the spectrum, was first observed in the 1940’s by physicists doing particle physics[13].

The first step in creating synchrotron radiation (SR) is accelerating the electrons. This is usually accomplished in stages using a linear accelerator and a booster synchrotron. After the initial acceleration, the electrons are injected into the storage ring
(figure 2.4). It is here that the electrons circulate in closed orbits producing radiation for use in experiments. However, because electrons are circulating around the storage ring in discrete groups, called bunches, the radiation is pulsed at a regular frequency ($\approx 1$MHz).

Dipole bending magnets supply a centripetal Lorentz force, $(-e/c)\mathbf{v} \times \mathbf{B}$ which constrains the electrons in their orbit. Because the dipole magnets are only located at a few locations, the ring takes on the shape of an $n$-sided polygon, rather than a circle, with the bending magnets at the vertices, and straight sections in between.

Beamlines, located at the bending magnets on the storage ring, are responsible for allowing the radiation produced at the bending magnet to propagate to the experiment. The beamline contains the optics necessary for making the light monochromatic and focused for experimental use. Because of the strong absorption cross section by almost all materials across the x-ray and ultra-violet portion of the spectrum, lenses similar to those used for visible light are not suitable. Instead, a series of grazing-incidence mirrors are used to focus, collimate, and in some cases filter the radiation incident on the monochromator in order to suppress excess power. Monochromators used in SR applications generally consist of a reflection grating with a periodic "saw-tooth" pattern of lines, or crystals which select photon energies based on Bragg diffraction.

Energy lost by the electrons as they traverse the storage ring is replaced by radio-frequency cavities which provide an electric field to accelerate the electrons. This electric field is pulsed in order to help maintain the longitudinal grouping of the
electron bunches. Thus it is not the loss of energy which is the primary cause of beam decay in the synchrotron, but the loss of electrons. To counter this, pressures in the storage ring are usually kept in the $10^{-10} - 10^{-11}$ torr range in order to reduce the number of interactions between the electrons and other gas molecules, thereby extending the beam lifetime.

![Figure 2.4: Schematic of a storage ring and beam line on a synchrotron-radiation source.](image)

The experiments done for this thesis (not including the TOF analyzer testing) were conducted with x-ray synchrotron radiation (SR) provided by the National Institute of Standards and Technology/Argonne National Laboratory beamline X-24A at the National Synchrotron Light Source (NSLS). Natural Si(111) crystals in the double-crystal-monochromator component of the beamline provide a resolution of $E/\Delta E =$
5000 to 10,000 in the 2-6 keV (6-2 Å) photon-energy range.

A toroidal mirror downstream from the monochromator provides focusing, while a spherical mirror upstream from the monochromator serves to collimate the beam and limit the amount of power incident on the monochromator. With these mirrors, a beam with a brightness of $10^{10}$ to $10^{11}$ photons $s^{-1}mm^{-2}mrad^{-2}eV^{-1}$ is achieved. Additional details of the design [3] and performance [4] are available elsewhere.

Because of the amount of energy incident upon the monochromator, a certain amount of heating occurs (primarily at the first crystal) causing energy drifts (typically <1eV) [4]. In order to compensate for this, calibration of the photon energy is checked periodically. This is done by scanning the monochromator through the inner-shell threshold region while monitoring total-ion yield with the TOF analyzer [6]. By comparing the subthreshold resonances and other features to previously measured photoabsorption results, the absolute energy calibration can be determined.

## 2.2 The Chamber

The chamber in which the experiment is performed consists of a six-way cross with 8” conflat-type flanges. Because the beam emitted from the synchrotron is relatively immobile, the primary concern in the design of the support for the chamber is the ability to position the interaction region of the mass spectrometer with respect to the x-ray beam. To achieve this, a platform was built that mounts the chamber on three greased skid plates. Horizontal motion, accurate to about 0.01 inch, is achieved by tightening or loosening three pairs of bolts. Two of these pairs are perpendicular to
the beam, and also allow compensation for a “twist” in the alignment. This platform is mounted on a Portelvator brand cart. This cart has built in vertical motion, and wheels which make shipping to and from the experimental site easier.

Gas is delivered to the mass spectrometer by means of a manifold setup. The manifold is constructed of stainless steel tubing and valves in order to allow for the study of corrosive gasses. A Convectron pressure gauge is used to determine the base pressure of the manifold prior to introducing the gas. The accuracy of this gauge makes it useful for leak testing of the manifold, and gives a qualitative measure of the rate at which the manifold is out-gassing. In addition, a 10 micron filter protects the experiment from dust contamination.

2.3 The Analyzer and Detector

The analyzer used to collect data is similar in design to the analyzer constructed for this thesis (Section ). The creation of ions was achieved by focusing the incoming x-rays near the tip of a gas inlet needle located at ground potential in the extraction region. From there, the ions were accelerated through a series of electric field and field-free (or drift) regions toward a pair of microchannel plates (MCPs).

Each MCP is an array of about $10^6$ electron multipliers oriented parallel to each other at an angle of 12° from the surface of the plate. An ion with a sufficient energy incident on the surface of one of the channels will cause the emission of secondary electrons. These secondary electrons are accelerated by the potential difference across the MCP, and will in turn cause the emission of even more electrons when they are
incident on the walls of a channel. In our setup, two MCPs are used in a chevron configuration (the MCPs are rotated 180° with respect to each other). This reduces ion feedback, where ions created at the second plate are accelerated back to the first plate and cause secondary pulses. The electron pulse is then collected by a 50Ω, matched impedance, conical anode made by the Galileo corporation (model TOF 2003).

2.4 The Electronics

2.4.1 The Constant Fraction Discriminator (CFD)

The pulse from the conical anode is first sent through a pre-amplifier, if necessary, then into the CFD. Because of the varying amplitude of the pulses out of the anode, a certain amount of time resolution would be lost if these pulses were used to trigger the TAC. The CFD corrects this situation by providing a logic pulse whose timing does not depend on the amplitude of the input signal. It achieves this by splitting the signal into two parts. One part of the signal is then multiplied by some predetermined constant fraction. The other part is delayed and subtracted from the first part. A bi-polar pulse results, and the zero crossing point provides precision timing for the output logic pulse (figure 2.5-2.6).

