Mass spectroscopy of molecules following deep-core-shell photoexcitation

David Linnemann Hansen

University of Nevada, Las Vegas

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UMI
MASS SPECTROSCOPY OF MOLECULES FOLLOWING DEEP-CORE-SHELL PHOTOEXCITATION

by

David L. Hansen

A dissertation submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Physics

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ABSTRACT

Mass Spectroscopy of Molecules Following Deep-Core-Shell Excitation

by

David L. Hansen

Dr. Dennis Lindle, Research Advisor
Professor of Chemistry
University of Nevada, Las Vegas

The relaxation dynamics of HCl, DCl, H₂S, and D₂S following photoexcitation in the vicinity of the Cl, and S K-shell thresholds (~2.8 keV for Cl, ~2.5 keV for S) were studied by means of ion time-of-flight mass spectroscopy using monochromatic synchrotron radiation. In all cases, the onset of pre-edge core-shell photoionization precedes the formation on resonance of a significant amount of neutral hydrogen as well as post-collision-interaction effects above threshold. At the lowest resonant excitation to the 6σ* antibonding orbital in HCl, almost half of the excited molecules decay by emission of a neutral H atom, mostly in coincidence with a highly charged Clⁿ⁺ ion. The present work demonstrates that neutral-atom emission can be a significant decay channel for excited states with very-short lifetimes (1 fs). The first detailed observations of molecular fragmentation mediated by post-collision interaction between a...
photoelectron and an Auger electron are also presented, evidenced by the re-
capture of Cl-K photoelectrons by either Cl$^{n+}$ or H$^+$ dissociation fragments.
In addition, examination of the width of the H$^+$ peak in HCl and H$_2$S spectra
taken with the analyzer parallel and perpendicular to the polarization vector
of the incident light indicate that the asymmetry parameter $\beta$ is positive on
resonance. Finally, the relaxation dynamics of CH$_3$Cl following core-shell ex-
citation in the neighborhood of the chlorine K edge ($\approx$ 2.8 keV) were studied
using multi-ion coincidence techniques. Analysis of the data provides evidence
for sequential fragmentation of the molecule. In addition, for higher ionic
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mination of error bars.
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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[1].

There are three primary probes of the electronic structure of a system:
ions, electrons, 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 continuum 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 advantage 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[2].

Of the light sources available, lasers can only operate at relatively long wavelengths. 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 ¹ 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[3].

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

¹ for example, \( H_{el} = 21.22 \text{eV} \), \( H_{el} = 40.8 \text{eV} \), the \( M_\gamma \) lines of Y to Mo=132-192eV, and the \( K\alpha \) lines F=676eV, Mg=1.25keV, and Al=1.49keV

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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 spectrum of wavelengths, and through the use of monochromators is highly tunable. In addition, with the advent of insertion devices in modern storage rings, synchrotron radiation provides a beam which may be more than $10^6$ times brighter (photons $\text{cm}^{-2} \text{s}^{-1} \text{eV}^{-1} \text{steradian}^{-1}$) than conventional x-ray machines[2].

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[3]. 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[4]. 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[5].

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[6]. Thus beside their usefulness in illuminating electron correlation, synchrotron radiation experiments are useful in such fields where atomic interactions in solids or molecules can have important implications in the properties of the system under study. Examples from two scientific disciplines will serve to illustrate this point. The first comes from the field of radiobiology where it has been recognized that radiation damage from the dissociation of a molecule following core-level excitation has a direct correlation with cell death. In addition, because the resonant-excitation and ionization energies are characteristic of an atom, it is possible to select an atomic site for excitation if the atoms are not chemically equivalent. With this in mind, it is not impossible to imagine the possibility of selectively dissociating a complex system, such as a DNA backbone, by tuning the photon energy to selectively excite the electrons localized around a specific atomic site (in this case, phosphorus) [7]. Second, in the field of astrophysics, there are a number of datasets with calculated reaction rates, and absorption lines [8]. In this context, an experimental understanding of the interactions between photons and atoms or molecules is
necessary to ensure the accuracy of the models used [9]. Furthermore, a close
link has been revealed between x-ray emission and the early stages of stellar
evolution [10]. Experiments involving large hydrocarbons and soft x-ray light
from SR sources, can help identify the nature of interstellar dust and fluores­
cent molecular species [7, 10] and thus clarify the role played by the interaction
of x-ray photons and the gas and dust surrounding young stellar objects.

**Theory**

When a photon interacts with matter to ionize an electron, the fundamental
relation governing the photoionization process is the Einstein equation[11],

\[ E_k = h\nu - \Phi \]  

(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 pho­
toionization 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

\[ h\nu = \Delta \Phi \]  

(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[11]

$$
\sigma_{ij}(\epsilon) = \frac{4\pi^2 \alpha a_0^2}{3g_i} (\epsilon + \epsilon_i)|M_{ij}|^2
$$

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, $\epsilon_i$ is the ionization energy, and the matrix element $|M_{ij}|$ is given by

$$
|M_{ij}|^2 = \frac{4}{(\epsilon_i + \epsilon)^2} \left| \sum_{i,j} \frac{\epsilon}{\epsilon_i} \sum_{\mu} \exp(ik_\mu \cdot r_\mu) \nabla_\mu |i\rangle \right|^2
$$

Where $r_\mu$ is the position coordinate of the $\mu$th electron, and $k_\mu$ is the propagation vector for the photon[11]. Since $k = 2\pi/\lambda$ and $\lambda \approx 5\text{Å}$, 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

$$
e^{-ik\cdot r} = 1 - ik\cdot r + \frac{(-ik\cdot r)^2}{2!} + \ldots
$$

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

$$
e^{-ik\cdot r} \rightarrow 1
$$

then by substituting

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

it can be shown that[12]

$$
|M_{ij}|^2 = \frac{4}{(\epsilon_i + \epsilon)^2} \sum_{i,j} \left| \langle f | \sum_{\mu} \nabla_\mu |i\rangle \right|^2 = \sum_{i,j} \left| \langle f | \sum_{\mu} r_\mu |i\rangle \right|^2.
$$
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 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[13]. These processes are shown schematically in figure 1.

![Figure 1: Decay pathways for atoms with a core shell vacancy.](image)

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

$$Ar + h\nu \rightarrow Ar(1s^{-1}, 4p^{1}) \rightarrow Ar(3p^{-1}, 4p^{3}) + h\nu',$$  \hspace{1cm} (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

$$Ar + h\nu \rightarrow Ar^+(1s^{-1}) + e^- \rightarrow Ar^{2+}(2p^{-2}) + e^- + e^-$$  \hspace{1cm} (10)

where $Ar^+(1s^{-1})$ 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[13],

$$< f | H_{interaction} | i > = e^2 \int \int \psi_f^*(2)\psi_f(1)(1 - \vec{a}_1 \cdot \vec{a}_2) \frac{e^{ikr_{12}}}{4\pi r_{12}} \psi_i(2)\psi_i(1)d^3r_1d^3r_2$$  \hspace{1cm} (11)
where $\vec{\alpha}$ is the Dirac velocity, $\psi$ represents the initial and final wave function, and $r_{12}$ is the inter-electron distance. For the interaction operator:

$$\hat{I} = e^2(1 - \vec{\alpha}_1 \cdot \vec{\alpha}_2) \frac{e^{i\kappa r_{12}}}{4\pi r_{12}} (12)$$

The first term may be regarded as arising from the Coulomb repulsion, and the second from the relativistic current-current interaction. Because equation 12 does not have the same $r$ dependence as equation 8, dipole selection rules do not apply to Auger decay, instead, the selection rules governing these transitions in the L-S coupling representation are[13]

$$\Delta S = \Delta L = \Delta M_S = \Delta M_L = \Delta J = 0 (13)$$

$$\pi_i = \pi_f (14)$$

where equation 13 states that the projection quantum numbers for the whole state (ion and continuum electron) are unchanged and equation 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 $e^2/|\mathbf{r}_1 - \mathbf{r}_2|$ 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:

\[
Ar + h\nu \rightarrow Ar^+(1s^{-1}, 4p^1) \rightarrow Ar^{+1}(1s^2, 2p^{-1}, 4p^1) + e^-_{Auger}.
\] (15)

Such processes are energetically allowed only when

\[
E_f - E_i \geq E_{ionization}
\] (16)

where the left side of the equation refers to the energy of the resonant tran­
sition, 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-Kröning 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:

\[
Ar^{+}(1s^2 2s^1 2p^6 3s^2 3p^6) \rightarrow Ar^{+2}(1s^2 2s^2 2p^5 3s^2 3p^5) + e^- \] (17)

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

Finally, the yields for these decay processes are given in Table 1[14]
for each of the atoms studied in this thesis.
Table 1: Sulfur, chlorine, and argon radiative and radiationless pathway yields. Coster-Kröning 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>Process</th>
<th>Fluorescence</th>
<th>Coster-Kröning</th>
<th>Auger</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K  L$_1$ L$_2$,L$_3$</td>
<td>L$_1$-L$_2$</td>
<td>L$_1$-L$_3$</td>
</tr>
<tr>
<td>S</td>
<td>0.078 7.4·10$^{-5}$ 2.6·10$^{-4}$</td>
<td>0.32 0.62</td>
<td>0.922 0.056</td>
</tr>
<tr>
<td>Cl</td>
<td>0.097 1.2·10$^{-4}$ 2.4·10$^{-4}$</td>
<td>0.32 0.62</td>
<td>0.903 0.061</td>
</tr>
<tr>
<td>Ar</td>
<td>0.118 1.8·10$^{-4}$ 2.2·10$^{-4}$</td>
<td>0.31 0.62</td>
<td>0.882 0.066</td>
</tr>
</tbody>
</table>

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CHAPTER 2

EXPERIMENTAL

The experiments were performed using x-ray SR from beamline 9.3.1 at the Advanced Light Source (ALS) in Berkeley, California[15, 16, 17], and at the National Institute of Standards and Technology/Argonne National Laboratory beamline X-24A at the National Synchrotron Light Source (NSLS) in Brookhaven, New York[18, 19]. Beamline 9.3.1 at the ALS is a bending magnet beamline covering the 2–6 keV (6–2 Å) photon energy range. It is designed to provide a flux of $10^{11}$ photons s$^{-1}$ in $\leq 0.5$ eV bandpass by means of a two-crystal [Si(111)] "Cowan-type" monochromator. Focusing is provided by a pair of matched toroidal mirrors placed before and after the monochromator. At beamline X-24A, 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 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.

Photon-energy calibration is achieved by scanning the monochromator through the 1s threshold region while monitoring total-ion yield (Fig. 2.2) with the time-of-flight (TOF) analyzer. Comparing features, particularly sub-threshold resonances, in these absorption-like spectra to previously measured photoabsorption results[20, 21, 22] determines the photon energy with an accuracy of 0.2 eV. The calibration is checked periodically over the course of the experiment to compensate for small drifts (<1 eV) primarily caused by heating of the first crystals of the monochromators[19].

The time-of-flight mass spectrometer (Fig. 2.3) 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, between the pusher plate and first grid, is known as the extraction region. It is here that a hollow grounded needle serves as an effusive source for the gas under study. The pusher plate and first grid are held at approximately equal but opposite voltages, providing a uniform electric field with only a minimal distortion due to the needle.

The second through fourth regions are known as the first acceleration, drift, and second acceleration regions respectively. As the names imply, the first and second acceleration regions are areas of constant electric field through which
Figure 2.2: Total-ion-yield spectrum for HCl.

The ions are accelerated, while the drift region is field free. The fifth and final region is a small, field-free buffer region immediately above the micro-channel plates (MCPs) which serves as a spatial barrier to prevent the feedback into the extraction region of the electrons produced by the impact of an ion on the micro-channel plates, thus preventing spurious ionization events.

