## Gas Phase Anion Photoelectron Spectroscopy

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# Declaration

I declare that this thesis is my own work, and has not been submitted for any degree or diploma.

I declare that any help recieved in preparing this thesis, and sources used, have been acknowledged in the thesis.

Duncan Beckham, October 2014

Duncan Wild, October 2014

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#### Abstract

Gas phase anion photoelectron spectroscopy has been a useful technique in exploring the interactions in various clusters and exotic molecules. It plays an important role in understanding the dynamics of solvation and reaction pathways. In this dissertation the results of comprehensive photoelectron spectra of halide acetylene species will be shown as well as techniques used to characterise the spectra. Previous calculations on the energies of these species have been performed and the agreement to these results will be discussed. Further work into elucidating the structure of solvation shells and advancements to the experimental techniques will also be explored.

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# Chapter 1

# Introduction

Chemistry is the science of molecular reactions. Central to this study is the quantum model of physics which describes the energies of electrons and the allowed states that exist in atoms and more complex molecular systems. A molecule represents a local minimum of energy for the collection of electrons in the system. If sufficient energy is provided to break the bonds inside the molecule, and a favourable geometry is achieved then the system can react to form new products. The measurement of molecular systems through experiment provides an insight both into the dynamics of chemical reaction and the fundamental quantum nature of the species involved. Combining this process with powerful computational methods, leads to a deeper understanding of these systems and predictions for the behaviours of other systems.

### Solvation Chemistry

An important field of chemistry is the dynamics of solvation. The solvation phenomena is responsible for the reactivity and stability of many species in liquid contexts. Solvation dynamics are characterised by the interactions between solvent and solute, as well as the interactions between solute and solute. The relative strength of these interactions determines the structures present in the solution. Systems where the two interactions are of similar strength exhibit interesting behaviours. When a solution of H<sub>2</sub>O and X<sup>-</sup> (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) is made the interaction between the H<sub>2</sub>O are stronger and form a network that the halide rests on, however in the case of F<sup>-</sup> the solvent-solute bond is stronger and the systems take on the character of a central halide surrounded by a shell of ligands (1). A deeper understanding of a complex system can come through the detailed interrogation of a more simple system. An analogy to complex solvation systems in bulk contexts can be found in that of cluster formation in the gas phase. Clusters are systems of two or more molecular species interacting without the formation of a chemical bond. The molecules that agglomerate around the central ion are referred to as ligands. These ligands will form shells of varying number around the central ion depending on steric hindrance and ligand-ligand interaction.

## 1.1 Atmospheric Chemistry

In a more direct way, the chemistry of clusters plays an important role in the reactions inside the atmosphere. A prominent example of this was the effects of Chloro Fluoro Carbons on the atmospheric depletion of ozone. The dominant driving forces behind reactions like this are temperature, pressure and the character of the electromagnetic radiation present. However an understanding of the potential energy surfaces of reactive complexes allows an insight into the mechanisms involved that drive reactions and can lead to predictions on how to monitor, control and forecast the behaviours of complex systems.

## **1.2** Photelectron spectroscopy

Spectroscopy has been a crucial experimental technique in probing the quantum nature of molecules and atomic systems throughout the 20th century. Since the development of the laser and synchrotron, a new horizon of possible spectroscopic techniques has become available. One of these techniques, Anion Photoelectron Spectroscopy, uses a laser to interrogate the energies of electrons emitted from an anion. By measuring the kinetic energy of these electrons, we can observe the change from the ion to neutral states, the associated binding energy, and any notable vibrational modes of the neutral potential energy surface. This gives access to neutral states that might be unfavourable or unstable and allows for further examination of the weakly interacting species that would be difficult to characterise in the bulk context. This technique couples extremely well with mass spectroscopy, allowing for a detailed analysis of the composition of complex gas mixes and confirming the presence of exotic species and clusters not often seen in bulk contexts. Investigating cluster science using gas phase anion PES involves creating mixes to form clusters of a central anion, usually a halide due to their high electronegativity, surrounded by weakly interacting ligands.

Prominent work in the field of gas phase anion PES has been performed by Lineberger (8), Neumark (27), Johnson (10), Kaya (17), Bowen (21), and Shen Wang. Previous work by the Wild group has looked at various ligands such as NO, CO (16) (14) and  $N_2$  with both spectroscopic and computational methodology.

Previous work into the acetylene (ethylyne) halide complexes has been performed

in experimental and computational contexts by Ault (9), Wild (22; 23; 25; 24), McMahon (19) and Botschwina (2) (3). The first studied the infrared matrix spectroscopy of various alkyne molecules co-deposited with halide caesium salts in a rare gas matrix. This study found intense vibrational modes of F<sup>-</sup>...HCCH, Cl<sup>-</sup>...HCCH and I<sup>-</sup>...HCCH at 2873, 3050 and 3182 cm<sup>-1</sup>. These modes were assigned to the C-H stretching mode of the halide bonded hydrogen. Weaker modes of an essentially free H-C stretching mode were also observed confirming the prediced linear structure. Gas-phase infrared spectroscopy was next used to probe the halide acetylenes. This study on the series of clusters of  $X^{-}...(HCCH)_n$  (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) refined the measure of the H-C stretching energy and made the predictions of the size of the first solvation shells of Cl<sup>-</sup> and Br<sup>-</sup> through experimental spectra. Computational studies on the 1:1 complex have been performed using a variety of basis sets and computational techniques. The highest level of calculations was performed by Botschwina et al and used CCSD(T) with the very large augmented correlation consistent basis sets of Dunning. This study elucidated very accurate structure for the anion complex and measure of the the binding energy  $D_e$ . Despite this significant body of work on the anion complex there has not been any previous work into the neutral complex either through theory or experiment.

## 1.3 Project Aims

Throughout this project, the time of flight photoelectron spectrometer (TOFPES) in the Laser Spectroscopy Laboratory in the School of Chemistry and Biochemistry department has provided access to gas phase anions: the halides, and clusters of these halides with weakly bonding acetylene. The focus of this work was in the detailed acquisition of mass and photoelectron spectra of the  $X^-...(HCCH)_n$  (X =  $Cl^-,Br^-,I^-$ ) and the analysis of these spectra. Such analysis of the spectra will be compared to calculations undertaken in the group of the structure, bonding energy and potential energy surfaces of the clusters. The stepwise addition of acetylene will also explore the solvation phenomena and suggest further improvements of the technique in order to potentially interrogate clusters of multiple solvation shells. A secondary focus on apparatus development will also play a key role in acquiring the best resolution and most reliable spectra with given resources.

# Chapter 2

# **Aparatus and Methods**

The time of flight photoelectron spectrometer (TOFPES) is an experimental aparatus built in the Wild Laser Spectroscopy Laboratory. Central to the function of the set up is the time of flight mass spectrometer based on the designs of Wiley and McLaren(26). Coupled to this is the photoelectron spectrometer which employs the magnetic bottle design of Smalley et al (4). Detailed writing into the specifications of the setup has been given previously in the study of the Cl<sup>-</sup>...CO cluster (16) by LaMacchia (12) with further improvements by Lapere (15). As such an overview of the aparatus will follow with focus mainly on operational conditons relating to experiments and additions made to the aparatus throughout the research period. See figure 1 for a schematic.