2.4.2 The Time to Amplitude Converter (TAC)

The TAC serves as the nanosecond stopwatch to determine the flight times of the
individual ions. When the TAC receives a start pulse from the CFD, an internal voltage is linearly increased. When the TAC receives a stop pulse, the TAC outputs an analog pulse to the ADC with an amplitude proportional to the time difference between the start and stop signals.

2.4.3 The Multi-Channel Analyzer

For this experiment, the MCA is run in pulse height analysis (PHA) mode. In this mode, the pulses of varying amplitudes from the TAC are input to an ADC. The ADC then gives an output which the MCA reads as a channel address and increments the number of counts in the corresponding channel by one. Then by using a computer, the MCA gives a graph with the number of counts as the vertical axis, and channel as the horizontal axis, with the channel number being directly proportional to the time measured by the TAC.
2.5 Data Collection and Analysis

There are four modes of data collection for the spectra: total ion yield, singles, total coincident ion yield, and photoion-photoion coincidence (PIPIO). A total ion yield spectrum is recorded by scanning the monochromator over a set energy range around the ionization threshold energy for a core-shell electron of the species under study. The total number of ions detected during the scan is then recorded and plotted as a function of photon energy, producing a pseudo-photoabsorption curve. 3

Singles spectra derive their name from the fact that in order to collect this type of spectrum, the storage ring must be running in single-bunch or a similar mode. In this mode, a single bunch of electrons circulates in the storage ring producing one burst of x-rays each time the bunch passes through a bending magnet. This results in a periodic pulsing of the SR with a period depending upon the dimensions and operating parameters of the synchrotron (567ns at NSLS, 656ns at ALS). When collecting data in singles mode, the photon energy remains constant while data is being collected. The signal produced when an ion is detected by the spectrometer starts the "stopwatch" in the TAC, while the ring provides the stop signal. Thus what is actually measured is not the time of flight for the ions, but the time between detection of the ion, and the following ring pulse. In other words, it is the difference between the ion flight time and period of the ring when running in single bunch.

A true photoabsorption curve is obtained by placing a sample in the path of the light source. By comparing the light intensity before and after the sample, the absorption can be determined. In our case, we are measuring the interaction of the light and sample by collecting ions. Because a small fraction (<1%) of the interaction between the gas and photons do not produce ions, a total ion yield spectra cannot, by the most strict definition, be called an absorption spectra.
mode (figure 2.7). This results in faster moving ions having higher channel numbers. Because the ring pulses are regularly spaced, the flight times can be determined, thus allowing the identification of the peaks observed based on their charge-to-mass ratio.

![Figure 2.7: Schematic of how signal is measured in singles spectra.](image)

Total coincident ion yield and PIPICO spectra are used only in the study of molecules. A total coincident ion yield spectra is similar to a total ion yield spectra. The difference is that instead of counting the total number of ions, the total number of ion pairs which arrive within a certain time interval is measured, again, usually while the energy is scanned over a range near the inner-shell threshold of one of the atoms of the molecule. PIPICO spectra are similar to singles spectra, except that the stop signal for the TAC is provided when a second ion from the same molecule is detected. Thus the time measured by the TAC is the difference in flight time between the 2 ions. Because these spectra do not depend on the ring for timing, the mode of
operation of the storage ring is irrelevant. Because of the method by which PIPICO spectra are collected, the detection discriminates against recording processes where the molecule does not dissociate, and a molecular ion is formed, or where the molecule dissociates, and one of the fragments is neutral.

The data analysis procedure is essentially the same for both PIPICO and singles spectra. For each spectrum, the individual peaks are integrated, and the background subtracted. Then, the ratio of the intensity of a particular ion to the total number of ions produced at a specific energy is calculated. Since the spectra are taken at a number of different energies, we can then determine the fractional abundance of the different ions as a function of energy, and make conclusions based on the trends observed.
Chapter 3

The Time of Flight Mass Spectrometer

The time of flight analyzer (Figure 3.8) is divided by stainless steel plates into five regions of differing width and electric field strength. In the center of each plate is a round aperture covered with high transmission (90%), conducting wire mesh which serves to minimize field distortion. The first region, which lies between the pusher plate and first grid, is known as the extraction region. It is here that a grounded needle serves as an effusive source for the gas upon which the x-rays will be incident. The pusher plate and first grid are held at approximately equal but opposite voltages. This provides a uniform electric field with only a minimal distortion due to the needle.

In the second through fourth regions (referred to as the first acceleration, drift, and second acceleration regions), the voltages and widths are adjusted in order to achieve the maximum time resolution. As the names imply, the first and second acceleration regions are areas of constant electric field through which the ions are accelerated, while the drift region is an area of zero electric field. The fifth and final region is a field-free buffer region immediately above the micro-channel plates (MCPs). When ions are
incident upon the micro-channel plates, a cascade of electrons is excited. The voltages which accelerate the positive ions toward the MCPs will accelerate the electrons back toward the extraction region. If these electrons collide with the stainless steel plates of the analyzer, or with the sample gas, photons or ions would be created adding noise to the signal. The buffer region has no field across it, so it serves as a spatial barrier to prevent feedback by the electrons produced by the micro-channel plates.

![Figure 3.8: The time of flight mass spectrometer](image)

The width and field strength for each region is selected in order to achieve the greatest amount of spatial resolution. This principle, known as space focusing [1],
results in ions with the same charge and mass having the same time of flight regardless of their location of formation in the extraction region. That is to say, differences in flight path length due to the finite width of the ionizing radiation beam cause negligible differences in the ion time of flight.