The width and field strength for each region of the time-of-flight mass spectrometer was optimized for the 656 ns period of the ALS single-bunch mode while maintaining optimal resolution. This was achieved by adjusting the an-
alyzer voltages to compensate for the finite beam-spot size by a process known as space focusing[23]. In addition, acceleration voltages and discriminator settings were selected to ensure uniform detection efficiency for all ions and charge states[24]. The ion TOF mass spectrometer was constructed with apertures of 2.54 cm, the diameter of the MCPs. Simulation showed that at the nominal operating extraction voltages, there would be no discrimination against ions created at the tip of the needle and ejected perpendicular to the analyzer axis with a kinetic energy of less than 50 eV. In order to determine the effect of the
angular distribution on the collection efficiency of the analyzer, ion-TOF data were taken in the singles mode with the axis of the analyzer both parallel (0°) and perpendicular (90°) to the polarization vector of the SR. The branching ratios of the ionic fragments observed for HCl and H2S proved nearly identical for both analyzer orientations, indicating that discrimination in the detection of H+ as a result of angular effects was negligible.

Detection of the ions was accomplished using two MCPs in a chevron configuration. The signal pulse is collected by a 50 Ω, matched impedance, conical anode made by the Galileo Corporation (model TOF 2003). While the electronics for the multi-coincidence measurements will be described in further detail in Chapter 6, for the singles measurements in Chapters 2-5 the pulse from the conical anode is first sent through a pre-amplifier, if necessary, then into a constant-fraction discriminator (CFD) which provides a time-to-amplitude convertor (TAC) with a logic pulse whose timing is not affected by the amplitude of the input signal. The TAC serves as the nanosecond stopwatch to determine the flight times of the individual ions, and outputs an analog pulse to an analog-to-digital convertor (ADC) with an amplitude proportional to the time difference between the start and stop signals provided by the CFD. The ADC then converts the signal to a digital number and outputs it to a multi-channel analyzer.

The experimental setup was tested at the ALS. The results are shown in
Fig. 2.4. 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. There are four modes of data collection for the spectra when not performing multicoincidence measurements: total-ion yield (TIY), singles, total-coincident-ion yield (TCY), and Photoion-Photoion Coincidence (PIPICO). 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 photoabsorption-
Figure 2.4: Argon spectrum taken at a photon energy above the K-shell threshold (3205 eV) at beamline 9.3.1 during ALS two-bunch operation. See text for an explanation of x-axis scaling.

like curve (Fig. 2.2). A total-coincident-ion yield curve is taken in much the same way, the difference being that rather than measuring the total number of ions detected, the total number of coincidences between two ions is measured (Fig. 2.5). In the “singles” mode, time-of-flight spectra (Fig. 2.6) are collected with only one or two electron bunches circulating in the storage ring. The start pulse for the timing circuit is provided by the detection of an individual ion, while the ring timing pulse, produced by the periodic pulsing of the SR
Figure 2.5: Total coincidence yield spectra for H₂S.

(328 ns for ALS 2-bunch, 567 ns at NSLS), provides the stop signal. Thus the ion-TOF spectra are inverted relative to actual flight times (i.e. slower ions appear to the left). In addition, because the ALS operates in 2-bunch mode, peaks due to the slowest ions “wrap around” in the narrower time window (Fig. 2.6). These spectra show a high degree of ionization of the atoms (Cl⁺, S⁵⁺) and that fragmentation of the molecule occurs following nearly all interactions. 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
Figure 2.6: TOF spectra of HCl and H$_2$S taken above threshold. Two isotopes of chlorine and sulfur are visible.

A 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 $^{35}$Cl (75.77%) and $^{37}$Cl (24.23%) are well resolved. $^{32}$S (95.02%) and $^{34}$S (4.21%) can also be distinguished in the H$_2$S spectra. Because the ions are measured in coincidence with the timing signal, this method has an advantage over electron-ion coincidence measurements in that there is no need to correct for differences in detection efficiency which

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arise from the differing numbers of electrons produced by the different charge states [25].

![Figure 2.7: Branching ratios as a function of energy for HCl singles spectra. The Cl+6 peak was omitted for clarity.](image)

In the PIPICO mode of operation, two ions from the same molecule provide the start and stop signals for the timing circuit (in this case, H+ provides the start, and Cln+ or Sn+ provide the stop). Thus the difference in flight time between the two ions is measured, and the operation mode of the storage ring is irrelevant. These measurements inherently discriminate against decay processes where the molecule does not dissociate, or where the molecule dis-
sociates but one of the fragments is neutral. The data analysis procedure is essentially the same for both PIPICO and singles spectra. Spectra were taken at a number of photon energies in the Cl and S K-shell region. Peaks in these spectra were integrated in order to calculate fractional yields as a function of energy. An example of this for HCl singles is shown in Fig. 2.7.
CHAPTER 3

NEUTRAL DISSOCIATION OF HYDROGEN FOLLOWING
PHOTOEXCITATION OF HCL AT THE CHLORINE K' EDGE.  

Application of mass spectroscopy and coincidence techniques to photoexcited atoms and molecules has begun to unravel some of the multitude of electronic and fragmentation decay pathways available to core-excited systems. Studies of Br M-shell excitation in HBr[26] gave the first evidence of the fast dissociation of a molecule into neutral fragments followed by atomic Auger decay. Subsequent studies found rapid neutral dissociation to be a decay mechanism in a number of other core-excited molecules[27, 28, 29, 30]. and, more recently, estimates of the branching ratios between "molecular" and "atomic" Auger decays have been made [31]. Essentially all of these measurements focus on shallow-core levels (e.g., Br 3d, Cl 2p), defined herein as levels in which a core hole can decay electronically only through interactions with valence-shell electrons. In contrast, holes in deeper core levels (e.g., Cl 1s) have shorter lifetimes and typically relax by means of a stepwise series of de-

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cays known as a vacancy cascade, where the initial decay step usually creates one or more shallow-core holes leading to highly charged residual ions[32].

As a simple diatomic with deep-core electrons, HCl was chosen for the present experiment because the core-level spectroscopy is well understood[20], and because of the relatively few ion fragments possible, facilitating interpretation of the subsequent mass spectra. Also, electron-spectroscopy measurements for the shallow-core Cl 2p level of HCl[28, 31] as well as ion-spectroscopy measurements of the K-shell of Ar[33, 34], which is iso-electronic with HCl, are available for comparison. One conclusion from the shallow-core measurements on HCl was that excitation of a Cl 2p electron to the lowest antibonding molecular orbital (6σ*) can lead to dissociation of neutral hydrogen in competition with electronic decay modes. Upon similar excitation of a Cl 1s electron we also find this to be a significant decay pathway. This result seems rather surprising considering the Cl K-hole lifetime is only 17% that of a Cl L2,3-hole.

Neutral dissociation occurring competitively with Cl-K Auger decay would be the fastest neutral-atom dissociation observed in photofragmentation to date.

The experiments were performed using x-ray synchrotron radiation (SR) from beamline 9.3.1 at the Advanced Light Source (ALS) in Berkeley, California[15, 16], and beamline X-24A at the National Synchrotron Light Source (NSLS) in Brookhaven, New York[18, 19]. An ion time-of-flight (TOF) mass spectrometer, comprised of five cylindrical regions of differing length and electric-field
strength, was used to measure charge distributions of photoions produced following x-ray absorption. In the first (extraction) region, a grounded needle served as an effusive source for the gas through which the x-ray beam is focused. Voltages on all regions were selected to achieve maximum time resolution by satisfying space-focusing conditions[23]. Ions formed in the extraction region of the analyzer were accelerated toward a dual micro-channel plate assembly which provided an electron cascade with a gain of about $10^6$. The signal was then further amplified, and timing information, related to the pulsed SR, was extracted. Acceleration voltages and discriminator settings were selected to ensure uniform detection efficiency for all ions and charge states.

Photon-energy calibration is achieved by scanning the monochromator through the Cl 1s threshold region while monitoring total-ion yield (Fig. 2.2) with the TOF analyzer. Comparing features, particularly subthreshold resonances, in these absorption-like spectra to previously measured photoabsorption results[20] determines the photon energy with an accuracy of 0.2 eV. The calibration is checked periodically over the course of the experiment to compensate for small drifts (<1 eV) primarily caused by heating of the first crystals of the monochromators[19].

The first peak (2823.9 eV) in Fig. 2.2 corresponds to the $1\sigma$ (Cl 1s)→$6\sigma^*$ transition, where $6\sigma^*$ designates the lowest-unoccupied molecular orbital which, in this case, is anti-bonding. The second peak is the result of contributions
from a number of Rydberg-like excitations. The Cl-K threshold at 2829.8 eV is indicated in the figure.

Two modes of operation are used to collect ion-TOF data. In the “singles” mode, spectra (Fig. 2.6) are collected with the storage rings operating with only one or two electron bunches. The start pulse for the timing circuit is provided by the detection of an individual ion, while the ring timing pulse, produced by the periodic pulsing of the SR (328 ns for ALS 2-bunch, 567 ns at NSLS), provides the stop signal. Thus the ion-TOF spectra are inverted relative to actual flight times (i.e. slower ions appear to the left). In addition, because the ALS operates in 2-bunch mode, peaks due to the slowest ions “wrap around” in the narrower time window (Fig. 2.6).

In the second mode of operation, two ions from the same molecule provide the start and stop signals for the timing circuit (in this case, H⁺ provides the start, and Cl²⁺ provides the stop). Thus the difference in flight time between the two ions is measured, and the operation mode of the storage ring is irrelevant. These Photo-Ion Photo-Ion Coincidence (PIPICO) measurements inherently discriminate against decay processes where the molecule does not dissociate, or where the molecule dissociates but one of the fragments is neutral.

Singles and PIPICO spectra were taken at a number of photon energies in the Cl K-shell region. Peaks in these spectra were integrated in order to
calculate fractional yields as a function of energy. Results from the singles spectra are shown in Figs. 2.7-3.8, while the results for the PIPICO spectra are shown in Fig. 3.9.

![Graph](image)

Figure 3.8: Ratio of hydrogen ions detected to the sum of all chlorine ions detected in singles mode.

The most prominent feature in Figs. 2.7-3.8 is the dip in the fraction of hydrogen produced on the $6\sigma^*$ resonance. Fig. 3.8 shows a drop in the $H^+/Cl^{n+}$ ratio of about 40% ($Cl^{n+}$ denotes the sum of all chlorine charge states detected.) All but one possible fate of the missing hydrogen ions can be ruled out. One possibility is that fewer $H^+$ ions appear on resonance because
dissociation occurs less often. However, if hydrogen remains part of the HCl molecule, and the molecule forms a molecular ion, then HCl\(^{++}\) peaks would be seen in the “singles” spectra. Analysis shows that HCl\(^{+}\) yields are consistently less than 1% of all ions detected, too small to explain the dip in H\(^{+}\) yield. On the other hand, if the molecule remains intact and neutral, then it also would escape detection. Only radiative decay of the resonantly excited state could produce uncharged molecules, and the radiative yields for such processes are known to constitute less than 1% of the possible decay processes of Cl K-
holes [14]. In addition, any process which leaves an intact HCl molecule would exhibit a matching decrease in Cl$^{a+}$ yields, which is clearly not the case. So, resonant excitation leads primarily to dissociation.

For resonant photofragmentation producing an H$^+$ ion, the 0° TOF spectra show a splitting in the H$^+$ peak (Fig. 2.6), which can be explained as follows. The molecules in the gas jet are randomly oriented, but because of the well-defined symmetry of the excited orbital (i.e., 6σ$^*$), molecules which have their axes parallel to the polarization vector of the SR preferentially interact with the incident photons. Because decay and dissociation of the molecule occur rapidly compared to the rate of molecular rotation, fragments are ejected along the molecular axis, and the double peaks reflect orientation of the molecule following excitation. (This effect will be dealt with more completely in a future publication.)