### 2.1 Gas Mix

Examining exotic molecules and clusters requires gas mixtures which enable the formation of these species. To achieve this, a gas bottle and vacuum line set up is used. A mix of three components is typically used: halide source molecule, ligand gas, and backing gas of argon. The halide parent molecule comes from a volatile liquid of either  $CH_3I$ ,  $CH_2Br_2$  or  $CCl_4$ . This mix is purified through a series of freezepump-thaw cycles in which the liquid is frozen, opened up to vacuum, then isolated again and heated. Dissolved gaseous impurities, such as  $O_2$  and  $N_2$  will be more volatile than the halide source and their solubilities will decrease with temperature. Once cooled the liquid becomes more pure, and once the pressure of vapour is evacuated the impurities will become more volatile and the process repeats. The gas mixing line is pumped down to 10 mTorr and a small amount of volatile halide parent molecule is allowed into the line. In order to calibrate the photoelectron spectra it is helpful to have a small amount of halide source seeded from a previous experiment (the calibration scheme will be discussed in a later section). This is obtained via



Figure 1— The Schematics of the TOFPES

a small amount of the previous gas mix adsorbing onto interior surfaces of the gas mixing station during vacuum cycles between experiments. Once an acceptable amount of halide-parent is present in the mixing bottle, the line is opened to the ligand gas until the desired pressure is present and finally the line is opened to the backing gas until. Typically gas mixtures will be 90-95% argon, 5-10 % ligand and 1% halide source.

The mixture enters the vacuum of the source chamber through the pulsed solenoid nozzle. Once exposed to the vacuum the pulsed gas mixture undergoes a supersonic expansion (7) which serves to cool the species entrained in the expansion via collisions with the argon gas, transferring internal degrees of freedom to linear motion. As the expansion of the gas continues, the local speed of sound in the expansion falls. In order to prevent shock disk formation in the expansion, a skimmer is employed which extracts the collimated mid section of the conical expansion and absorbs the barrel shocks. Typical temperatures in the gas beam are around the 20K mark which is important when calculating the predicted vibrational spectra.

### 2.2 Mass Spectra

By coupling mass spectrometry with the photoelctron spectrometry, a preliminary analysis of species and the mass discriminated timings can be attained.

#### 2.2.1 Ion formation

In order to produce ions the neutral molecules are bombarded with a pulse of electrons at 500eV ejected from a rhenium filament, housed in the ion source. The entire ion source is coated in a graphite covering, while this contributes to a vapour pressure in the chamber, it reduces the effect of surface charges and ensures the beam of nascent ions and ion molecule complexes are undeflected. An einzel lens focuses the electrons onto the beam. This process causes ionisation of the molecules and fragmentation from the parent molecules through slow electron interactions (5). This process occurs as follows where M is the buffer gas:

$$M + e_{fast}^{-} \longrightarrow M^{+} + e_{fast}^{-} + e_{slow}^{-}$$
(2.1)

$$CH_3I + e_{slow}^- \longrightarrow [CH_3I^-]^* \longrightarrow I^- + CH_3$$
 (2.2)

The slow electron then proceeds to attach to a halide containing molecule (iodide chosen as an example) and fragments through a process called dissociative electron attachment (5). Ligand solvation, which is essential to the aims of the project may occur in two ways. Either the ligands may aggregate around the nascent anion or highly solvated neutral species aggregate during the supersonic expansion of the form  $CH_3I(Ar)_n(HCCH)_m$ . In the latter case these species may then undergo further cooling via the evaporation of ligands after the process of dissociative electron detachment.

#### 2.2.2 Time of Flight

Once a charged constituent of the gas mix has been formed it is able to be manipulated by the use of electric fields. A series of three plates (TOF plates) differentiate the neutral and positive ions from the packet and accelerate the negative ions along the flight length. The primary time of flight plate is held at 1000V, followed by a second plate which provides spatial focusing at 90% the voltage of the first. The final plate is held at ground to ensure an even field is experienced by the ions. The spatial focusing plate accounts for the spread of timing that the beam arrives at the plates as well as the angular distribution of the beam. A set of X/Y deflecting plates give control over the trajectory of the beam throughout flight. Finally a set



**Figure 2**—Diagram illustrating the magnetic fields of the photoelectron detector courtesy of D. Wild. The x marks the point of intersection between lasers and ions. The field becomes more dense in the direction of the magnet housing

of einzel lenses focusses the beam to maximise the density of the beam at the laser interaction point. A schematic of the set-up is given in 1. Notably the mass gate and ion decelerator are absent in the current experimental setup. The purpose of these are to discriminate the ion beam into a single mass signal via a timed pulse and to slow the ion pulse to reduce velocity broadening effects

### 2.3 Photoelecton Spectroscopy

In this type of photelectron spectroscopy the aim is to collect 97% of all ejected electrons in order to maximise signal. The design of the PE detector is based of that of Cheshnovsky (4). By coupling the flight tube with a homogeneous magnetic field throughout to a permanent divergent field source near the point of detachment the mapping of the fields creates what is essentially a magnetic bottle trap see fig 2.

#### 2.3.1 Magnetic mirror effect

Electrons that are ejected with an orientation opposite to the detector are turned around by the magnetic mirror effect. For an electron with constant energy and magnetic moment, as is the case in the experimental setup, the magnetic moment is given as:

$$\mu = \frac{mv_t^2}{2B} \tag{2.3}$$

where  $v_t$  is the tangential velocity to the magnetic field. The other conserved quantity energy is given as:

$$E = \frac{1}{2}mv_t^2 + \frac{1}{2}mv_p^2 \tag{2.4}$$

Therefore as an electron moves into a greater B the parallel velocity must be converted to tangential velocity until the electron is turned around. This also leads to the result (11) that the particles that are not able to be turned around satisfy the inequality

$$\frac{v_t}{v_p} < \frac{1}{\sqrt{\frac{B_{max}}{B_{min}}}} \tag{2.5}$$

After a small delay the trajectories of the electrons have become parallelised and therefore the energies can be well calculated by a measure of time of flight through the detector.

### 2.3.2 Laser

Photodetachment is achieved via the 1064nm Nd:YAG laser. The fourth harmonic of the laser is amplified in the optical set-up to achieve photons of 266nm, sufficient to excite an electron from the halide ions. To maximise interactions between the laser and ions, as well as minimising the pressure inside the vacuum chambers, the whole setup is pulsed at 10Hz with laser pulses lasting several nano seconds. The diameter of the laser beam is quite broad, 7mm, and can be reduced by the use of a telescopic optical element. However during experiments this was found to be ineffective at improving the signal noise ratio. A polariser is also employed to allow a selective orientation of electron ejection.

#### 2.3.3 Spectral limitations

This type of spectroscopy is limited by the binding energy of species that the laser can ionise. As will be seen from experimental results, the accetylene complexes of greater than two clusters are likely to have binding energies close to or beyond the limit of the laser. Despite the technique having a much higher yield of collected electrons compared to similar techniques there is still a threshold below which a signal is not recognisable above the noise. Typically species that have mass spectra intensities of at least 25mV will have detectable photoelectron spectra.