3.1 Space Focusing

An ion produced in the extraction region will reach the detector with a flight time:

$$TOF = T_{\text{extraction}} + T_{\text{acceleration1}} + T_{\text{drift}} + T_{\text{acceleration2}} + T_{\text{buffer}}.$$ (3.18)

Assuming zero initial kinetic energy and treating the detector as a one dimensional electrostatics problem, it can be shown that [1]

$$T_{\text{extraction}} = \left(\frac{2smd_1}{q\Delta V_1}\right)^{1/2}$$ (3.19)

$$T_{\text{acceleration1}} = \frac{d_2}{\Delta V_2} \left(\frac{2m}{q}\right)^{1/2} \left(\left[\frac{s}{d_1} \Delta V_1 + \Delta V_2\right]^{1/2} - \left[\Delta V_1 \frac{s}{d_1}\right]^{1/2}\right)$$ (3.20)

$$T_{\text{drift}} = d_3 \left(\frac{m}{2q}\right)^{1/2} \left[\frac{s}{d_1} \Delta V_1 + \Delta V_2\right]^{-1/2}$$ (3.21)

$$T_{\text{acceleration2}} = \frac{d_4}{\Delta V_4} \left(\frac{2m}{q}\right)^{1/2} \left(\left[\frac{s}{d_1} \Delta V_1 + \Delta V_2 + \Delta V_4\right]^{1/2} - \left[\frac{s}{d_1} \Delta V_1 + \Delta V_2\right]^{1/2}\right)$$ (3.22)
where $q$ is the charge on the ion; $m$ is the mass of the ion; $s$ is the distance between the first grid and the location of ion formation; and $d_n$, $\Delta V_n$ refer to the width and voltage across the $n$th region.

The space focusing of the analyzer utilizes the fact that ions closer to the source backing plate (larger $s$ value) during formation gain a greater energy than ions formed further away from the backing plate (smaller $s$ value). These more energetic ions will eventually pass the less energetic ions. Thus we see that the purpose of the drift region, which is the longest part of the analyzer, is to give the faster ions an opportunity to "catch up". Finally, by placing the detector at the location where the ions pass each other, the difference in flight path length produces no difference in flight time. In order to find the location such that ions formed at $s_0 \pm \Delta s$ have the same flight time (where $s_0$ is the location of the gas inlet needle), we select voltage and region widths such that $\frac{dT_{\text{TOF}}}{ds} = 0$.

\begin{equation}
T_{b_{\text{f,te}}} = d_s \left( \frac{m}{2q} \right)^{\frac{1}{2}} \left[ \frac{s}{d_1} \Delta V_1 + \Delta V_2 + \Delta V_3 \right]^{-\frac{1}{2}} \tag{3.23}
\end{equation}

3.2 Design

A number of factors, aside from maximizing resolution, were taken into consideration in order to reduce the number of possible combinations of region lengths and voltages. The first parameter was that the ion time of flight needed to be kept under 656ns in order to take advantage of the period of the ALS when it is operating in single-bunch mode. Second we wanted the top of the micro-channel plate stack (and
consequently the bottom of the analyzer assembly) to be at a negative potential with a magnitude no less than 4600 volts. This voltage was chosen in order to achieve an acceptable level of detection efficiency for different ions and charge states. This value was chosen based on measurements taken with a similar device at the NSLS[2]. Third, the voltages on the extraction region are not to exceed ± 1000 volts in order to avoid added expense in power supplies. Finally, the sizes of commercially available parts were taken into consideration.

With these restrictions in mind, the first step in designing the analyzer was to do a number of calculations to determine the relationship between the voltages used and the region widths. Since the analyzer to be constructed was modeled after a device used in previous experiments [6], the dimensions and voltages of the previously constructed analyzer served as a starting point for our calculations. With the goal of optimizing this design for use at ALS, the amount by which the analyzer parameters could be varied while maintaining space focusing was determined. The dimensions determined in this part of the design process could then be used in Monte-Carlo simulations to test the resolution. An example of the relationship between detector dimensions and voltages is shown in Figure 3.9

For the Monte-Carlo simulations, the goal was to determine which space-focused configuration of the TOF analyzer would provide the greatest resolution. A number of analyzers with different dimensions were simulated, as were different energy uncertainties for the ions formed. The ability to resolve the $^{35}Cl^+$ and $^{37}Cl^+$ was used as a measure of the quality of the detector. Some of the results are shown in figures
The testing shows that the entire detector length should be extended as much as possible. Extending the acceleration regions improves peak sharpness, while extending the drift region, causes greater broadening in both the inter-peak spacing, and the peak width. Because the inter-peak minimum is lower when the second acceleration
region was extended, we concluded that extending this region improves resolution more than extending the drift region.

Further simulations were then conducted to determine what minimum size for the apertures is required to prevent the ions from colliding with the stainless steel plates of the TOF analyzer. These tests showed that during their travel through the analyzer, only a very small fraction of the ions ever travel beyond 0.5 cm in the beam-needle plane (equivalent to an aperture of diameter 1 cm). Since the smallest apertures available on the commercially supplied stainless steel plates used to construct the analyzer is 2.54 cm, there is no conflict with aperture size.

The final dimensions adopted, and examples of corresponding voltages are listed in Table 3.2. The voltages given in Table 3.2 are not the only voltages for which the detector will be space focused. Other combinations of voltage differences which satisfy equations 3.19-3.23 will work. Experience has shown that the sensitivity to variations in these voltages is not high.

Table 3.2: Dimensions and Voltages for the TOF analyzer. Unusual decimal lengths are a result of purchasing parts measured in English rather than metric units.
3.3 Testing

With the detector assembled, we were then able to proceed with testing. Testing was done using a Kimball Physics EFG-7F-2015 electron gun substituting for the pulsed synchrotron radiation. On this model the beam energy can be adjusted from 0 to 5 kV, with a minimum pulse width of 10 ns. Beam current, location, and divergence are also controllable. Count rates were determined by connecting a counter to the output signal of a constant fraction discriminator (CFD) and setting it to count for one second. Using a Leybold model TMP 361 turbo-molecular pump, we achieved a base pressure of about $10^{-8}$ torr. We proceeded to do the following:

1. Increase the voltage to the MCPs, and check to see if they are working. Using a digital oscilloscope we examined the output of the pre-amplifier. With the pressure gauge off, we observed occasional negative pulses (rate $\ll 1$ Hz). When the pressure gauge was turned on, the count rate increased (the precise rate depends on a number of variables, pressure, gauge used, etc., although rates of 10-40 kHz are typical). Negative pulses observed on the scope had amplitudes between about 20-140 mV, and fall times of about 1 ns. From this we concluded that the MCPs were working correctly.