It is possible that this angular-distribution effect is sufficient to enable H$^+$ ions to escape extraction and detection by the analyzer. Two tests were done to examine this possibility. First, the ratio of H$^+$ to Cl$^{3+}$ was measured for extraction voltages in the interaction region as high as 2.2 kV/cm, and as low as 1 kV/cm (data in Figs. 2.6–3.9 were collected at approximately 2 kV/cm), at photon energies both on resonance and just above threshold. In all cases, as the extraction voltage was changed, the H$^+$/Cl$^{3+}$ ratio did not change significantly, strongly suggesting that extraction efficiency is unaffected by the on-resonant
angular distributions. Second, the measurements were performed with the analyzer parallel and perpendicular to the polarization vector of the SR beam. For the parallel orientation, the two peaks which result from $H^+$ ions being ejected toward and away from the detector have identical intensities within experimental error, indicating that the collection efficiencies for ions ejected in either direction are equal. With the analyzer in the perpendicular orientation, $H^+$ ions are ejected perpendicular to the detector axis, presumably making it more likely that the extraction voltage would be insufficient to collect all the $H^+$ ions. However, the data show that the relative $H^+$ yields on-resonance and above-threshold are the same for both orientations of the analyzer. In addition, simulations indicate that at the nominal operating extraction voltages, there would be no angular discrimination against $H^+$ ions ejected with less than 50 eV kinetic energy. We conclude that $H^+$ ions are not escaping the extraction fields of the TOF analyzer. Thus, the only plausible explanation of the dip in $H^+$ yield on the $6\sigma^*$ resonance is the dissociation of HCl, yielding neutral atomic hydrogen, which the analyzer cannot detect. The magnitude of this effect is particularly surprising considering the short lifetime of a Cl K-shell hole (1.1 fs), and that there is enough energy in the system to form highly charged chlorine ions (up to Cl$^{6+}$).

Corresponding to the decrease in the $H^+$ yield is an increase in the relative yields of Cl$^{3+}$ and Cl$^{4+}$ (Fig. 2.7), suggesting an association with formation
of neutral hydrogen on resonance. This hypothesis is confirmed by the HCl PIPICO yields (Fig. 3.9). While for the singles spectra (Fig. 2.7) the yield of Cl$^{3+}$ ions is greater on resonance than above threshold, the PIPICO spectra show that the coincidence yield between H$^+$ and Cl$^{3+}$ on resonance is lower than the coincidence yield above threshold (Fig. 3.9). This is expected if the neutral hydrogen is being ejected in coincidence with Cl$^{3+}$; coincident detection of an ion pair is impossible, therefore reducing the coincidence yield on resonance.

These results suggest one or some combination of the following types of decay paths following resonant excitation of HCl:

$$HCl^*(1σ^-16σ^*) \rightarrow H^0 + Cl^*(1s^-13p^6)$$ (3.18) \textit{(Fragmentation)}

$$Cl^*(1s^-13p^6) \rightarrow Cl^{++}(2p^-23p^6) + e^-$$ (3.19) \textit{(Atomic KLL Auger)}

Auger decay of the two L-shell holes leads to the formation of a Cl$^{3+}$ ion. Dissociation prior to relaxation of the K-shell hole is the key point in this mechanism. Another option is Auger decay of the Cl K-hole prior to dissociation of the molecule:

$$HCl^*(1σ^-16σ^*) \rightarrow HCl^{++}(1π^-26σ^*) + e^-$$ (3.20)
From the present experiments, it is impossible to determine which of these paths is more probable. The higher electron density around the H atom in the excited $\sigma^*$ orbital, coupled with the fact that the H atom has very little time to move during the lifetime of the core hole, opens up the possibility that the excited electron in the $\sigma^*$ orbital remains as a spectator electron, localized around the H atom. The spectator electron which is not ejected in the subsequent Auger decay, thus allows the H atom to fragment as a neutral. Electron spectroscopy of the KLL-Auger electrons would reveal if the Auger decay takes place from an atomic or molecular species, and in the case of molecular decay, if the electron in the $\sigma^*$ orbital is a spectator or participator in the Auger decay, thus determining if the dissociation of the molecule occurs on the same time scale as the Auger decay. Studies done at the Cl L-edge of HCl[28] indicate that at the Cl 2p$\rightarrow$ 6$\sigma^*$ resonance, dissociation followed by Auger decay of the atomic Cl fragment is the dominant decay path. However, the fact that a Cl K-shell hole has a shorter lifetime than an L-shell hole by a factor of about 6 [for a K-shell hole, the lifetime $\Gamma=0.6$ eV (1.1 fs); for an
L-shell hole, $\Gamma = 0.1 \text{ eV (6.6 fs)}[14]$ may allow Auger decay to compete more favorably as the first step in the decay process.

In conclusion, following photoexcitation of a Cl K-shell electron in HCl to the $6\sigma^*$ anti-bonding orbital, a significant decrease in the amount of H$^+$ observed is attributed to an increase in the amount of neutral hydrogen dissociation. The increase in neutral hydrogen corresponds to an increase in the amount of Cl$^{3+}$ detected. Observation of a decrease in the amount of Cl$^{3+}$ detected during PIPICO measurements confirms this interpretation. While electron spectroscopy is required to conclusively determine the decay mechanism, the present results suggest that the dissociation time for resonantly excited HCl may be competitive with the decay time of a Cl K-shell hole.
CHAPTER 4

PHOTOFRAGMENTATION OF THIRD-ROW HYDRIDES FOLLOWING PHOTOEXCITATION AT DEEP-CORE LEVELS

Time-of-flight mass spectroscopy and coincidence measurements of atoms and molecules are relatively well understood techniques\cite{23, 35, 36}. Coupled with the high brightness and high resolution of synchrotron radiation (SR) sources, these techniques have proven useful in elucidating some of the multitude of electronic and fragmentation decay pathways available to core-excited systems. To date, the majority of these studies have concentrated on relaxation of systems following excitation of a shallow-core electron, where shallow-core levels are those which can electronically decay only through interaction with valence-shell electrons (e.g., Cl 2p, Br 3d). In contrast, the measurements done for this paper focus on deep-core level excitations (e.g., Cl 1s, S 1s). Deep-core holes have shorter lifetimes, and typically relax through Auger decay, creating shallow-core holes. Because of this extra step in the decay process, deep-core excited systems have a much wider array of decay pathways by which they can relax, and usually produce much more highly charged residual ions by means
of a stepwise series of decays known as a vacancy cascade[32].

HCl and H₂S serve as interesting systems to study for a number of reasons. In both cases, the core-level spectroscopy is well understood[20, 21, 22], and electron-spectroscopy measurements[28, 31, 37, 38] following shallow-core-level excitation have been performed. Both molecules are also iso-electronic with Ar for which ion-spectroscopy measurements following K-shell excitation are available[24, 34, 33] thus allowing the useful comparison between atomic and molecular decay pathways. Because HCl and H₂S are chemically identical to DCl and D₂S, it is also useful to study the deuterated systems, in order to determine the changes in the kinematics of the fragmentation which result.

Results and Discussion

HCl, DCl

A total-ion yield spectrum for HCl near the chlorine K-edge is shown in Fig 2.2. The molecular orbital notation for the ground state electronic configuration of both HCl and DCl is

\[
\begin{align*}
\text{Core Shells} & \quad 1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 \\
\text{Valence Shells} & \quad 4\sigma^2 5\pi^2 2\pi^4 6\sigma^*^0.
\end{align*}
\]

(4.22)

Following the lead of previous experiments[20], the first spectral line in Fig. 2.2 is attributed to a resonance transition from a core-shell chlorine 1s orbital to a 6\(\sigma^*\) anti-bonding orbital. This orbital is composed primarily of the atomic
chlorine $3p$ and hydrogen $1s$ orbitals. The second spectral line in Fig. 2.2 results from a superposition of transitions to the Rydberg orbitals $7\sigma^*, 3\pi^*$. and $8\sigma^*$ derived from the Cl $4p$ orbital. Again, it seems likely that most of the intensity of this peak is due to the $s \rightarrow p$ dipole transitions which have a higher probability due to the dipole selection rules.

![Graph](image)

Figure 4.10: Branching ratios as a function of energy for DCl singles spectra. The Cl$^{+6}$ peak was omitted for clarity.

Figure 2.7 and Fig. 4.10 show the fractional ion yields obtained for HCl, and DCl singles spectra, while Fig. 3.9 and Fig 4.11 show the yields obtained using the PIPICO spectra. As is to be expected the yields of the Cl$^{3+}$, Cl$^{4+}$,
Figure 4.11: Branching ratios as a function of energy for DCI PIPICO spectra. The Cl$^{+6}$ peak was omitted for clarity.

and Cl$^{5+}$ increase across threshold, while yields of Cl$^{2+}$ and Cl$^{+}$ charge states decrease. This is easily explained by the fact that at photon energies below the 1s $\rightarrow$ 6$\sigma^*$ resonance, the photoexcitation is primarily a result of interactions with electrons in molecular orbitals derived from the Cl 2p and valence orbitals. At energies above the resonance, interaction with a Cl 1s electron becomes more likely, thus adding an additional step in the relaxation cascade, and making higher ionic charge states more probable.
In the photon energy regime below the $1s \rightarrow 6\sigma^*$ resonance changes in the relative abundances of the different ionic states are visible in the fractional ion yields for both the singles (Fig. 2.7, 4.10) and PIPICO spectra (Fig. 3.9, 4.11). The trend is reflected in the sharp increase in the average charge state (Fig. 4.12) at energies which are several linewidths below the resonance (linewidth = 1.86 eV [20]). Following the lead of previous studies[39], we attribute this effect to pre-edge inner-shell ionization, where the photoelectron is excited to the Lorentzian profile of a continuum state[40]. Previous studies have observed the onset of this effect at tens of eV below the $1s \rightarrow 4p$ resonance for Ar[41] and for more than 10 eV below the first sulfur K-edge resonance in OCS and CS$_2$[39]. While in this study, the data does not allow for an accurate determination of the onset of pre-edge ionization, it can be safely said that it occurs at energies more than 5 eV below the $1s \rightarrow 6\sigma^*$ resonance.

The most prominent feature in Figs. 2.7, 4.10 is the dip in the fraction of hydrogen produced on resonance, which has been attributed in a previous paper to the production of neutral hydrogen [42]. The ratio of hydrogen ions to chlorine ions (Fig. 4.13) shows a drop in the hydrogen to chlorine ratio of as much as 40% for HCl, and 20% for DCl. It should be noted that although the DCl 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 explained by the fact that the heavier deuterium does not escape the
Figure 4.12: Average chlorine charge state for HCl and DCl singles and PIPICO spectra. Circles represent the HCl data, triangles represent the DCl data.

The attractive potential of the Cl$^{+\alpha}$ ion as quickly as the hydrogen atom, and it is thus more difficult for the deuterium atom to carry away an electron in the presence of the more electronegative chlorine ion.

In the energy regime immediately ($\sim 7$ eV) above the Cl 1s threshold, the fractional ion yields (Fig. 2.7) for Cl$^{3+}$, Cl$^{4+}$, Cl$^{5+}$, and H$^+$ increase, while for Cl$^{2+}$, there is a decrease in yield. The effect is particularly pronounced in the yields for the PIPICO spectra (Figs. 3.9, 4.11). Similarly, the average
Figure 4.13: Ratio of hydrogen or deuterium ions detected to the sum of all chlorine ions detected in singles mode. Circles represent the HCl data, triangles represent the DCl data.

charge state shows an increase in the same regime (Fig. 4.12). These trends have been explained in a previous paper[43] by an electron correlation effect known as post collision interaction (PCI) where the photoion recaptures the photoelectron following Auger decay.