The theoretical limiting resolution in this method of spectroscopy is in the finite time taken to turn around and parallelise the electrons. However, in many setups the limiting factor is the non-zero velocity of the ions. Without a functioning mass decelerator this will be the dominant source of spectral broadening apparent in the work. In order to minimise the effect of this broadening the polarisation of the laser is chosen to be perpendicular to the ion velocity. Thus having the maximum and minimum velocity differences at the lowest probability angles of ejection. However, a consequence of this choice is the larger number of electrons satisfying the inequality



**Figure 3**— The Schematics of the Laser courtesy of Lapere (13). P1 is a steering prism. P2 is used as a dispersing element to separate 532nm wavelengths from the 266nm. The rotatable object is a BBO crystal for second harmonic generation from the 532nm output of the laser

2.5. In the alternate case of polarising co-axial to the velocity the most likely ejections would have minimum and maximum energy. The resulting spectra would have two clearly distinct peaks that may have some degree of overlap

### 2.4 Recording the spectra

Spectra are recorded via measuring collisions at the microchannel detectors at the end of the magnetic bottle flight tube. These spectra are recorded over 10000 shots of the laser (1000s) and are collected via the FastComTec P7888 Multiscaler Time of Flight card. Typically three to five repeats of spectra are taken to ensure a proper calibration can be made.

It is necessary to take background spectra in which the laser timing is such that there are no ion-laser interactions (typically 300ns before the halide peak). Any photoelectrons detected in this spectrum are due to either stray electrons drifting in the flight tubes, or photodetachment from the metal surface of the flight tubes caused by the laser. In theory the magnet housing is the only surface in the laser interaction chamber that has a field that maps onto the detector, although imperfections in the design might invalidate this assumption. By recording this background spectra at the same laser intensity as other species, it is possible to rule out certain spectral features as artefacts of the background. It is also possible to subtract the background fully to reveal peaks that may be covered by the background. Although, the resolution is generally too low for this to be an effective technique.

## 2.5 Analytical Methodology

In order to extract meaningful data from the recorded spectra a calibration scheme needs to be implemented. This method is chosen as it overcomes the need to have highly replicable conditions between daily cycles of experiments. By comparing known values such as binding energies of the bare halides and the splitting between spin orbit states, a calibration curve can be implimented.

A fitting scheme using the Mathematica non-linear model fit has been used to find the gaussian curve that best approximates the data series. Various improvements to this base method are employed to try to create better schemes, such as different statistical fits as well as multiple peak fitting.

## 2.6 Improvements to the TOFPES

Due to significant machine failure, an addition by Conran(6) of a permanent rare earth magnet to the setup was not able to be fully tested during their research. The apparatus involves replacing an existing electro-magnet with a powerful rare earth permanent magnet. As the magnitude of field strengths designed for the apparatus are easily obtainable by modern materials this was chosen as a way to reduce the need for external cooling of the existing electro magnet. Additionally the magnet aperture is designed in a way such that there is a degree of freedom in the positioning of the source of the magnetic field. This allows for small adjustments to be made to optimise yield at the detector. It was thought that early attempts to find a suitable field were producing a field that was too divergent near the detachment point. As such a range of magnets were purchased in an attempt to best map onto the magnetic bottle. Completing a detailed analysis of the predicted field structures inside the machine could provide an accurate estimate of optimal operating conditions. Due to seemingly large variations between the experimental conditions of each day, an approach which had a larger degree of freedom was favoured.

During the experiments an Ortec 935 Quad 200-MHz Constant-Fraction Discriminator was aquired. This allowed for a more precise measurement of collisions at the photoelectron detector by converting the electron signals from the microchannel plates and outputs them as fast NIM pulses. The effect of this addition will be discussed in a further chapter.

An improved voltage supply to drive the electron filament and einzel lens was also completed during the experimental period. This allowed for a better response of the filament in terms of pulse duration and timing.

# Chapter 3

# Experimental

## **3.1** Opperating Conditions

Due to the work of Conran (6) a gas mix of 5% acetylene was known to be reasonable for cluster creation, as well as minimising an unwanted blocking effect at the nozzle.

While at rest the source chamber is under a vacuum of  $1 \times 10^{-8}$  Torr and the laser interaction chamber is at  $1 \times 10^{-9}$  Torr. During experiments the source chamber reaches  $1 \times 10^{-5}$  Torr and the laser interaction chamber is at  $1 \times 10^{-7}$  Torr. During the course of a day the settings of the machine could drift significantly. Typical settings for the various voltage supplies will be provided below for the purpose of future reference:

Element	Set	Settings		
Electron Fillaments	4.00	А	-500	V
Gas nozzle	216	V	100	$\mu { m s}$
TOF Plates	1000	V	900	V
Einzel lenses	-27	V	-82	V
X Deflection plates	-6	V	6	V
Y Deflection plates	-20	V	10	V
TOF plates timing	710	$\mu s$		

Previous to the start of experiment a failure of the pressurised air source lead to the machine being flooded with large amounts of gas mixture. The effects of the flooding created a deflection of the beam path, possibly due to some surface localised residues. With the compromised beam path, a complete scouring of the machine was required.

During experiments the pressure in the source chamber could sometimes drift over time. It is thought that this was due to an issue that occurs in the nozzle. As mentioned the nozzle had previously become blocked possibly due to the stratisfication of the gas mix in the narrow pipe leading to the nozzle. A clean of the nozzle in a sonic bath seemed to alleviate the issue suggesting that this problem may have been occurring again resulting in a residue clogging the nozzle.

### 3.2 Mass spectra

### 3.2.1 Chloride

Initial measurements were undertaken on a chloride acetylene gas mix. Chloride containing species are easily identifiable by the characteristic 3:1 splitting of the isotopic peaks in the mass spectra arising from the natural abundances of <sup>35</sup>Cl and <sup>37</sup>Cl. In the initial testing, the chloride signal was at 1.4V, indicating that previous issues with ion deflection had been overcome. Noticeably the isotope ratio of bare  $Cl^{-}$  in the spectra is not actually representative of the natural abundance. This is due to saturation occurring at the detector, which in turn is caused by the large volume of Cl<sup>-</sup>. A significant volume of ions saturates the detector and so limits the maximum output voltage and causes ringing which can also be seen in the change in the baseline of the spectrum. Clusters had intensities starting at 700mV but rapidly dropping off to 100mv for  $(HCCH)_2$  and by a similar factor for increasing numbers of ligands. In figure 4, the spectra with full intercity of chloride is shown and in 5, the spectra is focussed in on the region with lower intensity clusters. Due to its explosivity in a homogeneous mixture, acetylene is stored solvated in acetone (propanone) and as such signals for acetone complexes will be present in the spectra. The pairwise clusters of acetylene and acetone have similar intensities and are labelled in the figures. There was little appreciable seeding of bromide or iodide into the mixture which indicates that calibrating the spectra would be problematic.

The stability of the apparatus setting was poor even during a single day.Figure 6 shows the mass spectra taken in the afternoon, compared to the morning spectrum of figure 4 and 5 the relative ratios of species present had shifted, many clusters were no longer distinguishable, and a signal at 127 amu, Iodide, had grown dramatically. The resolution of the spectra is also poor compared to previous works by the group. A likely explanation is that after the machine was completely opened up to atmosphere there were numerous settings that were not yet optimised in the apparatus. Only two days of meaningful data were taken for the gas mix and a re-graphetisation of the skimmer was seen as necessary.