2. Increase the gas pressure and observe the effects it has on the count rate. The pressure was raised to about $10^{-6}$ torr by allowing Argon to flow into the chamber.

\footnote{The pressure gauge is a Bayard-Alpert type nude ion gauge. The way it works is this. A filament is heated so that it emits electrons. These electrons are accelerated by a potential difference to a grid. As the electrons transverse this path, they collide with and ionize residual gas molecules in the chamber. The rate at which the ions created are collected determines the pressure. Because of the method by which this gauge works, it is no surprise that it causes an increase in the count rate.}
ber through the gas inlet needle of the TOF analyzer. With the ion gauge off, the counts were still only occasional. With the ion gauge on, the count rate increased as expected.

3. Pump gas out of the chamber and turn on the analyzer voltages. This had no noticeable effect on the count rate when the ion gauge was off, and caused a higher count rate than previously observed with the ion gauge on. This was as expected.

4. With no gas flowing into the chamber, and no voltage on the analyzer, turn on the electron gun. Although the electron gun was intentionally aimed at the metal parts of the analyzer in order to produce more noise, no increase in the count rate was observed.

5. Turn on the electron gun, and analyzer voltages (no gas). The number of dark counts increased. When the electron gun hit either the stainless steel plates or the gas inlet needle, the number of counts was seen to increase by one or two orders of magnitude, as expected.

6. Turn on the electron gun, the analyzer voltages, and allow gas to flow in to the analyzer. After doing this, spectra were collected.

3.4 Results and Discussion

Because an electron gun was used for testing, the voltage across the extraction region was reduced to between 100 and 200 volts in order to minimize deflection of
the electron beam. The top of the MCP stack was held at -1.7 kV. An example of
the spectra collected is shown in figures 3.13-3.14. The gas used for the experiment
was argon, charge states up to +5 were observed.

The data shown in figures 3.13-3.14 have been converted from channel number
to time of flight.

From Newton's Equations of motion in one dimension, we know:

\[ x = x_0 + v_0 t + \frac{1}{2}at^2. \]  

(3.24)

For our case, we can set \( x_0 = v_0 = 0 \) and because we are dealing with regions of
uniform electric field, we can substitute:

\[ a = \frac{qE}{m} \]  

(3.25)

and

\[ E = \frac{V}{x}. \]  

(3.26)

Then, by solving we find:

\[ t = A\sqrt{\frac{m}{q}}. \]  

(3.27)

where \( A \) is a constant. Thus the position of the peaks relative to each other is
determined by the square root of ionic mass to charge ratio.

The peak labeled "prompt" in figure 3.13 is caused by photons emitted when
electrons strike the stainless steel plates of the analyzer or some other piece of metal
Figure 3.13: Spectrum collected at 3kV using the electron gun.

Figure 3.14: Spectrum collected at 3kV using the electron gun. The region around the Ar +3, +4, and +5 peaks is expanded.
near the detector. This is highlighted by the fact that if, while taking spectra, the phosphor-coated, copper beam-monitoring paddle is placed in the path of the beam. The count rate for the prompt peak increases dramatically, while the count rates for the other peaks remain unchanged. In addition to giving a reference point for time = 0, the prompt peak serves as a measure of the resolution achievable with the experimental setup. The width of the prompt peak is equivalent to the width of a pulse from the electron beam, and the asymmetry on the right side of the peak indicates that the pulses from the electron gun require longer to "turn on" than to "turn off".

The next four peaks visible in figure 3.13 are the +4 to +1 peaks. These peaks are between two and three times as wide (full width, half maximum) as the prompt peak. Because the mass of the Ar nucleus is so much greater than the electron mass, it seems unlikely that during ionization the recoil from the interaction of the electron and the ion is enough to cause broadening this large. Experience during the collection of data showed that the emission current of the electron gun, and the focus of the electron gun were not stable. In addition, resolution of the peaks was far more sensitive to the focus of the gun than to any other factor. It seems likely that this broadening is an effect produced by the electron gun. It is possible that apertures on the electron beam, upstream from the interaction region would produce narrower peaks.

Finally, the areas of the individual peaks were integrated, and compared to published results for ion spectroscopy using an electron gun[7]. Table 3.3 shows the results. The ratios observed during testing were about twice as large for all charge
states. Earlier studies [2] show that in order to get uniform ion detection, an accelerating potential of at least 4600 V is required for an ion with a +1 charge (qV = 4600). During these tests, a potential of only 1700 V was used in order to minimize beam deflection. Because of their higher charge states, the +3 and +4 ions experience a greater force, and therefore obtain enough kinetic energy to be detected efficiently (for +3 qV = 5100, for +4 qV = 6800), while the +2 state (qV = 3400) and +1 state (qV = 1700) do not obtain enough energy to be detected efficiently. This is evidenced by the fact that the ratios of +3 ions to that of ions in the +4 state for both this experiment and that done by Van Der Wiel agree to within 0.06%.

<table>
<thead>
<tr>
<th>Table 3.3: Ratio of Ar charge states at 3keV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van Der Wiel et al. [7]</td>
</tr>
<tr>
<td>This work</td>
</tr>
</tbody>
</table>

Finally, the spectrometer was tested at the ALS in August of 1995. The results are shown in figure 3.15. Because of the double-bunch mode of operation at ALS, two spectra, indicated by labels above or below the baseline, respectively, are shown. The time axis is scaled to give the correct flight time for the peaks with labels below the spectrum. All of the peaks in the second spectrum (labels above the spectrum) are shifted by 328 ns, the time separation between the two ALS bunches.

The maximum time resolution for the experiment can be determined from the width of the prompt peaks resulting from light scattered from the sample onto the detector. These peaks, which actually have a flight time near zero, have a full width
at half maximum (FWHM) of only 200 ps. The most intense peak in the spectrum, Ar$^{+4}$, shows a FWHM of 840 ps, while Ar$^{+7}$, which is the most efficiently space focused peak, shows a FWHM of 600 ps. The high degree of time resolution observed is a result of the excellent timing characteristics of the ALS, as well as an indication that the design and construction processes were successful in achieving good analyzer resolution.