It is also worth noting that some structure is visible in the region between the first resonance and threshold. This is particularly true of the PIPICO yield curves (Figs. 3.9, 4.11). While the intensities of the higher charge states (Cl^{3+},
Cl^{+}, Cl^{5+}) tend to follow the structure of the TIY spectrum, the yields for the lower charge states (Cl^{+}, Cl^{2+}) follow the TIY inversely, that is to say that maxima in the TIY spectrum correspond to minima in the ion yields for Cl^{+} and Cl^{2+}, which show sharp peaks corresponding to the energies in between the resonances. This can be explained by the fact that the lower charge states are produced primarily by valence photoionization. Because the cross section for K-shell photoexcitation increases on resonance, the yield of the higher charge states will increase, thus decreasing the fractional yield for the lower charge states. In the region in between the first and second resonance, the opposite is true, and the lower K-shell cross section results in an increase in the fractional yield of Cl^{+}, Cl^{2+}. The same effect is visible in the average charge curves (Fig. 4.12), where the sub-threshold structure follows that of the absorption cross section.

Figure 4.14(a) shows the H^{+} peaks from HCl TOF spectra taken on the 6σ^{*} resonance, and at 50 eV above resonance, with the analyzer parallel to the orientation of the polarization vector of the SR. The areas in all spectra were normalized to one in order to obviate differences in the H^{+} peak shape caused by changes in the β parameter or the amount of kinetic energy released as a function of photon energy. In this context, β is the parameter which describes the angular distribution of photofragments in the well-know expression for the
differential photoionization cross section [44]

\[ \frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[ 1 + \frac{\beta}{2} \left( 3\cos^2 \theta - 1 \right) \right]. \] (4.23)

Here \( \sigma \) is the partial photoionization cross section, \( \Omega \) is the solid angle, and \( \theta \) is the angle between the ejected fragment and the polarization vector of the SR.

Within experimental error, both plots in Fig. 4.14(a) have the same baseline width, indicating that both are the result of fragments ejected with the same kinetic energy, and that differences in peak shapes are a purely angular effect. These differences arise from the fact that the molecules in the gas jet are randomly oriented, but because of the well defined symmetry of the excited orbital (i.e. \( 6\sigma^* \)), molecules which have their axes parallel to the polarization vector of the SR preferentially interact with the incident photons. Following photoabsorption by HCl, the molecule will, in most cases, fragment. and because decay and dissociation of the molecule occur rapidly compared to the rate of molecular rotation, fragments are ejected along the molecular axis, and the double peaks reflect orientation of the molecule following excitation. Because of its smaller mass, the H\(^+\) ion will be ejected with a much higher velocity than the Cl\(^{a+}\) ion, and H\(^+\) ions ejected toward and away from the detector make up the peaks at faster and slower flight times respectively. The same effect was observed in ion-TOF studies of HCl after excitation of a Cl 2\( p \)
Figure 4.14: H\(^+\) peaks from HCl singles spectra. (a) Data taken on resonance (dotted line), and 50 eV above resonance (solid line) with the analyzer parallel to the polarization vector of the SR. (b) Data taken 10 eV below resonance (dotted line), and 50 eV above resonance (solid line) with the analyzer parallel to the polarization vector of the SR. (c) Data taken on resonance (dotted line) and 50 eV above resonance (solid line) with the analyzer perpendicular to the polarization of the SR. The labels on the top x-axis correspond to the 0° plots, while labels on the bottom correspond to the 90° plot.
Following the lead of a previous paper [23] the energy released in fragmentation can be determined from the peak width using the expression

\[
U_0 = \left( \frac{qEt}{2} \right)^2 \frac{1}{2m}
\]

where \( q, E, t, \) and \( m \) are the charge, electric field in the interaction region, peak width in ns, and mass of the ion. It also assumes that fragments are perfectly space focussed, and that the electric field in the extraction region is uniform. Deviations from ideal conditions increase the peak width, thus the values calculated are upper bounds. On resonance, the average energy released as measured by the time between maxima of the split peaks is \( 11 \pm 2 \) eV, while the most energetic ions have an energy of about \( 48 \pm 4 \) eV as measured by the width of the peak where it returns to the background intensity.

Figure 4.14(b) shows the \( \text{H}^+ \) peaks from HCl TOF spectra taken 10 eV below and 50 eV above resonance, with the analyzer in the 0° orientation. It is clear that below resonance the \( \text{H}^+ \) peak is narrower than above resonance. At 50 eV above resonance, the \( \text{H}^+ \) peak has a width of \( 25 \pm 3 \) eV (FWHM), while the \( \text{H}^+ \) peak for the 10 eV below resonance spectra is \( 18 \pm 2 \) eV wide (FWHM). An identical change in width can also be observed in the spectra taken with the analyzer in the 90° orientation. This indicates that the change in peak width is a result of a change in the amount of energy released in fragmentation and electron [45].

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that this is not an angular effect. This observation is in line with the fact that below the \(6\sigma^*\) resonance, and above the \(K\)-shell threshold, we would expect \(\beta=0\). In both of these energy regimes we are dealing primarily with excitations into the continuum, and thus there is no specific orbital symmetry associated with these interactions. It is also interesting to note that the energy released due to the repulsion between an \(H^+\) and \(\text{Cl}^{n+}\) ion is \(n \cdot 11.3\) eV.

In order to gain a more quantitative description of the dissociation picture, we treated the data to determine the \(\beta\) parameter on resonance. In order to do this, we first determined the ratio of the yield of \(H^+\) detected on resonance, to the yield of \(H^+\) detected below resonance. The areas of the \(H^+\) peak on resonance (Fig 4.14(a)) and below resonance (Fig 4.14(b)) were normalized to this ratio, and the peaks were subtracted in order to remove the effects of valence and shallow-core level excitations. The new background-subtracted peak was then fit using a commercial peak fitting program. The background subtracted \(H^+\) peak was accurately fit by two Gaussian peaks, indicating that the \(H^+\) intensity was entirely a result of HCl molecules aligned with the polarization vector of the SR, which leads us to conclude that for resonantly excited molecules, within experimental error, \(\beta=2\). Figure 4.14(c) shows the \(H^+\) peaks from TOF spectra taken on the \(6\sigma^*\) resonance, and at 50 eV above resonance, with the analyzer perpendicular to the orientation of the polarization vector of the SR. The resonant \(H^+\) peak is significantly narrower than the 50 eV
peak. In this orientation, the H$^+$ peak maintains the same width in both on resonance, and below resonance spectra. This is in sharp contrast to the shape of the H$^+$ peak observed with the analyzer in the 0° orientation [Fig 4.14(a)], but is as we would expect for $\beta = 2$.

$H_2S, D_2S$

Figure 2.5 shows the total-coincidence-yield spectra for $H_2S$. The ground state electronic configuration of $H_2S$ is

$$
\begin{array}{c}
\text{Core Shells} \\
1a_1^2 2a_1^2 1b_1^2 3a_1^1 1b_1^2 \\
\text{Valence Shells} \\
4a_1^2 2b_2^2 5a_1^2 2b_1^2 3b_2^2 6a_1^0 \\
\text{Empty Shells}
\end{array}
$$

(4.25)

In previous studies[21, 22], the first peak in Fig. 2.5, is attributed to the excitation of electrons from the sulphur 1s to the 6a$_1$ (derived from the hydrogen 1s and sulphur 3s, 3p$_z$, 3d) and 3b$_2$ (derived from hydrogen 1s and sulphur 3p$_z$) anti-bonding molecular orbitals. As a result of dipole matrix elements, the contribution of the a$_1$ orbital is only about 20% as intense as that of the b$_2$ orbital[21]. The lines from the two orbitals are separated by only 0.5eV[46], 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[22]. The second peak in Fig. 2.5 is attributed to excitations from the sulphur 1s to the 4p$b_1$, 4p$b_2$, and 3d$_z$a$_1$ orbitals[20]. Finally, for $H_2S$ a third peak, just below threshold, resulting from transitions to 5p derived Rydberg orbitals[47] is visible in the total coincidence yield spectrum.
Figure 4.15: Branching ratios as a function of energy for $\text{H}_2\text{S}$ singles spectra. The $S^{5+}$ peak was omitted for clarity.

In the singles data for both $\text{H}_2\text{S}$ (Fig. 4.15) and $\text{D}_2\text{S}$ (Fig. 4.16), the branching ratios are nearly identical. As the photon energy is increased from below resonance to above the $K$-shell threshold, we see the fractional ion yields for $S^{3+}$ and $S^{4+}$ increasing while the yields for $S^+$ and $S^{2+}$ decrease. The only notable difference between the $\text{H}_2\text{S}$ and $\text{D}_2\text{S}$ data is a decreased $D^+$ yield below resonance which is at least partially a result of a larger yield for the molecular ion, $\text{DS}^+$ at below-resonance energies. In addition, trends in the average charge state of the $S^{n+}$ ion (Fig. 4.17) are nearly identical for both $\text{H}_2\text{S}$ and...
Figure 4.16: Branching ratios as a function of energy for D$_2$S singles spectra. The S$^{5+}$ peak was omitted for clarity.

D$_2$S, and show a similar, although different in magnitude, enhancement on resonance, when compared to the average charge state plot for Cl$^{n+}$ in HCl and DCl. Again, a sharp increase in the average charge state below resonance indicates the onset of pre-edge inner-shell ionization. As in the case for HCl it can be safely said that the onset of this effect is at least 5 eV below resonance.

On the first and Rydberg resonances Figs. 4.15, 4.16 show a significant
Figure 4.17: Average sulfur charge state for \( \text{H}_2\text{S} \) and \( \text{D}_2\text{S} \) singles and PIPICO spectra. Circles represent the \( \text{H}_2\text{S} \) data, triangles represent the \( \text{D}_2\text{S} \) data.

depletion in the yield of \( \text{H}^+ \). Again, we attribute this to the neutral dissociation of hydrogen. For this energy regime, the magnitude of the \( \text{D}_2\text{S}^+ \) peak in the time-of-flight spectra indicate that this is not a result of an increased molecular ion yield. Furthermore, the charge states which show an enhanced yield on resonance relative to their above threshold values in the singles spectra (Fig. 4.15, 4.16) show a smaller yield on resonance than above threshold in the PIPICO spectra (Fig. 4.18, 4.19). For both \( \text{H}_2\text{S} \) and \( \text{D}_2\text{S} \), Fig. 4.20 shows
that on resonance, about 30% less hydrogen is produced on resonance than above threshold.

Figure 4.18: Branching ratios as a function of energy for H₂S PIPICO spectra. The S⁵⁺ peak was omitted for clarity.

Because H₂S is a triatomic molecule, the dissociation picture is slightly more complicated, and interpretation of the data must reflect this. Auger decay competes with dissociation of one or both hydrogen atoms:

\[ H₂S + hν \rightarrow H₂S^*(1a₁⁻¹ 3b₂⁺¹⁺) \]

(4.26)
Figure 4.19: Branching ratios as a function of energy for D₂S PIPICO spectra.