**Figure 4**—Spectra of the Cl<sup>-</sup> Ion (\*) at full intensity. The series of  $Cl^- \cdots (HCCH)_n$  is shown with  $Cl^- \cdots Ar$  (#) appearing, and after the n=2 peak the acetone series is concurrent to the acetylene.  $Cl^- \cdots CCl_4$  (@) and related complexes appear later in the series.



**Figure 5** — Spectra of the Cl<sup>-</sup> Ion (\*) at full intensity. The series of  $Cl - \cdots (HCCH)_n$  is shown the n= 3 peaks are overlapped by  $Cl^- \cdots Ar_2$ . Iodide is identified by the arrow.  $Cl^-.CCl_4$  (@) and related complexes appear later in the series.



**Figure 6**— Afternoon spectrum. The lack of clusters beyond 100 amu suggests some settings in the apparatus are no longer ideal. The signal at 127 amu is Iodide

### 3.2.2 Iodide

The Iodide gas mix was prepared after an experiments on a Cl NO mix were carried out by a colleague. It appears that during this phase any remaining bugs in the apparatus had been resolved and some very high resolution mass spectra of the Cl NO gas mix was taken. The Iodide acetylene gas mixtures had significantly more extensive mass spectra than the chloride. Iodide and its clusters have no isotopologues in their spectra due to the single stable isotope of <sup>127</sup>I. Although the intensity still drops off to less than 0.1V for the  $I^{-}(HCCH)_{2}$  ligand the series of peaks is nonetheless easily resolved from the background up to n=9. Figure 7 shows the  $I^$ peak at full intensity where as figure 8 highlights signals of the clusters. The pairs of peaks that appear after the n=3 cluster are due to the  $C_3H_6O$  (acetone) in the mix, while the first peak is  $I^- \cdots C_3 H_6 O$  the subsequent series is  $I^- \cdots (C_3 H_6 O) (HCCH)_n$ with the  $I^-...(C_3H_6O)_2$  peak barely distinguishable from the background. The large peak at 267 amu is the MeI-I<sup>-</sup> complex and has an associated series in the same way the I<sup>-</sup> does. Before the Iodide peak it is possible to make out the faint Cl and Br signals. Throughout the measurement the iodide clusters grew more intense in signal however the other two halides were never in significant enough abundance to record spectra. Another noteworthy element is the very weak signal of  $I^-...Ar$ . Whereas, in the chloride spectra the Cl<sup>-</sup>...Ar peak has greater intensity than the Cl<sup>-</sup>...HCCH peak.



**Figure 7**— The spectrum with  $I^-$  (\*) at full intensity. What can be seen of the HCCH<sub>n</sub> series is labeled.  $I^-$ .CH<sub>3</sub>I (\*\*) is also shown.



**Figure 8**—I<sup>-</sup> mass spectrum focused on the clusters labelled up untill n=9. The I<sup>-</sup>.CH<sub>3</sub>I (\*\*) and its related acetylene complex series are also clearly defined. Also shown are the Chloride (#), Bromide (@), and I<sup>-</sup>...Ar (X) peaks.



**Figure 9**—The Br<sup>-</sup> spectrum at full intensity. Br<sup>-</sup>...HCCH series is labelled. Br<sup>-</sup>.CH<sub>3</sub>Br<sub>2</sub> (#) is also shown

### 3.2.3 Bromide

Characteristic of the bromide mass spectra are the pairs of peaks separated by two mass units which correspond to the bromide mass isotope ratio of 1:1 <sup>7</sup>9Br and <sup>8</sup>1Br. The bromide spectra had excellent signal of 1.6-2V. Once again saturation occurs at the detector and thus the abundances of each isotope was not representative. The gas mixture remained stable for the course of a few weeks and over this time the intensities of the clusters improved significantly through overall optimisation. Initially Br<sup>-</sup>(HCCH) was at 200mv and improved to 500mV. The clusters for bromide had a similar drop off in intensity similarly to the Iodide spectra and clusters up to n=6 were observable. Even if the signal for the n=7 was more intense it would be unfortunately covered by the Br<sup>-</sup>.CH<sub>3</sub>Br<sub>2</sub> cluster and its related acetylene complexes. The splitting pattern of the Br<sup>-</sup>.CH<sub>3</sub>Br<sub>2</sub>, and similar molecules with one repeated atom of multiple isotopes, is the binomial distribution corresponding to the probabilities of each mass.

### **3.3** Photoelectron spectra

Acquisition of photoelectron spectra requires a significant quantity of the species of interest in order to resolve a signal above the background. The spectra of background should be virtually empty, except for a small amount of random noise, due to the collection technique only mapping electrons from the collection region to the



**Figure 10**—Br<sup>-</sup>...HCCH spectra at reduced intensity. Br<sup>-</sup>...(HCCH)<sub>n</sub> series is labelled up to n=6. Br<sup>-</sup>.CH<sub>3</sub>Br<sub>2</sub> (#) and the first accetylene complex appear prominently. Br<sup>-</sup>...Ar (@) and I<sup>-</sup> (\*\*) are also shown.

detector. It is apparent though, that with increasing laser intensity, a distinct energy signal emerges in the backgrounds. This is likely to be caused by stray laser shots reflecting until they cause ionisation of the metal interior of the magnet housing, as this is the only location that could be mapped onto the detector. If this signal were situated at an energy that was vastly different to the species of interest then there would be less impact. By chance the energies of the clusters with multiple ligands tend to coincide with the background and these are also the species with the lowest abundance. Effectively this rules out maximising laser power as an effective means to increase signal for these species.

### 3.3.1 Chloride

Due to the significant broadening, the chloride spectra does not resolve two spin orbit states. A technique to try to fit the unresolved spectra to overlapping gaussians is discussed later. In combination with the lack of seeded halides the resulting spectra have very poor accuracy once calibrated. Detecting the chloride, and to a less extent  $Cl^{-}...(HCCH)$ , was a simple task as both had signals that appear relatively constant when averaged over eight sweeps on the oscilloscope. The  $Cl^{-}$  spectra are very broad with an average fwhm of 0.42 eV. The fitted mean to the curve is by construction 1.048 eV, to equal the known chloride electron detachment energy from a 4.66 eV laser. Using this calibration scheme the  $Cl^{-}...HCCH$  ion was found to have a binding



Figure 11 - PES of the Cl<sup>-</sup> Ion

energy of  $3.61 \,\mathrm{eV}$  with a fwhm of  $0.30 \,\mathrm{eV}$ .