![Argon spectrum taken at a photon energy above the K-shell threshold (3205 eV) at beamline 9.3.1 during ALS two-bunch operation in August 1995.](image)

Figure 3.15: Argon spectrum taken at a photon energy above the K-shell threshold (3205 eV) at beamline 9.3.1 during ALS two-bunch operation in August 1995.
Chapter 4

Results and Discussion

4.1 Total Ion and Total Coincidence Yield

Total ion yield spectra for HCl and DCl near the chlorine K-edge are shown in figure 4.16. Because the only difference between the two molecules is the isotopic change in the hydrogen atom, we would expect the resonances to be a result of identical electronic transitions. This is reflected in the similarity of the two spectra.

The molecular orbital notation for the ground state electronic configuration of both molecules is

\[
\begin{align*}
\text{CoreShells} & : 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 \\
\text{ValenceShells} & : 4\sigma^2 5\sigma^2 2\pi^4 6\sigma^* 0 .
\end{align*}
\]  

To emphasize that the molecular orbitals can be considered as being derived from atomic (particularly chlorine) orbitals, this configuration is frequently written as follows

\[
\begin{align*}
\text{CoreShells} & : 1\sigma^2 2\sigma^2 2\sigma^* 2\pi^4 \\
\text{ValenceShells} & : 3\sigma^2 3\sigma^2 3\pi^4 3\sigma^* 0 .
\end{align*}
\]
From this configuration, the first spectral line (labeled 1 in figure 4.16) is attributed to a resonance transition from a core-shell chlorine 1s orbital to a $3p\sigma^*$ anti-bonding orbital. This orbital is composed primarily of the atomic chlorine 3p and hydrogen 1s orbitals. This transition obeys the atomic dipole selection rules, and as a result, the large matrix elements for K-shell excitation give a cross section for this transition which is large compared to the cross section of the continuum\[^{19}\]. With the $3p\sigma^*$ orbital filled, by a core electron, valence electrons see the core hole as an additional positive nuclear charge, and we can treat the chlorine atom in terms of its core equivalent species\[^{21, 22, 23}\]. The core equivalent molecule for HCl is ArH. The

---

\[^5\text{Molecular orbital notation is similar to atomic orbital notation. For example, a } 3p\sigma^4 \text{ orbital has quantum numbers } n=3, \ell = 1 (\ell=0 \text{ for } s \text{ orbitals, } \ell = 1 \text{ for } p \text{ orbitals etc.}), m_\ell=1 \text{ (similarly } m_\ell = 0 \text{ for } \sigma \text{ orbitals, } m_\ell = 1 \text{ for } \pi \text{ orbitals, etc.) and the superscript denotes the number of electrons in the orbital, in this case, four.}\]
ground state for this molecule has an essentially repulsive potential curve due to a filled anti-bonding orbital. Because of this repulsion, the fragmentation of core excited HCl into H and a core excited Cl* is likely to compete with Auger decay of the 1s hole[19].

Following the lead of previous absorption experiments[19], we can attribute the second spectral line (labeled 2 in figure 4.16) to a superposition of transitions to the Rydberg orbitals 4sσ, 4pπ, and 4pσ. Again, it seems likely that most of the intensity of this peak is due to the s → p dipole transitions which have a higher probability due to the dipole selection rules.

Finally, the roughly constant part of the spectrum represents energies above the ionization threshold. With sufficient resolution, and at high enough energies above the threshold, spectral peaks for multiple electron interactions can be observed. However, that is beyond the scope of the present work.

Figure 4.17 shows the total coincidence yield spectra for H₂S. The ground state electronic configuration of H₂S is

\[
\begin{array}{cccc}
\text{Core Shells} & \text{Valence Shells} & \text{Empty Shells} \\
1a_1^2 2a_1^2 1b_1^2 3a_1^2 1b_2^2 & 4a_1^2 2b_2^2 5a_1^2 2b_2^2 & 3b_2^0 6a_1^0 \\
\end{array}
\]

(4.30)

The largest peak, labeled 1 in figure 4.17, has been attributed to the excitation of electrons from the sulphur 1s to the 6a₁ (derived from the hydrogen 1s and sulphur 3s, 3pₓ, 3d) and 3b₂ (derived from hydrogen 1s and sulphur 3pₓ) anti-bonding molecular orbitals. With H₂S a system for labeling molecular orbitals is used which makes reference to the symmetry. The two hydrogen 1s orbitals combine with the sulphur orbitals in this way: hydrogen 1s + sulphur s or sulphur pₓ → a₁ orbital; hydrogen 1s + sulphur pₓ → b₁ orbital; and the hydrogen 1s + sulphur pᵧ → b₂.
orbitals in earlier studies[25, 24, 18]. The $b_2$ orbital is the dominant contributor to the intensity of this line. The orbital with $a_1$ symmetry is only about 20% as intense as a result of the amplitudes of the dipole matrix elements[24]. The lines from the two orbitals are separated by only 0.5eV[18], and are unresolved due to broadening from the lifetime width of the energy levels (0.3-0.5 eV), the photon energy width ($\approx 0.4$ eV), and the Franck-Condon effect[25], which can be explained as follows. When an electron undergoes a transition causing the molecule to go from the ground state to an excited state, the equilibrium displacement between the atoms in the molecule changes. When a photon interacts with a molecule, the interaction occurs much faster than the relaxation time for the nuclear positions in the molecule. As a result, the
excited molecule no longer has an equilibrium bond length, and begins to oscillate. In other words, in the most probable transition for the molecule, the ground state separation of the atoms becomes the classical turning point for the oscillating excited molecule. These oscillations add or remove energy from the ions produced by the fragmenting ion, causing the energy broadening observed.

The peak labeled 2 in figure 4.17 is attributed to excitations from the sulphur 1s to the 4pb1, 4pb2, and 3d2a1 orbitals[19]. Finally, for H2S a third peak just below threshold is visible in the total coincidence yield spectrum. This peak results from transitions to 5p derived Rydberg orbitals[20].

4.2 The Time of Flight Spectra

Spectra taken on resonance for HCl, DCl, and H2S are shown in figures 4.18-4.20.