In Eq. 4.26 the notation 3b₂ is shorthand for excitations into either the 3b₂ or 6a₁ orbital since the two excitations cannot be resolved.

\[
H₂S^*(1a₁⁻¹ 3b₂⁺₁*) \rightarrow H^0 + H^{n+} + S^*(1s⁻¹ 3p⁺₁*)
\]

\[
\rightarrow H^0 + H^{n+} + S^{++}(2p⁻² 3p⁺₁*) + e^-
\]  \hspace{1cm} (4.27)

In Eq. 4.28 we have dissociation of both hydrogens prior to Auger decay, and
Figure 4.20: Ratio of hydrogen or deuterium ions detected to the sum of all sulfur ions detected in singles mode. Circles represent the $\text{H}_2\text{S}$ data, triangles represent the $\text{D}_2\text{S}$ data.

one or both of the hydrogens are neutral ($n=0$ or 1).

\[
\text{H}_2\text{S}^*(1\alpha_{\text{a}}^{-1} 3\beta_{\text{a}}^{+1*}) \rightarrow \text{H}^{n+} + \text{HS}^*(1\sigma_{\text{a}}^{-1} 3\pi_{\text{a}}^{+1*})
\]

\[
\rightarrow \text{H}^{n+} + \text{HS}^{+*}(1\pi_{\text{a}}^{-2} 3\pi_{\text{a}}^{+1*}) + e^-
\]  

(4.28)

One hydrogen dissociates prior to the Auger decay, the other dissociates after
Auger decay, with at least one of the atoms dissociating as a neutral, or

$$H_2S^+(1a_1^{-1} 3b_2^{+1*}) \rightarrow H_2S^{++}(1b_m^{-2} 3b_2^{+1*}) + e^-$$  \hspace{1cm} (4.29)

dissociation of both hydrogens occurs following the Auger decay of the 1s hole from the molecular ion, where $1b_m$ is shorthand for the $1b_1$ and $1b_2$ molecular orbitals derived from the S 2p atomic orbitals. Again, as in the chlorine case, the 2p derived holes will also subsequently relax, typically through Auger decay.

Ab-initio studies\[48\] 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. Furthermore, electron-spectroscopy studies\[37, 38\] of the decay channels for L-shell holes in H$_2$S show that the primary decay channel involves dissociation of one hydrogen atom followed by Auger decay from the excited HS molecule. 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 antibonding orbital 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.

Previous studies\[43\] have shown that when HCl fragments, into H$^+$ and
Cl\textsuperscript{n+} the decay process can be similar to that for the Ar\textsuperscript{(n+1)+} ion. The data suggest that a similar analogy can be made between the Cl\textsuperscript{n+} ion and the S\textsuperscript{(n-1)+} ion. The fractional ion yield for H\textsubscript{2}S singles (Fig. 4.15) S\textsuperscript{3+} shows an enhancement on both the first and Rydberg resonances in a manner which is qualitatively similar to Cl\textsuperscript{4+} in the HCl case (Fig. 2.7). Thus it seems likely that the relaxation pathways which create the enhanced Cl\textsuperscript{4+} yield following resonant excitation are analogous to those causing the enhancement in the S\textsuperscript{3+} yield. In the case of S\textsuperscript{2+} the fractional yield for the singles spectra (Fig. 4.15) shows only a slight resonant enhancement, while the H\textsubscript{2}S PIPICO spectra (Fig. 4.18) shows a distinct enhancement in yield on the 6\textit{a}_{1}-3\textit{b}_{2} resonance, indicating that at least one of the hydrogens fragments as H\textsuperscript{+}. If the other H atom fragments as a neutral, the increase in the S\textsuperscript{2+} PIPICO yield (Fig. 4.18) can then be explained as being analogous to the enhanced Cl\textsuperscript{3+} yield (Fig. 2.7) on excitation to the lowest unoccupied molecular orbital.

The H\textsuperscript{+}/Cl\textsuperscript{n+} and H\textsuperscript{+}/S\textsuperscript{n+} ratios (Figs. 4.13, 4.20) also point out inherent uncertainties in our method of taking data. Above threshold, where we believe the molecules are completely fragmented, the H\textsuperscript{+}/Cl\textsuperscript{n+} ratio should be one, and the H\textsuperscript{+}/S\textsuperscript{n+} ratio should be two. However, in the present experimental setup, only one ion from a fragmentation event, can be detected. Both the H\textsuperscript{+} and its sister ion (Cl\textsuperscript{n+} or S\textsuperscript{n+}) from the same molecule have approximately equal probabilities to reach the detector. However, because of its smaller mass,
the H\(^+\) ion will reach the detector first. If the H\(^+\) ion is detected, no more ions will be detected from that fragmentation event. Thus the Cl\(^n+\) ion or S\(^n+\) ion has a smaller probability of being detected dependent on the detection efficiency for H\(^+\). This effect is in competition with a smaller extraction efficiency for the H\(^+\) ions. Earlier we mentioned that all H\(^+\) ions created at the tip of the gas needle with an energy of less than 50 eV would be collected. In practice, because the photon beam transverses the entire aperture, not all H\(^+\) ions are created at the tip of the needle, and some are lost. It appears that for the HCl case (Fig. 4.13) the second effect dominates as evidenced by the fact that the above threshold ratio is < 1. On the other hand, for H\(_2\)S, the faster H\(^+\) flight time and the fact that there are two H\(^+\) ions, causes some discrimination against the S\(^n+\) ion causing H\(^+\)/S\(^n+\) > 2.

Figures 4.21(a)-(b) show the H\(^+\) peaks from TOF spectra of H\(_2\)S taken with the analyzer oriented parallel to the polarization vector of the SR, while Fig. 4.21(c) shows H\(^+\) peaks taken with the analyzer in the perpendicular orientation. The data is shown from spectra taken 50 eV above, 10 eV below, and on the \(6a_1-3b_2\) resonance. The peaks in these spectra show an asymmetry with the right side (shorter flight time) having a higher intensity. This can be explained by the fact that when H\(_2\)S fragments, one of the H\(^+\) ions will reach the detector faster than the other. If the faster H\(^+\) ion is detected, it will not be possible for the slower H\(^+\) ion to be detected resulting in the difference in
Figure 4.21: H⁺ peaks from H₂S singles spectra. (a) Data taken on resonance (dotted line), and 50 eV above resonance (solid line) with the analyzer parallel to the polarization vector of the SR. (b) Data taken 10 eV below resonance (solid line), and on resonance (dotted line) with the analyzer parallel to the polarization vector of the SR. (c) Data taken on resonance (dotted line) and 50 eV above resonance (solid line) with the analyzer perpendicular to the polarization of the SR.
intensity[49].

Trends in the widths of the hydrogen peaks in these spectra are similar to those observed for HCl. For the parallel analyzer orientation, within experimental error, the widths of the on resonance and above resonance H\(^+\) peaks are identical (15 ± 2 eV and 17 ± 2 eV FWHM respectively), while the below resonance peak is narrower (11 ± 2 eV FWHM). Furthermore, for spectra taken with the analyzer in the perpendicular orientation the H\(^+\) peaks from the on-resonance and below-resonance spectra are nearly identical in width (13 ± 2 eV FWHM) while the above-resonance H\(^+\) peak is wider [18 ± 2 eV FWHM Fig. 4.21(c)]. The fact that H\(_2\)S is a "bent" triatomic molecule with C\(_{2v}\) symmetry, and the fact that the first resonant peak is the result of excitations to two orbitals of different symmetry (6\(a_1\) and 3\(b_2\)) makes data interpretation more difficult. However, the data presented here are consistent with previous K-shell measurements of H\(_2\)S which report a positive \(\beta\) on the 6\(a_1\) – 3\(b_2\) resonance[50].

Conclusions

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, H\(_2\)S, and D\(_2\)S. On resonance, a positive \(\beta\) was observed, as well as a significant decrease in the yield of hydrogen.
detected. The decrease in the H⁺ yield was attributed to an increase in the amount of neutral hydrogen created. This increase in the formation of neutral hydrogen corresponds to an increase in the Cl⁺⁺ or S⁺⁺ yield. 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 determine if fragmentation of the molecule occurs on the same time scale as Auger decay of the inner-core hole. In addition, evidence was found for the occurrence of pre-edge ionization of a K-shell electron below resonance, as well as post-collision-interaction effects in the energy regime immediately above the K-shell threshold.
CHAPTER 5

POST-COLLISION-INTERACTION EFFECTS IN HCl FOLLOWING
PHOTOFragmentATION NEAR THE CHLORINE $\kappa$ EDGE. ³

Following photoionization of an inner-shell electron in the energy region just above threshold, the photoion is left in a highly excited state and, in most cases, relaxes by means of radiationless decay. In this context, the slow-moving photoelectron, having an energy $E_{exc}$ equal to the difference between the photon energy and the ionization potential, interacts with the more energetic Auger electron and exchanges energy in the continuum. This post-collision interaction (PCI) manifests itself through changes in the Auger line shape and energy shifts in the electron spectra, as well as through trends in ion-yield spectra.

In atoms, PCI is a relatively well understood effect. Experimental,[51, 52, 53, 54, 55, 33, 56] as well as semiclassical[57, 58, 59, 60] and quantum-mechanical theoretical work[61, 62, 63, 64] has been done for both shallow and deep core levels. In contrast, PCI effects in molecules are less well understood.

Electron-spectroscopy measurements have been obtained following shallow core-shell excitation\cite{65, 66, 67}, and some qualitative results have been presented regarding PCI following deep core photoexcitation in molecules\cite{34, 25}. In this work, we present the first detailed quantitative analysis describing PCI-moderated dissociation of molecules. We find that recapture effects observed in the ion yields of Cl\textsuperscript{n+} following photodissociation of HCl are related to K-shell-Auger emission, and that these effects in molecules can be described with a hydrogenic PCI model. In addition, we also find that the H\textsuperscript{+} yield increases in the first few eV immediately above threshold, suggesting that this fragment sometimes captures the Cl 1s photoelectron; an effect which cannot be described using conventional atomic-PCI models.

The experiments were performed using x-ray synchrotron radiation (SR) from beamline 9.3.1 at the Advanced Light Source (ALS)\cite{15, 16}, and beamline X-24A at the National Synchrotron Light Source (NSLS)\cite{18, 19}, both of which have a photon-energy resolution $E/\Delta E \approx 7,000$. An ion time-of-flight (TOF) mass spectrometer, comprised of five cylindrical regions of differing length and electric field strength and oriented with its axis parallel to the polarization vector of the incident SR, was used to measure relative ion yields following x-ray absorption. In the first (extraction) region, a grounded needle serves as an effusive source of the gas through which the x-ray beam is focused. Voltages on all regions are selected to achieve maximum time resolution by
satisfying space-focusing conditions[23]. Ions formed in the extraction region of the analyzer are accelerated by a 2kV/cm field toward a dual micro-channel plate assembly which provides an electron cascade with a gain of 10^6. The signal from an individual ion is further amplified and used as the start pulse for a timing circuit in which the storage-ring timing pulse, related to the periodic pulsing of the SR (328 ns at the ALS, 567 ns at the NSLS), provides the stop signal. The resultant timing information is used to produce a TOF spectrum in which peaks for all ions are accumulated simultaneously. Acceleration voltages and discriminator setting were selected to ensure uniform detection efficiency for all ions and charge states. In addition, measurements were taken with the analyzer parallel or perpendicular to the polarization vector of the SR as well as at several different extraction voltages to ascertain if ions escape the extraction fields of the TOF analyzer. The full extent of these tests, which demonstrated that the extraction efficiency is unaffected by angular distributions, is described elsewhere[68]. Photon-energy calibration is checked periodically over the course of an experiment by scanning the monochromator through the Cl 1s threshold region while monitoring total-ion yield (TIY) and comparing subthreshold resonances in these absorption-like spectra[20].

Ion-TOF spectra were collected at a number of different photon energies in the Cl 1s threshold region in the “singles” mode, where spectra (Fig. 2.6) are collected with only one or two electron bunches in the storage ring. Peaks
in these spectra, representing individual photofragments (i.e., \(H^+\), \(Cl^{n+}\)), were integrated and fractional ion-yields as a function of energy were determined. Then, by multiplying the TlY curve by the fractional ion-yields for each ion, it was possible to determine partial ion-yield (PIY), or the intensity of each ion-TOF peak as a function of energy. The relative contributions of the interaction of incident photons with L-shell and valence electrons were determined by the magnitude of the PIY intensity below resonance, and were subtracted from the PIY to give the results shown in Fig. 5.22.