### 3.3.2 Iodide

Iodide spectra were seamless to record, in addition the I<sup>-</sup>...(HCCH)<sub>2</sub> cluster was interrogated. The shape of the Iodide spectra in energy space is quite interesting. The pronounced low energy wing is an indicator that the spectra likely has the remnants of electrons that were not parallelised in a sufficiently short time period. The spin orbit states are easily resolved by the spectra and are very stable values over the period of recording for a day. This implies that the calibration should be accurate for the clusters. I<sup>-</sup>...HCCH was recorded to have an electron binding energy of 3.40 eV for the  ${}^{2}P_{3/2}$  state and 4.32 eV for the  ${}^{2}P_{1/2}$  state. The lower binding energy state had a fwhm of 0.29 eV while the higher energy state had the relatively sharp fwhm of 0.14 eV. The I<sup>-</sup>...(HCCH)<sub>2</sub> spectra had no second measurable spin orbit state. If there was a trend of increase in ligand number corresponding to an increase in binding energy then this would indicate that the energy of this particular state is likely to be close to the emission threshold given by the laser energy of 4.66 eV and thus either too low in intesity or completely unattainable via the laser.

### 3.3.3 Bromide

When recording spectra for the bromide and clusters it was also possible to detect the remnant iodide signal. It was during the measurement of this series that the Quad







Figure 13 — Spectra of the  $\mathrm{I}^-$  Ion







Figure 15 — Spectra of the  $\rm I^-...(\rm HCCH)_2$  Cluster



Figure 16 - Spectra of the Br<sup>-</sup> Ion

CFD was trailed. The bromide iodide calibration curves had very good correlation .9990, indicating that this method is reasonably reliable. Br<sup>-</sup>...HCCH was recorded to have energy for  ${}^{2}P_{3/2}$  of 3.78 eV and  ${}^{2}P_{1/2}$  of 4.24 eV. Br<sup>-</sup>...(HCCH)<sub>2</sub> was recorded with only one peak. Once again this is likely that the energy is shifted into the non-detachment or low energy section of the spectra. The  ${}^{2}P_{3/2}$  state had an energy of 4.16 eV.

## **3.4** Broadening in the Spectra

The most significant cause of broadening is due to the relative motion of the ion beam with respect to the direction on the electron ejection. In the frame of emission there should be a spread of velocities depending on a  $\cos^2(\phi)$  distribution about the the polarisation axis. Transforming back to the laboratory frame leaves a distribution with velocities ranging from  $v_e + v_i$  to  $v_e - v_i$ . Calculating the predicted spread for bromide mass 79amu and energy 1000 eV ejecting a 1.30 eV electron finds that the difference between maximum and minimum energy electrons should be 0.378 eV. The previous value should be reasonably close to the full-width at 1/10th maximum of the corresponding spectra. When compared however these two measures are not close with the fw1/10m being 0.5 eV. There are ofcourse other sources of broadening which will contribute to the full picture. The intrinsic vibrational spectra takes up a spectral space of 0.05 eV as seen later. Under the assumptions of the magnetic mirror effect as described previously the turn around time is proportionate to  $\frac{1}{\sqrt{E}}$ 



Figure 17 — Spectra of the  $\rm Br^-...HCCH$  Cluster



Figure 18 — Spectra of the  $Br^-...(HCCH)_2$  Cluster



Figure 19—Spectra of the Bromide ion at four energies

so a better resolution should be seen for the lower energy electrons, which is what is observed in the spectra. Potentially the exact configuration of the magnetic fields is not ideal and so there is a much greater effect of the reflection and parallelisation process than expected.

In order to understand the velocity broadening a set of spectra were recorded for the Br<sup>-</sup> ion with varied beam energy. Spectra were taken at varying beam energies of (200, 300, 1000, 2000)eV see figure 19. The predicted trends would be a slight shift in mean position of the peaks as well as a large variance in the fwhm of the curves. The fitted curves to these spectra reveal that the predicted shift in mean and fwhm is observed. The magnitude of these shifts however is significantly greater than expected. The asymmetrical nature of the curves is also similar across different energies compounding the suggestion this must be an artefact of other spectral features, likely the parallelisation, and not solely due to velocity broadening.

### 3.5 Fitting to the data

In choosing a function to fit to the data it was important to consider both the physical sources of the data and something which was computationally easy to work with. In the end guassian fitting was chosen as the physical situation seems too complex to find a neat mathematical form and guassian fitting is not computationally intensive. The fits seemed to represent the low intensity data the best, possibly because the random fluctuations present disguise the true form of the spectra. For the spectra of the halides it is clear there is a large mismatch in terms of the chosen fit. The leading higher energy wing of the curve seems to be of guassian nature but the trailing edge is different in form. Overall this method still produced repeatable estimates for the parameters of the curve and allowed for an accurate calibration.

### 3.5.1 Resolving Chloride

Due to poor resolution, the two chloride peaks were unresolved in their spectra. Despite this, it seemed plausible that the fit to the data could be optimised by instead modelling it to two overlapping guassians. As both the spin states are so close in energy, it can be assumed that the area under the curves would be indicative of the natural abundance for each state. The forms of the curves found using the new fitting scheme showed a wide range of behaviours with respect to the areas of each guassian see fig 20. The ratios of the two areas ranged from 5:1 to almost 1:1, while this is in the right order of magnitude it is not conclusive either way as to whether or not the fit was approximating the two energy states. The second comparison was to test if the mean point of each peak matched up with the predicted value. After roughly calibrating the energy scale it was seen that the energy gap between the two predicted peaks was about double what it should be and was constant across the various spectra. It is quite reasonable that this technique could accurately determine the two peaks from within the overlapping spectra. However, the limiting factor seems to be the complex interplay of many sources of broadening and the resulting spectral distortion. Instead of approximating the two energy peaks the guassians seemed to approximate the two wings of the broad spectra, hence explaining the larger separation of mean positions. Potentially if a form was found that better approximated the curves this technique could be extended quite easily to resolve the chloride spectra.

### **3.6** Spectral Details

The spectra of the halide acetylene complexes were able to characterise the binding energy of these complexes. The low resolution and inability to access clusters of greater than two ligands meant the vibrational structure and other spectral features were not able to be interrogated. In the work of Conran there was a observed a small hump in the spectra of Br<sup>-</sup>...HCCH and was thought to possibly be the emergence of a hot band. However, it seems likely that this was the peak of the background spectra as seen in figure 21. In previous works the appearance of a hotband has



**Figure 20** — PES of Cl<sup>-</sup> raw data (transformed from time of flight BIN to  $1/\text{TOF}^2$  ie energy) with the two curve approximation fit. The spectra is reversed with respect to the binding energy.

occurred as the number of ligands increased (14).



Figure  $21 - Br^-$ ...HCCH PES in blue with background in red. Giving the illusion of a possible hot band in the spectra

# Chapter 4

# Computational

Previous work on the theoretical energies of the halide acetylene complex will be discussed in brief and compared to the experimental results gained from this work.

### 4.1 Theoretical work

Calculations of the halide and halogen acetylene complexes were completed by the group to the CCSD(T)/aug-cc-pVTZ level of theory. The halide complexes were compared to the results of Botschwina's CCSD(T)/aug-cc-QZ results. There were two local minima found on the potential energy surface of the neutral: a T-shaped complex with  $c_{2v}$  symmetry and a linear complex with  $c_{\infty v}$  symmetry. The anion was found to have only one stable geometry, the linear  $c_{\infty v}$  state. The geometries are given in figure 22 and the dissociation energies and bond lengths are given in tables 4.1- 4.3.