The most notable feature of these spectra is the high degree of ionization of the atoms (+6 for chlorine, +5 for sulphur). In addition, fragmentation of the molecule is nearly complete. On resonance, for both HCl and DCl, the molecular ion (HCl+ or DCl+) is a product of less than 1% of the interactions, while for H2S, the molecular ion (HS+) is produced in fewer than 3% of the interactions. These spectra also give an indication of the resolution of the spectrometer. For the HCl and DCl spectra, the isotopes Cl35 (75.77%) and Cl37 (24.23%) are well resolved. S32 (95.02%) and S34 (4.21%) can also be distinguished in the H2S spectra.

Spectra, similar to those in figures 4.18-4.20 were taken at a number of different
Figure 4.18: Spectrum taken on resonance for HCl. The prompt and H+ peaks appear at the long time of flight end of the spectra due to an arbitrary choice of time delays in TOF measurement. Actual H+ flight time is its distance from the prompt peak.

Figure 4.19: Spectrum taken on resonance for DCI. For an explanation of the prompt and H+ peaks, see figure 4.18.
Figure 4.20: PIPICO spectrum taken on resonance for H$_2$S.

energies. The peaks in these spectra were integrated in order to calculate the ion fractions as a function of energy as described in section 2.5. For chlorine, the results are shown in figures 4.21-4.24

The most prominent feature in these graphs is the dip in the fraction of hydrogen produced on resonance. A change from approximately 50% to 45% was observed for HCl, 51% to 43% for DCI. The effect is even more pronounced when the ratio of hydrogen ions to chlorine ions is examined. Figure 4.24 shows a drop in the hydrogen to chlorine ratio of 40% for HCl, and 20% for DCI. The fact that the amount of hydrogen detected decreases only on resonance indicates that this effect is not the result of the H$^+$ ions being “lost” by the TOF analyzer. The incident photon energy has no effect on the collection efficiency of the detector. The absence of H$^+$ in the
Figure 4.21: Ion fraction as a function of energy for HCl singles spectra. The Cl$^{+6}$ peak was omitted for clarity.

Figure 4.22: Ion fraction as a function of energy for HCl PIPICO spectra. The Cl$^{+6}$ peak was omitted for clarity.
Figure 4.23: Ion fraction as a function of energy for DCI. The Cl$^{+6}$ peak was omitted for clarity.

Figure 4.24: Ratio of hydrogen and deuterium ions to chlorine ions.
spectrum could also be explained by the formation of the molecular ion HCl⁺. If this were the case, we would observe an increase in the amount of HCl⁺ detected. This is not the case. HCl⁺ fractional yields are consistently less than 1% of the ions detected. Formation of excited, neutral HCl also would reduce the amount of H⁺ detected on resonance, however the decay to HCl⁰ only occurs through radiative decay, and the yields for this process are far too small to account for this effect (see table 1.1). Thus it seems that the most likely explanation for this effect is the formation of neutral atomic hydrogen. The magnitude of this effect is particularly surprising considering that there is enough energy in the system to form highly charged chlorine ions.

Corresponding to the drop in the hydrogen fraction for HCl is an increase in the percentage of Cl³⁺ and Cl⁴⁺, in part due to the increased cross section of the K-shell holes on resonance. The much larger increase in the percentage of Cl⁺³ formed suggests that it has a much greater association with the formation of the neutral hydrogen on resonance (figure 4.21). This hypothesis is confirmed by the HCl PIPICO ion fractions. While for both HCl and DCl the fraction of Cl⁺³ ions is greater on resonance than above resonance, the fraction of coincidences between hydrogen and Cl⁺³ on resonance is about 7 percentage points lower than the fraction above threshold (figure 4.22).

This suggests either of the following decay paths following resonant excitation:

\[ HCl + \hbar \nu \rightarrow HCl^*(1s^{-1}\sigma^*) \]
\[ HCl^*(1s^{-1}\sigma^*) \rightarrow H^0 + Cl^*(1s^{-1}3p^{+1}) \]
\[ \rightarrow H^0 + Cl^{-1}\cdot(2p^{-2}3p^{+1}) + e^- (KLL Auger). \]  

The K-shell hole then Auger decays to form two L-shell holes, which would each
in turn Auger decay leaving a Cl$^{+3}$ ion. The dissociation before relaxation by the K-shell hole being the key point of comparison. Another option is core-shell Auger decay prior to dissociation of the molecule:

$$HCl^* (1s^{-1}\sigma^*) \rightarrow HCl^* (2p^{-2}\sigma^*) + e^- \quad (KL_{2,3} Auger)$$

$$\Rightarrow H^0 + Cl^+ (2p^{-2}3p^{+1}) + e^- \quad (Fragmentation).$$

From our experiments, it is impossible to determine which of these paths is more probable. However, using electron spectroscopy of the KLL-Auger electron we would be able to discern if the autoionization takes place from an atomic or molecular species, thus differentiating the preferred decay path. Studies done at the Cl L-edge[26] indicate that for those transitions, dissociation followed by Auger decay of the Cl fragment is the dominant decay path. However, the fact that a K-shell hole has a lifetime that is shorter than that of an L-shell hole by a factor of about five (for a K-shell hole, the lifetime $\Gamma=0.4$ eV$\approx1.6$ fs, for an L-shell hole, $\Gamma=0.1$ eV$\approx6.6$ fs[14]). may allow Auger decay to compete more favorably as the first step in the decay process. At this point, it also should be noted that although the DCI molecule undergoes the same decay transitions as the HCl molecule, the amount of neutral hydrogen produced is less by almost a factor of two. This is easily explained by the fact that the heavier deuterium does not escape the attractive potential of the Cl$^{+n}$ ion as quickly as the hydrogen atom.

As with HCl and DCI, in H$_2$S we see the same dip in the fraction of hydrogen produced, (figures 4.25- 4.26), and the same drop in the fraction of coincidences on resonance (figure 4.27).
Figure 4.25: Ion fraction as a function of energy for \( \text{H}_2\text{S} \) singles spectra.

Figure 4.26: Ratio of hydrogen ions to sulphur ions in \( \text{H}_2\text{S} \) singles spectra.
Figure 4.27: Ion fraction as a function of energy for H$_2$S PIPICO spectra.