It is interesting to compare the present results with a previous study[33] where Ar photoion spectra were measured in coincidence with K-LL and K-LM Auger electrons in order to ensure that primary vacancies were in the K-shell. These challenging electron-ion-coincidence measurements permitted a detailed view of PCI effects on individual charge states in Ar. In the present experiment, the data-analysis procedure outlined below permits isolation of PCI effects in the Cl K-shell of HCl using simpler non-coincidence measurements. Because HCl is isoelectronic with Ar, it is not unreasonable to expect that when the molecule fragments into \(H^+\) and \(Cl^{n+}\) the relaxation processes may be similar to those which lead to \(Ar^{(n+1)+}\). We see this upon examination of the Cl\(^{2+}\) PIY (Fig. 5.22), one can observe that this charge state essentially appears only due to resonant enhancement below threshold and photoelectron recapture by \(Cl^{3+}\) just above threshold. Outside of this narrow energy region,
Figure 5.22: Partial ion yields for different Cl charge states formed after photoexcitation of HCl. Valence and L-shell background subtracted.
and particularly at higher energies, little or no Cl$^{2+}$ yield is apparent. This result is similar both qualitatively and quantitatively to the Auger electron-ion-yield measurements of the Ar$^{3+}$ charge state in the Ar K-shell threshold region [33].

In the region just above the K-shell threshold at 2829.8 eV, each Cl$^{n+}$ PIY is affected by two PCI-induced electron-recapture effects; a decrease resulting from the loss of Cl$^{n+}$ ions to the Cl$^{(n-1)+}$ charge state, and an increase arising from Cl$^{(n+1)+}$ ions recapturing electrons to become Cl$^{n+}$. For example, the yield of Cl$^{4+}$ will be reduced by Cl$^{4+}$ ions which recapture electrons and become Cl$^{3+}$, but will be augmented by Cl$^{5+}$ ions which recapture and become Cl$^{4+}$. In order to isolate the recapture effect on each charge state, we first assume that because the Cl$^{6+}$ yield is negligible, PCI trends in the Cl$^{5+}$ PIY (Fig. 5.23(a)) reflect only the loss of Cl$^{5+}$ ions through electron recapture. Thus, an estimate of the Cl$^{5+}$ relative recapture cross section at energies just above threshold is obtained from the Cl$^{5+}$ PIY by subtracting the near-threshold PIY values from the asymptotic Cl$^{3+}$ yield. The asymptotic yield was taken as the average of the data points around 7 eV, above the energy regime where PCI effects are most prevalent, while below the energy where double-ionization effects begin. This recapture cross section for Cl$^{5+}$ is then subtracted from the Cl$^{4+}$ PIY to give an adjusted PIY curve with the contribution of Cl$^{5+}$ recapture removed (Fig. 5.23(b) circles). The procedure is then repeated using each adjusted PIY
curve, in turn, to isolate the recapture effect on each Cl\textsuperscript{n+} charge state.

In order to interpret the results in Fig. 5.23, we have attempted to reproduce the modified PIY curves using electron escape probabilities calculated with a hydrogenic model using a core-hole width $\Gamma = 0.6$ eV [14]. The hydrogenic model is based on the assumption that once a K-shell hole localized around the Cl atom is created, the intermediate states are localized far from the molecule (i.e. $\langle r \rangle \geq 50$ a.u.). Thus the structure of the core is unimportant, and the electron in the excited state sees an HCl\textsuperscript{+} ion. The escape probabilities plotted in Fig. 5.23 were normalized to the PIY curves above threshold. Within the experimental uncertainties for Cl\textsuperscript{3+}, Cl\textsuperscript{4+}, and Cl\textsuperscript{5+} charge states, the data agree with the K-shell PCI curves indicating that PCI recapture occurs in conjunction with K-shell Auger decay, and that the process of PCI recapture for the Cl\textsuperscript{n+} ions in HCl is similar to that observed in ions formed following relaxation of excited atomic species. The disagreement between the model and the data for the first two eV above threshold is at least partially explained by the excitation of the Cl K electron to Rydberg orbitals, and the photon and natural line widths. It is also clear from the modified PIYs for Cl\textsuperscript{2+}, and Cl\textsuperscript{+} (not shown) that, within our uncertainties, the Cl\textsuperscript{2+} ion does not typically recapture an electron to become Cl\textsuperscript{+}. The same can be said for the recapture of an electron by Cl\textsuperscript{+} to become a neutral. Our inability to observe electron recapture by the lower charge states is in part a result of
Figure 5.23: (a) Partial ion yield (circles) for Cl$^{5+}$. (b) Partial ion yield (diamonds), and partial ion yield modified for PCI recapture (circles) for Cl$^{4+}$. (c) Partial ion yield (diamonds), and partial ion yield modified for PCI recapture (circles) for Cl$^{3+}$. The solid line represents the hydrogenic model for PCI following K-shell Auger electron ejection. No modifications were made to the Cl$^{5+}$ yield because the Cl$^{6+}$ yield was negligible. The dashed line represents the asymptotic limit for single electron ionization. The shaded region represents the loss in intensity as a result of PCI recapture.
the low K-shell-related intensity for these charge states above threshold and in part a result of the fact that Cl⁺ and Cl²⁺ are formed primarily through x-ray emission, and as a result, cannot show a K-shell PCI-recapture effect because the system does not relax through a Cl K-shell Auger decay.

Figure 5.24: Partial ion yield for hydrogen (circles), and total ion yield for HCl (diamonds). The TIY has been normalized to the H⁺ PIY in order to facilitate comparison. The solid line represents the hydrogenic model for PCI following K-shell Auger electron ejection, the dotted line represents a semiclassical model.

Fig. 5.24 shows the PIY for H⁺ (circles) following K-shell photoexcitation, and the TIY (diamonds) normalized to the H⁺ PIY. The yield for H⁺ increases with energy just above threshold similar to, but over a shorter energy range than, the yields for the Clⁿ⁺ (n≥3) charge states. Comparison to the TIY

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for HCl indicates that this is not merely a result of a change in cross-section for K-shell excitation of the HCl molecule. Because of the atomic-like PCI behavior for the Cl\textsuperscript{n+} ions it seems that a likely explanation for the data is recapture of the photoelectron by H\textsuperscript{+} following dissociation of the molecule, suggesting that the H\textsuperscript{+} fragment also is involved in PCI, occasionally recapturing the Cl 1s photoelectron. This marks the first observation of PCI-mediated fragmentation, where the photoelectron is recaptured by an ion around which the initially excited orbital is not localized.

Comparison of the H\textsuperscript{+} yield to the hydrogenic model, as well as to a semiclassical model\cite{62} for PCI shows a clear deviation of the data from PCI theory. This is hardly surprising because the empirical formula is based on the assumption that the electrons are receding in a spherical Coulombic potential. This is not the situation at the time of Auger decay due to perturbations in the potential well resulting from the close proximity of the H\textsuperscript{+} ion, and the fact that recapture by H\textsuperscript{+} is a molecular effect, and is not included in the current models; an entirely new physical effect is being observed.

The possibility that the photoelectron is recaptured while the hydrogen atom is still part of the molecule is worthy of mention. The H\textsuperscript{+} PIY shows the greatest deviation from the TIY in the first 2.5 eV above resonance. We previously noted that the PIY's for the Cl\textsuperscript{n+} ions did not follow the PCI curves in this energy regime and attributed it to excitations to Rydberg orbitals, cou-
pled with photon and natural line widths. In most cases, if the photoelectron is recaptured in a molecular orbital, the molecule will still dissociate, and because of its higher electronegativity, the Cl\textsuperscript{n+} ion would most likely retain the electron instead of the hydrogen. This process produces an identical result to the case where recapture by Cl\textsuperscript{(n+1)+} follows fragmentation. An exception to this may arise if the electron is recaptured in an anti-bonding orbital, leading sometimes to neutral dissociation, as observed previously following resonant excitation to the \(6\sigma^+\) orbital \[42\]. In addition, in cases where the photoelectron is ejected in the direction of the H\textsuperscript{+} ion, it is possible for recapture by H\textsuperscript{+} to occur whether or not an Auger electron is emitted. Regardless of the explanation(s) for the PCI effect on the H\textsuperscript{+} PIY, it is clear that a novel physical effect, unexplainable by conventional models of PCI, has been observed.

In conclusion, time-of-flight mass spectroscopy was used to study the relaxation dynamics of HCl following photoexcitation of the Cl K shell. Following a straightforward analysis of the data, partial ion yields for Cl\textsuperscript{3+}, Cl\textsuperscript{4+}, and Cl\textsuperscript{5+} were found to agree with a hydrogenic model of PCI, while for H\textsuperscript{+} it did not. This indicates that while this PCI model was developed for recapture of a photoelectron following core-shell excitation in atoms, the model also can be extended to apply to photoexcitation of molecules at deep core-levels when the orbital is localized on the ionic fragment under study. However, for fragments around which the orbital is not localized, current PCI models are inapplicable.
CHAPTER 6

MULTI-ION COINCIDENCE MEASUREMENTS OF METHYL CHLORIDE FOLLOWING PHOTOFRACTONATION NEAR THE CHLORINE K' EDGE

Multi-ion coincidence techniques, often referred to as charge-separation mass spectroscopy (CSMS), provide a powerful experimental tool for the determination of the dissociation dynamics of photoexcited molecules. The detection of several fragments from a single dissociation event allows a differentiation between specific processes when there are a multitude of decay paths possible, and thus simplifies the characterization of the fragmentation mechanism. Synchrotron radiation (SR) provides an excellent counterpart for these types of measurements. Because it is both tunable and monochromatic, using SR it is possible to excite a specific core level localized around one atom in a molecule and thus provide a site specific probe of the molecular chemistry. Because of the localization of the initial excited state, it is possible to determine if site-selective fragmentation effects, where the fragmentation pathway changes as the result of the excitation of electrons in chemically different sites, are
present [69]. Such effects do exist, however, the mechanisms are not uniform. In different systems, it is possible to observe both extremes where either the decay pathway is dependent on the location of the initial excitation [70, 71], or where the system has no memory of the initially excited state [72, 73]. Studies of this type are of particular importance in biophysics, since the dissociation of molecules following core-level excitation has been found to be a cause of radiation damage in biological tissues, as well as in astrophysics, where it becomes necessary to identify the interstellar photochemistry of dust and large hydrocarbon molecules [7].

The majority of coincidence studies have focussed on the photofragmentation dynamics of molecules following valence or shallow-core level excitation, where a shallow-core level is defined as one in which a core hole (e.g., C 1s−1, Cl 2p−1) typically decays by means of an interaction with one or more valence electrons. In contrast, few studies [74] have used multi-ion coincidence techniques to study the fragmentation dynamics of molecules following the formation of a deep-core-level hole (e.g., Cl 1s−1). Here a deep-core-hole is one which can decay by first interacting with a shallow-core-level electron. The decay of these deep-core holes often leads to highly charged residual ions due their propensity to experience a stepwise series of decays known as a vacancy cascade [32, 75, 76]. The creation of these highly-charged ions in highly-excited states frequently causes the rupture of one or more bonds in the molecule and
in most cases leads to dissociation.