	$r_{\mathrm{X}\cdots   }*$	$r_{\rm C-H}$	$r_{\rm C\equiv C}$	$\angle_{(\mathrm{X}-   -\mathrm{H})}*$	$\angle_{\rm H-C-C}$	$D_e$	$D_0$	
	Å	Å	Å	0	0	$\rm kJmol^{-1}$	${\rm kJmol^{-1}}$	$\mathrm{cm}^{-1}$
$\mathrm{Cl}\cdots\mathrm{HCCH}$	2.670	1.066	1.216	90.4	179.4	16.5	13.9	1162
							16.5	$1379 \ \dagger$
$\mathrm{Br} \cdots \mathrm{HCCH}$	2.855	1.066	1.214	90.4	179.4	17.1	15.8	1321
							17.0	1421 †
$\mathrm{I}{\cdots}\mathrm{HCCH}$	3.188	1.066	1.213	90.2	179.6	14.7	13.6	1137
							16.3	1363 †
HCCH		1.065	1.210					
			a a	1 1				

**Table 1**—Structural parameters of the  $C_{2v}$  halogen-acetylene gas phase complexes predicted from CCSD(T) calculations

\* — is the mid point of the  $C \equiv C$  bond

 $\dagger CCSD(T)/CBS$  and CCSD(T)/aug-cc-pVTZ zpe

The T-shaped complex was found to be the more stable geometry of the neutral as reflected by the higher  $D_0$  values. There is an interesting trend in the  $D_0$  values



Figure 22 — The predicted geometries for the neutral T-shaped, neutral linear, and anion linear complexes. Courtesy Marcus Kettner

Table 2 — Structural	parameters of the	$C_{\infty v}$ halogen-acety	lene gas ph	ase complexes
predicted from CCSD	O(T) calculations			

	$r_{\rm H_bX}$	$r_{\rm C_b-H_b}$	$r_{\rm C\equiv C}$	$r_{\rm C_a-H_a}$	$D_{e}$	$D_0$		
	Å	Å	Å	Å	$\rm kJmol^{-1}$	${ m kJmol^{-1}}$	$\mathrm{cm}^{-1}$	
$\mathrm{Cl}\cdots\mathrm{HCCH}$	2.916	1.066	1.211	1.065	3.3	2.4	201	
						2.2	184*	
$\mathrm{Br} \cdots \mathrm{HCCH}$	2.987	1.066	1.211	1.065	4.6	3.5	293	
						2.9	242*	
$\mathrm{I}{\cdot}{\cdot}{\cdot}\mathrm{HCCH}$	3.190	1.066	1.211	1.065	5.1	4.3	360	
						4.7	393*	
HCCH		1.065	1.210	1.065				
* CCSD(T)/CBS and CCSD(T)/aug-cc-pVTZ zpe								

**Table 3**—Structural parameters of the  $C_{\infty v}$  anion halide-acetylene gas phase complexes predicted from CCSD(T) calculations

	$r_{\rm H_bX}$	$r_{\rm C_b\cdots H_b}$	$r_{C\equiv C}$	$r_{\rm C_a\cdots H_a}$	De	D	0
	Å	Å	Å	Å	$\rm kJmol^{-1}$	$\rm kJmol^{-1}$	${\rm cm}^{-1}$
$\mathrm{Cl}^-\!\cdots\mathrm{HCCH}$							
This work	2.258	1.093	1.216	1.064	44.9	43.1	3602
						43.2	3611*
(2)	2.2521	1.0919	1.2118	1.0623			3600(36)
$\mathrm{Br}^{-}\cdots\mathrm{HCCH}$							( )
This work	2.454	1.085	1.216	1.064	39.5	37.6	3143
						37.3	3188*
(3)	2.4800	1.0860	1.2117	1.0627			$3020(3)^{\dagger}$
I <sup>-</sup> ···HCCH							
This work	2.774	1.082	1.215	1.064	31.8	30.0	2507
21000 00110		1.002	1.210	1.001	01.0	31.0	2591*
(3)	2,7626	1 0809	1 2108	1.0626		01.0	2450(74)
HCCH	2.1020	1.0005	1.2100	1.0020 1.065			2100(11)
110.011		1.000	1.410	1.000			

\* CCSD(T)/CBS and CCSD(T)/aug-cc-pVTZ zpe

<sup>†</sup> Experimental value from reference (22)

as the halogen increases in atomic number. Chlorine nestles closest to the  $C \equiv C$  bond but has the lowest polarisability of these halides. Similarly iodine occupies the opposite characteristics with bromine in-between. The calculated values has bromide with the highest  $D_0$  value which indicates that the character of the bond is strongly influenced both by the size of the atomic radius, thus the closeness of the bond, and the polarisability of the atom.

In the situation pertaining to the experimental conditions it is unlikely that the transition from anion to neutral would involve a dramatic shift in geometry. Therefore the comparison to the photoelectron spectra is best made between the anion linear, and neutral linear complexes. Immediately it is clear that the differences between the two values are quite large. The character of the two bonds are quite different in nature. In the neutral linear complex there is little disturbance in the  $r_{C_b-H_b}$  length compared to the bare acetylene complex. In the anion linear complex the bond is significantly stretched suggesting there is effectively a hydrogen bond occurring. The trend of dissociation energies for the different halides is as expected. In the anion case the dominant forces are the ion-quadrupole moment and the ion induced dipole moment. The first drops of as  $\frac{1}{r^3}$  and the latter  $\frac{1}{r^4}$  hence as the atomic radius increases the dissociation energies decrease.

### 4.2 Comparison to experimental results

Species	$^{2}\mathrm{P}_{3/2}$	$^{2}\mathrm{P}_{1/2}$	$\mathbf{E}_{stab}$	ADE $C_{\infty v}$	ADE $C_{\infty v}$
Cl <sup>-</sup>	3.6(4)	-			
$Cl^HCCH$	4.1	-	0.5	4.037	3.889
$\mathrm{Br}^-$	3.39(6)	3.85(3)			
Br <sup>-</sup> HCCH	3.78	4.24	0.39	3.721	3.574
$\mathrm{Br}^{-}(\mathrm{HCCH})_2$	4.16	-	0.38		
Ι-	3.05(4)	4.02(6)			
I <sup>-</sup> HCCH	3.40	4.32	0.35	3.332	3.212
$I^(HCCH)_2$	3.69	-	0.29		

Table 4.2 shows the experimentally measured binding energies as well as the energies of stabilisation for the complexes. There are also the adiabatic detachment energies.

The trend down the halides for binding energy is similar to that of  $D_0$  as expected. When comparing the experimentally derived values for binding energy and the computationally determined values for the adiabatic detachment energies it is clear the values more closely agree with the  $c_{\infty v}$  geometry as predicted. The chloride case has a very larger uncertainty due to the unresolved energy peaks making the  $e_{stab}$  unreliable. The differences between the ADE values and the  $e_{stab}$  values are similar for iodide and bromide.

The limited data set for multiple acetylene complexes shows an interesting initial trend. Where as the bromide complex has the binding energy of the two acetylene complex of very close to the value of the single acetylene, the iodide has a larger difference. This could be put down to the low sample size, or possibly the spectrometer being unreliable for low energy electrons. The predicted solvation structure for bromide (22) has them at 180°. This should minimise any interaction hence it would be unlikely that the behaviour of the two ligand complex is markedly different in energies to the addition of the one ligand values.