Because H$_2$S is a triatomic molecule, the dissociation picture suggested by these facts is slightly more complicated. Auger decay competes with dissociation of one or both hydrogen atoms:

$$H_2S + h\nu \rightarrow H_2S^*(1s^{-1}3p^{+1*}) \quad (4.33)$$

$$H_2S^*(1s^{-1}3p^{+1*}) \rightarrow H^0 + H^0 + S^*(1s^{-1}3p^{+1*})$$
$$\quad \rightarrow H^0 + H^0 + S^{++}(2p^{-2}3p^{+1*}) + e^- \quad (4.34)$$

$$H_2S^*(1s^{-1}3p^{+1*}) \rightarrow H^0 + HS^*(1s^{-1}3p^{+1*})$$
$$\quad \rightarrow H^0 + HS^{++}(2p^{-2}3p^{+1*}) + e^- \quad (4.35)$$

$$H_2S^*(1s^{-1}3p^{+1*}) \rightarrow H_2S^{++}(2p^{-2}3p^{+1*}) + e^- \quad (4.36)$$
Again, as in the chlorine case, the 2p holes will also subsequently relax through Auger decay.

Ab-initio studies[29] show that for L-shell decay, there is only a very small contribution from the decay channel which involves dissociation of both hydrogens prior to autoionization. This is due to the relatively high cost in energy that this process would require. On this basis, it seems that equations 4.35 and 4.36 give the most likely decay channels.

Previous electron-spectroscopy studies[28, 27] of the decay channels for L-shell holes in H₂S show that the primary decay channel involves dissociation of one hydrogen atom followed by Auger decay from the excited HS molecule. Again, as in the case of HCl, the data does not allow us to determine if the shorter K-hole lifetime is sufficient to cause a change in the primary decay path when compared to the L-core hole. Further studies will be required to determine if the 1s⁻¹, σ* state is repulsive enough to cause neutral fragmentation on a shorter time scale than the lifetime of the core shell hole as is the case for an L-shell hole.

Another notable trend in the ion fractions for both the chlorine and sulphur atoms is the decrease in prominence of the +1 and +2 charge state atoms with a concurrent increase in the prominence of the +3, +4, and +5 charge states as the energy is increased above threshold. This is easily explained by the increased cross section of the core holes at and above resonance. As a result, rather than ionizing valence or shallow core level electrons, K-shell electrons are ionized which lead to higher charge state ions through multiple Auger decay processes.
The fractional yield graphs also point out an inherent uncertainty in our method of taking data. Above threshold, where we believe the molecules are completely fragmented, the $\text{H}^+/\text{Cl}^{n+}$ ratio should be one, and the $\text{H}^+/\text{S}^{n+}$ ratio should be two. However, in the present experimental setup, only one ion from a fragmentation event, can be detected. Both the $\text{H}^+$ and its sister ion ($\text{Cl}^{n+}$ or $\text{S}^{n+}$) from the same molecule have approximately equal probabilities to reach the detector. However, because of its smaller mass, the $\text{H}^+$ ion will reach the detector first. If the $\text{H}^+$ ion is detected, no more ions will be detected from that fragmentation event. Thus the $\text{Cl}^{n+}$ ion or $\text{S}^{n+}$ ion has a smaller probability of being detected dependent on the detection efficiency for $\text{H}^+$. This issue is discussed in greater length in the appendix.

There is also evidence for an effect known as post collision interaction (PCI). PCI is an effect that occurs when an electron absorbs just enough energy to be ionized. However, following the formation of the core hole, an Auger electron is ejected. In the classical picture, if the photoelectron is moving slowly enough, the Auger electron will pass the photoelectron, at which time the photoelectron may be recaptured by the Coulombic attraction of the now more highly charged ion. As the energy of the incident photon is increased, the kinetic energy of the photoelectron increases, which makes recapture less likely. Eventually, the photoelectron will reach the “no passing energy” where the Auger electron will no longer be energetic enough to pass the photoelectron, and it cannot be recaptured by the ion.

The evidence that PCI is occurring comes from the PIPICO fractional yields (figures 4.22, 4.27). In both cases, the dominant charge state ($\text{Cl}^{3+}$ or $\text{S}^{2+}$) shows an
increase in its fractional yield immediately above the ionization threshold. At about 5 eV above threshold, the fractional yield reaches a constant value. There is a decrease in the fractional yield of the charge state one smaller in magnitude (Cl$^{2+}$ or S$^{1+}$) corresponding to the increase in the yield of the dominant ion. This is the trend we would expect to see if the more highly charged ions are recapturing the photoelectrons. The above threshold region where the fraction of Cl$^{3+}$ or S$^{2+}$ becomes constant is the photon energy where the photoelectrons have enough kinetic energy to escape. If further testing confirms that this result is PCI, it would mark the first observation of this phenomenon in molecules.

4.3 Conclusions

An ion time of flight mass spectrometer was designed, constructed, and tested. As the result of a successful design and construction process, and the timing characteristics of the ALS, a FWHM of 840 ps was measured for Ar$^{4+}$, and 600 ps for Ar$^{7+}$.

Following excitation of a K-shell electron by an incident photon, a high degree of fragmentation of the molecule, and ionization of the atom (chlorine or sulphur) was observed in HCl, DCl, and H$_2$S. A significant decrease in the amount of hydrogen detected on resonance was attributed to an increase in the amount of neutral hydrogen created. This increase in the formation of neutral hydrogen corresponded to an increase in the amount of Cl$^{+3}$ or S$^{+2}$. The observation of an increase in the fractional yield for PIPICO spectrum of Cl$^{3+}$ or S$^{2+}$ ions with a corresponding decrease in the
fractional yield of Cl$^{2+}$ or S$^{1+}$ respectively is believed to be the first evidence of the PCI effect in molecules.