In this work, an ion time-of-flight mass spectrometer and coincidence electronics were used to perform CSMS measurements on CH$_3$Cl following photoexcitation of a Cl 1s electron by x-ray SR. CH$_3$Cl was studied for a number of reasons. Peaks in the mass spectra are relatively straightforward to interpret because there are only three different atoms, and in most cases, the mass distribution between the different fragments makes it possible to unambiguously associate different ions with different peaks, the exception to this being Cl$^{3+}$ and C$^+$ ions which have m/q = 11.66 and m/q = 12 respectively. In addition, because of its relative simplicity as a singly substituted methane, an understanding of the fragmentation dynamics of CH$_3$Cl serves as a useful stepping stone toward understanding the fragmentation dynamics of chlorofluorocarbons and their “temporary” substitutes mandated under the Montreal Protocol. Furthermore, comparison of CH$_3$Cl with previous studies of HCl excited at the Cl 1s level [42] allows differentiation of the kinematic changes that take place as the result of interchanging the hydrogen with a much heavier methyl radical. In addition, for CH$_3$Cl, absorption measurements at the Cl K edge [77], as well as ion time-of-flight measurements at the Cl 2p edge [78] are available for comparison.
Experimental

The experiments were performed using x-ray synchrotron radiation from beamline 9.3.1 at the Advanced Light Source (ALS)[15, 16, 17]. This beamline is designed to provide a flux of $10^{11}$ photons s$^{-1}$ in a bandpass $\leq 0.5$ eV. Photon energy calibration is checked periodically over the course of an experiment by scanning the monochromator through the Cl 1s threshold region ($\approx 2.8$ keV) while monitoring total-ion yield (TlY) (Fig. 6.25). Because of the small probability ($< 1\%$) for relaxation strictly through fluorescence [14], the total-ion-yield spectrum obtained is in good agreement with previous absorption results [77]. The first peak in Fig. 6.25 is the result of $1a_1 \rightarrow 8a_1$ excitations. The Rydberg excitation and ionization thresholds are also labeled.

An ion time-of-flight (TOF) mass spectrometer described previously [68], and oriented parallel to the polarization vector of the incident SR, was used to detect ions created following x-ray absorption. To describe it briefly, the gas under study is supplied effusively by a grounded needle centered between two stainless-steel plates held at equal but opposite voltages. The ions then traverse a series of regions with electric fields of different strengths until they are detected by a pair of microchannel plates. Spectra were collected at photon energies in the vicinity of the K-shell ionization threshold and on several different levels of complexity. Singles, doubles, and triples data was stored.
as a combination of the number of counts, and one, two, or three ion flight times. The singles spectra presented here were collected using the electronic setup described previously[68]. A PC-based, multi-stop, time-to-digital converter (TDC) acted as the nanosecond stopwatch in recording the double and triple coincidence spectra. The ring-timing signal was used as the start for the TDC, and the detection of an ion was used as a stop. However, because the frequency of the ring-timing signal was much greater than the count rate for ion detection, it became necessary to use a series of electronics to reduce
the amount of dead time caused by TDC starts which had no corresponding stop. The setup and timing diagram are shown in Fig. 6.26. When an ion was detected, the signal was split. One pulse triggered "on" a gate generator [6.26(a)] while the other was sent through a delay [6.26(b)]. The combination of the "gate on", with the arrival of the subsequent ring timing pulse caused an "and" gate [6.26(c)] to output a pulse used to start the TDC [6.26(d)]. The delayed ion signal [6.26(b)] then served as the stop for the TDC. The constant fraction discriminators [6.26(e)], which output a NIM logic pulse with timing independent of the amplitude of the input pulse, improved the timing characteristics of signals, while the delay on the ring-timing signal [6.26(f)] served as a means to adjust the position of the spectra in the TDC window.

Results

Figure 6.27 shows singles time-of-flight spectra taken on and 8.4 eV above the $1s \rightarrow 8a_1$ resonance. Because of the short period between pulses of the ALS when running in "double-bunch" mode, the ions "wrap around" in the time window of the TAC, and thus do not appear in the order of their charge-to-mass ratios. The most notable difference between these two spectra is the splitting of the C$m^+$ and Cl$n^+$ peaks in the spectrum taken on resonance. Because of the well defined symmetry of the $8a_1$ excited orbital, molecules which have their axes aligned parallel to the polarization vector of the SR will
preferentially interact with the incident photons. Because the fragmentation of the molecule takes place rapidly relative to the rate of molecular rotation, and because the polarization vector of the SR is parallel to the axis of the analyzer, the double peaks arise from ions ejected toward and away from the detector. The strength of these features indicates that on resonance, $\beta$ is positive, and likely approaches a value of 2. This effect is in complete analogy with the observed splitting of the $\mathrm{H}^+$ peak following resonant excitation of $\mathrm{HCl}$ [68].

Figure 6.26: Setup and timing diagram for the electronics used in coincidence measurement.
However in the CH\textsubscript{3}Cl case, the splitting is observed for the C\textsuperscript{m+} and Cl\textsuperscript{n+} peaks indicating that it is the C-Cl bond which is aligned with the polarization vector of the SR rather than a C-H bond. Finally, the peaks from a number of different TOF spectra taken at different photon energies were integrated, and the branching ratios of the different charge states were determined. The results are shown in Fig. 6.28.

![Diagram](image-url)

**Figure 6.27:** Singles spectra of CH\textsubscript{3}Cl taken (a) on and (b) 8.4 eV above the 1s → 8a\textsubscript{1} resonance.
Figure 6.28: Branching ratios as a function of energy for CH₃Cl singles spectra.

Figure 6.29 shows a double coincidence plot of CH₃Cl. The x-axis of this plot gives the time of flight for the first ion detected in the coincident pair, while the y-axis gives the time of flight for the second ion detected. It is worthwhile to note several of the large scale features of the spectrum here. First, it is apparent that the structure of the spectrum repeats itself for first-ion flight times greater than about 300 ns. This is a result of the fact that the data was taken during two-bunch mode at the ALS. Second, looking at a first-ion flight time of about 100 ns, there are a series of peaks vertically aligned. These peaks represent coincidences between C²⁺ ions, and Clⁿ⁺ ions.
Figure 6.29: Double coincidence spectrum for methyl chloride. The repeating structure is a result of operation during two-bunch mode at the ALS. The dotted and dashed lines denote the coincident pairs in both spectra.

These peaks come in pairs as a result of the two chlorine isotopes ($^{35}\text{Cl} 75\%$, and $^{37}\text{Cl} 25\%$), with each pair of peaks having a different slope from the other pairs. This will be discussed more fully later. Finally, at a first-ion flight time of about 220 ns, there are two groups of horizontally aligned peaks. These are a result of coincidences between either $\text{Cl}^+$ (second-ion flight time $\approx 500$ ns), or $\text{Cl}^{2+}$ (second-ion flight time $\approx 300$ ns), and either $\text{C}^+$, $\text{CH}^+$, $\text{CH}_2^+$, or $\text{CH}_3^+$. Also, between the peak representing $\text{CH}_3^+ - ^{35}\text{Cl}^+$ coincidences and the peak representing $\text{CH}_2^+ - ^{37}\text{Cl}^+$ coincidences it is possible to observe a
small peak which represents coincidences between CH$_2^+$ and HCl$^+$, and with sufficient statistics, it is also possible to observe coincidences involving H$_2^+$. This indicates that in some cases there is rearrangement of atoms following core shell excitation. The fact that peaks from ions differing by 1 amu can be distinguished gives a good indication of the resolution of the experimental apparatus.

Figure 6.30 and 6.31 show data taken in the triple coincidence mode on resonance, and 5.5 eV above resonance respectively. The x-axis represents the time of flight of the second ion detected, while the y-axis represents the time of flight of the third ion detected. Because these plots are of triple coincidence data, each of the peaks represents coincidences between an H$^+$, C$^m+$, and Cl$^n+$ ion. There are several points worth noting here. In both figures, as in the case with the doubles spectrum, it is possible to see contours resulting from coincidences with both of the isotopes of chlorine. In addition, while the above-resonance plots show the typical cigar shaped contour, in the on-resonance spectra, the contours are split into two round peaks. This is a consequence of the alignment of the molecule during resonant excitation as mentioned earlier in the discussion of the singles spectra. Finally, it should be noted that in all of the spectra, the slopes of the peaks are different for the different charge states of the ionic triplets.
Figure 6.30: Coincidence peaks of the second and third ion of triple coincidence events taken on the $1s \rightarrow 8a_1$ resonance of CH$_3$Cl.
Figure 6.31: Coincidence peaks of the second and third ion of triple coincidence events taken 5.5 eV above the $1s \rightarrow 8a_1$ resonance of CH$_3$Cl.
Discussion

The most important parameter in determining the fragmentation mechanisms is the slope of the coincidence peak. This can be determined as follows. The time of flight of an ion detected by the spectrometer is given by [23]

\[ TOF = T^0 + \Delta t \]  \hspace{1cm} (6.30)

\[ \Delta t = \frac{k \cdot p}{q} \cos \Theta \]  \hspace{1cm} (6.31)

\( T^0 \) is proportional to \( \sqrt{m/q} \) and represents the flight time of an ion with no initial kinetic energy. The sign of \( \Delta t \) depends on the direction the ion was ejected either toward or away from the detector, \( k \) is a constant which depends on the configuration of the analyzer, \( q \) is the charge state, \( p \) is the momentum imparted to the ion during fragmentation, and \( \Theta \) is the angle between the bond axis and the analyzer axis [Fig. 6.32(a)]. In the case of a diatomic AB which fragments into \( A^{m^+} \) and \( B^{n^+} \), the momenta will be anticorrelated (\( P_A = -P_B \)). If \( A^{m^+} \) is the first ion detected, the coincidence map will show a cigar-shaped contour of slope \(-m/n\) [Fig. 6.32(b)], with the coincidences in the lower right hand side of the contour produced by \( B^{n^+} \) ions ejected toward the detector (reducing the TOF for \( B^{n^+} \)), and \( A^{m^+} \) ions ejected away from the detector (extending the TOF for \( A^{m^+} \)). The opposite is true for the coincidences in the upper left corner of the contour plot.

Previous studies have enumerated mechanisms for three [79, 36] and four [72]...
Figure 6.32: Schematic of the fragmentation geometry and resultant contour plot for ions ejected in multicoincidence measurement.

body decay. For the sake of clarity, it useful to first look at the mechanisms for three body decay before extending the explanation to the case of CH$_3$Cl. In the case of a triatomic molecule ABC fragmenting we first look at the reaction sequence known as deferred charge separation (DCS), where a neutral particle is ejected in the first step of dissociation, followed by charge separation in the second fragmentation step

$$ABC^{(i+j)+} \rightarrow AB^{(i+j)+} + C \ldots U_1$$  \hspace{1cm} (6.32)
Here, \( U_1 \) and \( U_2 \) are the energies released in each fragmentation step. If we can ignore \( U_1 \) relative to \( U_2 \), the momenta \( p_A \) and \( p_B \) are then anticorrelated \((p_A = p_B)\) and the peak will have a slope of \(-i/j\) analogous to the two-body case (\( A^{i+} \) is the first ion detected).

In another dissociation process known as secondary decay (SD), the detected fragments are ejected in different steps of the sequential dissociation

\[
AB^{(i+j)+} \rightarrow A^{i+} + B^{j+} \ldots U_2.
\]

\[
ABC^{(i+j)+} \rightarrow A^{i+} + BC^{j+} \ldots U_1
\]

\[
BC^{j+} \rightarrow B^{j+} + C \ldots U_2.
\]

In this situation, by conservation of momentum, we can write

\[
p_A = -p_{BC} \tag{6.34}
\]

\[
p_B = \frac{m_B}{m_B + m_C} \cdot p_{BC}
\]

\[
p_B = \frac{-m_B}{m_B + m_C} \cdot p_A
\]

where \( p \) and \( m \) represent the momentum and mass of the fragment. Then if \( A^{i+} \) is the first ion detected, we can write the slope as

\[
slope = \frac{\Delta t_B}{\Delta t_A} \tag{6.35}
\]
It is also necessary to consider non-sequential or concerted dissociation (CD) processes

\[ A^{i+j+k}C^+ \rightarrow A^{i+} + B^{j+} + C^{k+} \ldots U_1, U_2. \]  

(6.36)

In CD processes, the distribution of energies between the fragments is not necessarily unique. The contours are frequently "egg" shaped as a result of energy released by the ejection of the non-detected fragment, with fragmentation events involving three ions generally having a larger momentum release than those involving dissociation of a neutral[80].