**Figure 23** — The predicted spectra of the halide acetylene complexes. The black sticks represent progressions in the intermolecular stretching modes, and the red sticks are combination bands. Courtesy Duncan Wild

## 4.3 Simulated spectra

Anion photoelectron spectra were simulated by determining the Frank-Condon factors of the anion and neutral vibrational states. This spectrum was then convoluted with a guassian function of width 0.005 eV to simulate a high resolution spectrum. These are shown in fig 23. These spectra are two orders of magnitude more finely than the experimental work. Confirmation of the relative intensity of the various modes will be a matter for future research.

## Chapter 5

## **Future Work**

### 5.1 Piezo Driven Nozzle

It was hoped that construction of a piezo driven nozzle based on the designs of Proch (18) and later improved by Shieber(20) would be completed before the end of the experimentation period. Changing from the current solenoid to a piezo setup would have numerous advantages. Primarily piezo has a faster response time to electrical impulse and this allows for better control over the size of gas pulse into the vacuum as well as improving its homogeneity with respect to time. By achieving shorter more intense pulses the number of clusters formed after ion formation should be improved. Also the spatial resolution in the time of flight tube will be improved as the pulse entering the TOF plates will be more narrow in time. The combination of these effects will be increased volume of interactions with laser shots, ultimately improving the photoelectron spectra.

### 5.2 SEVI

Work on testing the SEVI was also performed. This involves extending the flight tube of the ions into a new arm of the detector. Ions were able to be detected at the new ion detector, through use of a secondary set of X/Y deflection plates subsequent to the initial Ion detector. The signal was relatively stable however it was uncertain exactly what the optimum setting would as the interdependence of various setting can make optimisation a difficult process. Despite the success at the ion detector there was no detectable signal that made it to the CCD. Potentially this could be due to a mis-alignment of some of the orifices or another kind of obstruction in the setup.

Future improvements to the setup will be to improve the resolution of the photo-

electron spectrometer. As discussed the primary limiting factor was the significant velocity of the ions. Various techniques to reduce the effect of this, such as the mass decelerator, can be used. A more novel approach is suggested by

# Chapter 6

# Conclusion

Comprehensive spectra of the halide acetylene clusters has been performed in this work. The combination of mass spectroscopy and photoelectron spectroscopy has allowed a piecewise addition of acetylene ligands to a halide central ion to be measured. The binding energies of the X<sup>-</sup>...HCCH complexes have been accurately determined using a fitting scheme and calibration to known values. The fitting scheme has also revealed various features of the spectra which reflect the conditions of the experiment. Notably the broadening in the spectra seems to have numerous source which each have a larger than expected effect. The results have been compared to the computational results derived by the group and has shown some promising agreement. For further work on these clusters to be undertaken significant advancements to the apparatus would be needed. It was shown that due to the relatively strong interaction between the halide and acetylene the energy of stabilisation afforded to the anion to neutral transition was high. In order to probe clusters of higher order of ligands a higher energy laser or synchrotron radiation source would be required. In order to probe the vibrational states, and indeed in the case of chloride to resolve the spin states, the issue of velocity broadening needs to be removed. Once new parts, such as the piezo nozzle and mass decelerator, are eventually installed and tested this should certainly allow access to much more in-depth photoelectron spectroscopy.

# References

- Evan J. Bieske. Spectroscopic studies of anion complexes and clusters: A microscopic approach to understanding anion solvation. *Chem. Soc. Rev.*, 32:231–237, 2003.
- [2] Peter Botschwina and Rainer Oswald. The anionic complex clhcch: Results of large-scale coupled cluster calculations. *The Journal of Chemical Physics*, 117(10), 2002.
- [3] Peter Botschwina and Hermann Stoll. The hydrogen-bonded cluster anions br-...hcch and i-...hcch: results of coupled cluster calculations. *Phys. Chem. Chem. Phys.*, 3:1965–1972, 2001.
- [4] O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, and R. E. Smalley. Magnetic timeofflight photoelectron spectrometer for masselected negative cluster ions. *Review of Scientific Instruments*, 58(11), 1987.
- [5] L. G. Christophorou. Electron-molecule interactions and their applications, vol. 1, 1984.
- [6] S. Conran. Investigating br... $(hcch)_n$ , cl... $(hcch)_n$  and i... $(hcch)_n$  using anion photoelectron spectroscopy and ab initio calculations, 2013.
- [7] P. Dub, M. J. Kiik, and B. P. Stoicheff. Spectroscopic study of vibrational relaxation and cooling of raregas excimers formed in a direct current discharge with supersonic expansion. *The Journal of Chemical Physics*, 103(18), 1995.
- [8] Kent M. Ervin and W. Carl Lineberger. Photoelectron spectroscopy of phosphorus hydride anions. The Journal of Chemical Physics, 122(19):-, 2005.
- [9] Mei Lee H. Jeng and Bruce S. Ault. Infrared matrix isolation studies of molecular interactions: alkynes with halide anions. *The Journal of Physical Chemistry*, 95(7):2687–2692, 1991, http://dx.doi.org/10.1021/j100160a013.

- [10] Jude A. Kelley, Gary H. Weddle, William H. Robertson, and Mark A. Johnson. Linking the photoelectron and infrared spectroscopies of the (h2o)6 isomers. *The Journal of Chemical Physics*, 116(3), 2002.
- [11] P Kruit and F H Read. Magnetic field paralleliser for 2 electron-spectrometer and electron-image magnifier. Journal of Physics E: Scientific Instruments, 16(4):313, 1983.
- [12] R. LaMacchia. Towards anion photoelectron spectroscopy of complexes and clusters, 2008.
- [13] K. M. Lapere. Anion photoelectron spectroscopy of clusters and complexes, 2013.
- [14] Kim M. Lapere, Robert J. LaMacchia, Lin H. Quak, Marcus Kettner, Stephen G. Dale, Allan J. McKinley, and Duncan A. Wild. Anion photoelectron spectra and ab initio calculations of the iodidecarbon monoxide clusters: I(co)n, n = 14. The Journal of Physical Chemistry A, 116(14):3577–3584, 2012, http://dx.doi.org/10.1021/jp300471x. PMID: 22420454.
- [15] K.M. Lapere. An investigation of the cl<sup>-</sup>...co and br<sup>-</sup>...co van der waals clusters with anion photoelectron spectroscopy and ab initio calculations, 2009.
- [16] K.M. Lapere, R.J. LaMacchia, L.H. Quak, A.J. McKinley, and D.A. Wild. Anion photoelectron spectroscopy and ab initio calculations of the gas phase chloridecarbon monoxide complex: Clco. *Chemical Physics Letters*, 504(13):13 – 19, 2011.
- [17] Atsushi Nakajima, Tetsuya Taguwa, and Koji Kaya. Photoelectron spectroscopy of iron carbonyl cluster anions (fen(co)m, n = 14). Chemical Physics Letters, 221(56):436 - 440, 1994.
- [18] D. Proch and T. Trickl. A highintensity multipurpose piezoelectric pulsed molecular beam source. *Review of Scientific Instruments*, 60(4), 1989.
- [19] M. Roy and T. B. McMahon. The anomalous gas phase acidity of ethyl fluoride. an abinitio investigation of the importance of hydrogen bonding between f and sp2 and sp ch bonds. *Canadian Journal of Chemistry*, 63(3):708–715, 1985, http://dx.doi.org/10.1139/v85-117.
- [20] Alexander Schieer and Rolf Schfer. Versatile piezoelectric pulsed molecular beam source for gaseous compounds and organic molecules with femtomole

accuracy for uhv and surface science applications. *Review of Scientific Instruments*, 80(8):-, 2009.