Because these are the first studies of this type on these molecules at K-shell energies, a number of questions remain. Electron spectroscopy studies of these molecules will be required to elucidate the decay paths, and confirm the observation of the PCI effect. Measurements of electron intensity as a function of electron kinetic energy would, based on the peak position, shape and width observed, indicate if the electrons were ejected by molecular or atomic species. Because of the vibrational energy inherent in molecules, broader electron lines are observed around Auger energies than is the case for atomic species. By studying these spectra, it is possible to determine if the Auger decay occurs from an atom or a molecule and thus know whether fragmentation occurs before or after the Auger decay. These studies would also confirm or refute the existence of PCI for these molecules. Since PCI causes Auger electrons to gain energy from the photoelectrons, electron spectroscopy would show an asymmetry toward the higher electron kinetic energy side of the Auger peak (the result of Auger electrons gaining energy), while the photoelectron peak would show an asymmetry toward the lower electron kinetic energy side.
Appendix

Analyzer Efficiency

In order to gain some insight into the efficiency of the mass spectrometer, we will first define $\epsilon_H, \epsilon_{Cl}$, and $\epsilon_S$, as the probability that an ion of hydrogen, chlorine, or sulphur, which is created through the interaction of a photon with an HCl or H$_2$S molecule is detected by the MCPs. We can write each of these detection probabilities as the product of the probability, $\epsilon_E(H)$ (for hydrogen), that the ion is extracted from the extraction region, and is not lost on the first aperture (that is to say that the ion is formed and extracted with a trajectory that sends it into the detector), and the probability $\epsilon_T(H)$, that the ion is successfully transported from the extraction region to the MCPs where it is detected:

$$
\epsilon_H = \epsilon_E(H)\epsilon_T(H). 
$$

(4.37)

Similar expressions can be written for sulphur and chlorine. The probability $\epsilon_T$ takes into account the likelihood that the ion will be lost to one of the wire meshes covering the apertures, or that it will impact on a region of the MCPs which will not result in an electron cascade, and therefore detection.
With the TOF setup used, if an ion is detected from the fragmentation of a molecule, no other ions from that same fragmentation event can be detected. Thus the slower sulphur and chlorine atoms can only be detected in the fragmentation events where hydrogen ions are not detected, and are therefore discriminated against in this detection scheme. For HCl, the probability of detecting a Cl^{n+} ion (where Cl^{n+} represents an ion of arbitrary charge state) is

\[ \epsilon_{Cl}(1 - \epsilon_H) \]  

(4.38)

where 1 - \( \epsilon_H \) is the fraction of events where a hydrogen ion is not detected. Thus we would expect the ratio of hydrogen to chlorine to be

\[ \frac{H^+}{Cl^{n+}} = \frac{\epsilon_H}{\epsilon_{Cl}(1 - \epsilon_H)}. \]  

(4.39)

For H\(_2\)S, we have a similar situation, except that we must take into account the fact that there are two hydrogens. The probability of detecting the first hydrogen is still \( \epsilon_H \). The probability of detecting the second hydrogen is, in analogy to the case with chlorine, \( \epsilon_H(1 - \epsilon_H) \). Then, the fraction of sulphur created which is detected is

\[ \epsilon_S (1 - \frac{1stH^+}{\epsilon_H} - \frac{2ndH^+}{\epsilon_H(1 - \epsilon_H)}) \]  

(4.40)

and the hydrogen-to-sulphur ratio is

\[ \frac{H^+}{S^{n+}} = \frac{\epsilon_H + \epsilon_H - \epsilon_H^2}{\epsilon_S(1 - 2\epsilon_H + \epsilon_H^2)} \]  

(4.41)

by completing the square in the numerator and factoring, we can rewrite this as

\[ \frac{H^+}{S^{n+}} = \frac{1}{\epsilon_S(1 - \epsilon_H)^2} - \frac{1}{\epsilon_S}. \]  

(4.42)
Then using the values $H^+/Cl^{n+}=0.95$ (figure 4.24) and $H^+/S^{n+}=2.25$ (figure 4.26), we can calculate $\epsilon_H$. It should be noted that we select the values of $H^+/Cl^{n+}$ and $H^+/S^{n+}$ above threshold because we believe at these energies, the molecules are completely fragmented. To calculate $\epsilon_H$, we assume $\epsilon_{Cl} = \epsilon_S$ and that $\epsilon_H$ is the same for both molecules. We make the assumption that $\epsilon_{Cl} = \epsilon_S$ on the basis of the fact that very little kinetic energy will be imparted to the sulphur and chlorine ions because they are so much more massive than the hydrogen ions. Thus the heavier ions will have trajectories which are essentially straight in to the detector. The statement that that $\epsilon_{H}(Cl)=\epsilon_{H}(S)$ assumes that in the fragmentation of the $H_2S$ molecule, both hydrogens are break off with the same kinetic energy as in the fragmentation of $HCl$. This seems reasonable, again, because of the large mass of the sulphur ion relative to the hydrogen ion.

\[
\frac{\epsilon_H}{.95(1-\epsilon_H)} = \frac{1}{2.25} \left(\frac{1}{(1-\epsilon_H)^2} - 1\right)
\]

\[
2.37(\epsilon_H - \epsilon_H^2) = 1 - (1 - 2\epsilon_H + \epsilon_H^2)
\]

\[
\epsilon_H^2(1 - 2.37) + \epsilon_H(2.37 - 2) = 0 \quad ; \epsilon_H = .27
\]

Next, we assume that because very little kinetic energy is imparted to the heavier ions during fragmentation, $\epsilon_E(Cl) = \epsilon_E(S) = 1$, and $\epsilon_T(H) = \epsilon_T(Cl) = \epsilon_T(S)$, then $\epsilon_{Cl} = \epsilon_S = \epsilon_T(H)$. If we assume $\epsilon_T(H) = 0.39$ and $\epsilon_E(H) = 0.69$. These strategically selected values, which still give $\epsilon_H=.27$ reflect the fact that the hydrogen ions are given a greater kinetic energy than the heavier ions, and are therefore extracted less efficiently. We then plug $\epsilon_{Cl}=.39$ into equation 4.39, and $\epsilon_S=.39$ into equation 4.42 to get the ratio $H^+/Cl^{n+}=0.94$ and $H^+/S^{n+}=2.23$ which is in good agreement with
Table 4.4: Efficiencies and ionic ratios presented in this appendix

Experimental value. Thus we have a good first approximation for the detection efficiency of H⁺, Cl⁺⁺ and S⁺⁺ in HCl and H₂S. These calculations are summarized in table 4.4

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