Figure 6.33 gives the slopes of the contours of the second and third ions detected as a function of photon energy, the numeric values are presented in Table 6.2. The slopes were determined through inspection of the contour diagrams. Previous studies have shown that because of uncertainties in the flight times, this is the most reliable method of determining the peak slopes [80, 81]. While Fig. 6.33 shows some change in the slopes of the peaks as a function of energy, these fluctuations are within the error bars of the measured values. The dotted lines in Fig. 6.33 represent the calculated values given in Table 6.2.
Figure 6.33: Peak slopes as a function of energy. Slopes are taken from the contour plots of the second and third ions detected in triples mode. Dotted lines represent the calculated values of slope. Poor statistics in the Cl^{4+} peaks prevented the determination of error bars.
Table 6.2: Slopes of the coincidence maps for the second and third ions detected following CH$_3$Cl fragmentation. Calculated slopes assume a SD process with negligible energy released in the second step of the decay process.

<table>
<thead>
<tr>
<th>2nd/3rd Ion</th>
<th>0 eV</th>
<th>3.6 eV</th>
<th>5.5 eV</th>
<th>7 eV</th>
<th>10 eV</th>
<th>30 eV</th>
<th>60 eV</th>
<th>Calc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$^{2+}$/C$^+$</td>
<td>-2.84</td>
<td>-2.64</td>
<td>-2.51</td>
<td>-2.69</td>
<td>-2.51</td>
<td>-2.60</td>
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<td>C$^{2+}$/Cl$^{2+}$</td>
<td>-1.23</td>
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</tr>
<tr>
<td>C$^{2+}$/Cl$^{3+}$</td>
<td>-0.90</td>
<td>-0.86</td>
<td>-0.90</td>
<td>-0.81</td>
<td>-0.88</td>
<td>-0.84</td>
<td>-0.89</td>
<td>-0.83</td>
</tr>
<tr>
<td>C$^{2+}$/Cl$^{4+}$</td>
<td>-0.63</td>
<td>-0.65</td>
<td>-0.66</td>
<td>-0.84</td>
<td>-0.71</td>
<td>-0.69</td>
<td>-0.72</td>
<td>-0.625</td>
</tr>
<tr>
<td>C$^+$/Cl$^+$</td>
<td>-1.35</td>
<td>-1.30</td>
<td>-1.33</td>
<td>-1.34</td>
<td>-1.41</td>
<td>-1.34</td>
<td>-1.32</td>
<td>-1.25</td>
</tr>
<tr>
<td>C$^+$/Cl$^{2+}$</td>
<td>-0.68</td>
<td>-0.65</td>
<td>-0.66</td>
<td>-0.68</td>
<td>-0.69</td>
<td>-0.69</td>
<td>-0.69</td>
<td>-0.625</td>
</tr>
<tr>
<td>Cl$^{+}$/C$^+$</td>
<td>-3.37</td>
<td>-2.85</td>
<td>-2.90</td>
<td>-2.78</td>
<td>-2.70</td>
<td>-2.98</td>
<td>-2.88</td>
<td>-3.2</td>
</tr>
</tbody>
</table>

These values were determined using the SD mechanism for dissociation with the first step being the rupture of the C-Cl bond, and assumed no energy release from the breaking of the C-H bonds. These calculated values show agreement with the experimentally measured values within the first approximation, however, there is not complete agreement with the measured values of the slopes.

There are two explanations for deviant slopes within the model of secondary decay [81]. In the first, the lifetime of the intermediate molecule is sufficiently short that it decays within the Coulomb field of the first fragment. The additional repulsion between the charged particles causes the two detected ions to have momenta which is more strongly anticorrelated, moving the peak slope nearer to -1. The second explanation for slopes which deviate from their nominal values is the release of momentum in the second reaction step. However, only cases where the momentum released in the second step is aligned
with the momentum released in the first step will manifest themselves in a change in the observed peak slope. This presupposes that the dissociation in the second step must take place on a time scale which is shorter than that for rotation of the intermediate. Because it requires a short time scale for dissociation, it is likely that the secondary step will take place within range of the Coulomb repulsion of the first fragment. Thus these two mechanisms are not completely separable as explanations of deviant slopes.

Generalization of the SD fragmentation mechanism to the case of CH$_3$Cl taking into account the energy released in both fragmentation steps can be done in the following manner. Keeping in mind that the energy released is shared between five particles, we first write

$$p_{Cl}^2 = \frac{2U_1 m_{Cl}(3m_H + m_C)}{m_{CH_3Cl}}$$ \hfill (6.37)

$$q^2 = \frac{2U_2 (m_H m_C)}{m_{CH}}$$ \hfill (6.38)

where $p_{Cl}$ represents the momentum of the Cl$^{n+}$ ion, $U_1$ represents the energy released in the rupture of the C-Cl bond, $m$ represents the mass of the individual fragments, and $U_2$ and $q$ are the energy and momentum released by the breaking of one H-C bond in the second step of fragmentation. The expression for $q$ assumes that all three H$^+$ bonds rupture simultaneously and that each hydrogen is pushing only against the carbon ion along the C-H bond axis. We
can then write

$$p_C = \sum_{i=1}^{3} q_i - \frac{m_C}{3m_H + m_C} p_{C1}$$  \hspace{1cm} (6.39)

$$p_H = -q - \frac{m_H}{3m_H + m_C} p_{C1}.$$  \hspace{1cm} (6.40)

The eventual goal of this is to use the ratios of these momenta to determine the slope of the coincidence peaks. In order to do this, we need only be concerned with the momenta of the fragments parallel to the analyzer axis. Using the subscript $z$ to denote momenta parallel to the axis of the analyzer we can write

$$p_{Cz} = \left[ 3 \cos \theta \left( \frac{2U_2 m_H m_C}{m_{CH}} \right) ^{\frac{1}{2}} - \frac{m_C}{m_{CH3}} \left( \frac{2U_1 m_{Cl} m_{CH3}}{m_{CH3Cl}} \right) ^{\frac{1}{2}} \right] z (6.41)$$

$$p_{Hz} = \left[ - \cos \theta \left( \frac{2U_2 m_H m_C}{m_{CH}} \right) ^{\frac{1}{2}} - \frac{m_H}{m_{CH3}} \left( \frac{2U_1 m_{Cl} m_{CH3}}{m_{CH3Cl}} \right) ^{\frac{1}{2}} \right] z(6.42)$$

where $\theta$ is the angle between the C-H bond and the C-Cl bond axis. We can then get an expression for the ratio of the momenta

$$\frac{p_{Cl}}{p_C} = \left[ 3 \cos \theta \left( \frac{U_2}{U_1} \right)^{\frac{1}{2}} \left( \frac{m_H m_C m_{CH3Cl}}{m_{Cl} m_{CH3} m_{CH}} \right)^{\frac{1}{2}} - \frac{m_C}{m_{CH3}} \right]^{-1}. \hspace{1cm} (6.43)$$

It is also possible to derive similar expressions for the ratios $p_{Cl}/p_H$ and $p_C/p_H$. It should also be noted that if $U_2 \ll U_1$ these expressions reduce to give the same values as Eq. 6.36. Using the experimentally measured slope of -1.35 for the $C^+ - Cl^+$ peak we can determine a value for the expression $\cos \theta \cdot \sqrt{(U_2/U_1)}$. Then using these values, we can calculate the slopes for the $C^{m+} - H^+$ and
The results are shown in Tables 6.3 and 6.4. It should also be noted that taking into account the kinetic energy released in both dissociation steps it was not possible to model the fragmentation of CH$_3$Cl with the ejection of the hydrogen as the first step of the process.

<table>
<thead>
<tr>
<th>1st/2nd Ion</th>
<th>0 eV</th>
<th>3.6 eV</th>
<th>5.5 eV</th>
<th>7 eV</th>
<th>10 eV</th>
<th>30 eV</th>
<th>60 eV</th>
<th>Calc</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$/$C^+$</td>
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<td>7.59</td>
<td>7.31</td>
<td>7.41</td>
<td>7.77</td>
<td>9.04</td>
<td>8.57</td>
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</tr>
<tr>
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<tr>
<td>H$^+$/$C^3+$</td>
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<td>1.22</td>
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</table>

Figure 6.34(a) shows a graph of the data presented in Table 6.3 while 6.34(b) shows the data from Table 6.4. For the singly charged ions (C$^+$, Cl$^+$) measured in coincidence with H$^+$ there appears to be little or no change in the mechanism as a function of energy, and the measured slopes show good agreement with the calculated values. However the situation is different for the more highly charged carbon and chlorine ions. The slopes of the H$^+$ - Cl$^{2+}$ and H$^+$ - C$^{2+}$ peaks clearly change in the first 5 eV above resonance, and only agree with the calculated values on resonance. It seems likely that the

<table>
<thead>
<tr>
<th>1st/3rd Ion</th>
<th>0 eV</th>
<th>3.6 eV</th>
<th>5.5 eV</th>
<th>7 eV</th>
<th>10 eV</th>
<th>30 eV</th>
<th>60 eV</th>
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</thead>
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<td>-.90</td>
<td>-.92</td>
<td>-2.89</td>
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Figure 6.34: Slopes of the coincidence peaks of the (a) first and second (H$^+$-C$^{n^+}$) or (b) first and third (H$^+$-Cl$^{n^+}$) ions detected in triples mode. Dotted lines represent the calculated values of slope. Poor statistics in the C$^{3+}$ and Cl$^{4+}$ peaks prevented the determination of error bars.
explanation for this is that on resonance, the excitation of the core electron into the $8\alpha_1$ antibonding orbital causes the C-Cl bond rupture in a manner analogous to the fast dissociation observed for resonant excitation of HCl [42]. In contrast, on excitation to the Rydberg orbitals (3.4 eV above resonance) or to the continuum (5 eV above resonance), rupture of the C-Cl bond results from electronic depletion following Auger decay. In addition, with the higher ionic charge states comes greater mutual repulsion between the ions making fragmentation a more CD process and bringing the slope closer to -1. In the limiting case, it is possible to imagine the ions undergoing a "Coulombic explosion" where the molecule fragments and each of the ions is simultaneously ejected with an energy that comes from their mutual Coulomb repulsion.

In conclusion, the fragmentation dynamics of CH$_3$Cl was studied using triple-coincidence CSMS methods. By measuring the slopes of the different coincidence maps, it was found that a sequential decay mechanism which was initiated by the rupture of the C-Cl bond described the dissociation process well. In addition, the slope of the coincidence maps of H$^+$ - Cl$^{2+}$ and H$^+$ - C$^{2+}$ were observed to change with photon energy. We attributed this to the fact that on resonance the electron is excited to the $8\alpha_1$ antibonding orbital, causing fast dissociation, while at higher photon energies the higher charge states of the ionic fragments causes the dissociation process to be more concerted.

There are still a number of questions left unanswered by the CH$_3$Cl data.
Some modeling will be necessary to determine if the fragmentation can be described as a Coulomb explosion [82, 83], or if it would be more accurately described by an impulsive model [7, 26], where the emphasis is placed on the breaking of chemical bonds and collisional effects are accounted for. There are also a number of other data analysis tools that need to be developed. Currently, examination of the triple coincidence plots with the first and second ion times of flight on the x and y axes, the data plotted represents the counts from the first, second, and all possible third ions. The same is true of the plots of the first and third ions, the data plotted represents all possible second ions. The ability to look at a coincidence map with all three ionic states specified would allow greater differentiation in determining the fragmentation mechanisms. Furthermore, when looking at the coincidence plots for two fragments, the lengths of the peaks provide information on the energy released during the separation of those two fragments [36], the widths of the peaks provide information on the energy released during other steps of the fragmentation and peak shape provides information on the molecular orientation during fragmentation [80]. It would also be useful to examine these parameters in order to determine the kinetic energies released in the different fragment steps. This information would provide another means to check the expressions used to describe the SD process (Eq. 6.43).
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