- [21] Jae Kyu Song, Sang Yun Han, Inho Chu, Jeong Hyun Kim, Seong Keun Kim, Svetlana A. Lyapustina, Shoujun Xu, J. Michael Nilles, and Kit H. Bowen. Photoelectron spectroscopy of naphthalene cluster anions. *The Journal of Chemical Physics*, 116(11), 2002.
- [22] P. S. Weiser, D. A. Wild, and E. J. Bieske. Infrared spectra of cl(c2h2)n(1n9) anion clusters: Spectroscopic evidence for solvent shell closure. *The Journal of Chemical Physics*, 110(19), 1999.
- [23] P.S. Weiser, D.A. Wild, and E.J. Bieske. Infrared spectra of i(c2h2)n (1n4) anion complexes. *Chemical Physics Letters*, 299(34):303 – 308, 1999.
- [24] D. A. Wild, P. J. Milley, Z. M. Loh, P. P. Wolynec, P. S. Weiser, and E. J. Bieske. Structural and energetic properties of the brc2h2 anion complex from rotationally resolved mid-infrared spectra and ab initio calculations. *The Journal of Chemical Physics*, 113(3), 2000.
- [25] D.A Wild, P.J Milley, Z.M Loh, P.S Weiser, and E.J Bieske. Infrared spectra of br-(c2h2)n complexes. *Chemical Physics Letters*, 323(12):49 – 54, 2000.
- [26] W. C. Wiley and I. H. McLaren. Timeofflight mass spectrometer with improved resolution. *Review of Scientific Instruments*, 26(12), 1955.
- [27] Yuexing Zhao, Ivan Yourshaw, Georg Reiser, Caroline C. Arnold, and Daniel M. Neumark. Study of the arbr, ari, and kri anions and the corresponding neutral van der waals complexes by anion zero electron kinetic energy spectroscopy. *The Journal of Chemical Physics*, 101(8), 1994.

# Appendix

The following is the code used to fit the experimental spectra.

```
Mile PEdata = "C:\\Users\\P151\\Dropbox\\Shared\\Spectra\\PE_data\\2013"
Out[1]= C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013
ln[2]:= SetDirectory[PEdata]
Out[2]= C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013
In[3]:= Months = Table[StringJoin[{PEdata, "\\",
         {"January", "February", "March", "April", "May", "June", "July", "August",
           "September", "October", "November", "December"}[[n]]}], {n, 1, 12}]
Out3]= {C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\January,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\February,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\March,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\April,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\May,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\June,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\July,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\August,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\September,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\October,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\November,
     C:\Users\P151\Dropbox\Shared\Spectra\PE data\2013\December}
In[4]:= WorkingMonths = Module[{}],
                   SetDirectory[PEdata];
                   FileNames[]]
Out[4]= {April, August, June, March, May, New Folder, November, October, September}
In[5]:= Days[x_] := Module[{DAYS, xo},
                   DAYS = { }; January = 1; February = 2;
      March = 3; April = 4; May = 5; June = 6; July = 7; August = 8;
      September = 9; October = 10; November = 11; December = 12;
                   xo = x;
                   SetDirectory[Months[[xo]]];
      AppendTo[DAYS, Table[StringJoin[{Months[[xo]], "\\", FileNames[][[n]]}],
                          {n, 1, Length[FileNames[]]}];
                   DAYS]
In[7]:= TEST[x_, month_] := Module[{y},
                        y = Flatten[Days[month]][[x]];
                        SetDirectory[y];
                            Table[StringJoin[{y, "\\", FileNames[][[n]]}],
                             {n, 1, Length[FileNames[]]}]
In[8]:= LIST[a , month ] := Module[{LISTT, p},
           LISTT = { } ; p = TEST[a, month] ;
           Do[If[StringSplit[StringSplit[p[[i]], "\\"][[-1]], "."][[-1]] == "asc",
                      AppendTo[LISTT, p[[i]]], {i, 1, Length[p]}];
           LISTT]
```

2 Untitled-2

This section imports my data and then converts it from time of flight to Kinetic Energy. I was smoothing the data by using a moving average function. It will allow for better aquisition of peaks, though possibly it may lead to loss of information?

```
h[9]:= Imp[x_] := Flatten[Import[x, "CSV"]];
h[10]:= data[x_, y_, month_] := Imp[LIST[x, month][[y]]][[1;; 5000]]
h[11]:= datavector[x_, y_, month_] :=
Transpose[{Table[i, {i, 1, Length[data[x, y, month]]}], data[x, y, month]}];
h[12]:= mdatavector[x_, y_, month_] :=
ReplaceList[datavector[x, y, month], ({___, {a_, b_}, __} \implies {1/(a^2, b})];
```

Here I am finding the maximums of the list with the condition that the point is greater than the surrounding 400 points, in the future I can make this manipulatable to ensure the correct number of peaks is found.

I'm then implementing a gaussian fit function that I will test the data with, It gives weighting to the peaks rather than the wings of the guassian.

Could be made more manipulatable in the future to change the amount of points for the fit.

```
ln[13]:= Maxms[x_, y_, month_] :=
```

h[15]:= Approx[maxno\_, x\_, y\_, month\_] := Module { {www, ooo} ,

www = TOFVect[maxno, x, y, month]; ooo = Maxms[x, y, month]; NonlinearModelFit[www,  $\frac{A}{\sqrt{(2\pi)\sigma}} e^{\frac{-(var-\mu)^2}{2\sigma^2}}$ ,

{ $\mu$ , mdatavector[x, y, month][[ooo[[maxno, 1]], 1]]}}, var, Weights  $\rightarrow$  (#2 &)]]

In[16]:= GApp[n\_, x\_, y\_, month\_] :=

```
Show[(Plot[#, {z, TOFVect[n, x, y, month][[Length[TOFVect[n, x, y, month]], 1]],
	TOFVect[n, x, y, month][[1, 1]]}, PlotRange → All] &/@
	({Normal[Approx[n, x, y, month]] /. var → z})),
	ListPlot[TOFVect[n, x, y, month]], PlotRange → All]
```

Here I am creating some fits that only take a slice of the region around a peak, hopefuly when these approximations are taken together they will better represent the enitre data

```
In[17]:= NewApproxL[maxno_, x_, y_, month_] := Module {www, ooo},
```

www = TOFVect[maxno, x, y, month][[Floor[Length[TOFVect[maxno, x, y, month]] / 3]
;; Length[TOFVect[maxno, x, y, month]]]];

ooo = Maxms[x, y, month];

NonlinearModelFit  $\begin{bmatrix} www, \frac{A}{\sqrt{(2\pi)\sigma}} e^{\frac{-(var-\mu)^2}{2\sigma^2}}, \\ \left\{ \left\{ A, 000 [[maxno, 2]] * \frac{(www[[1, 1]] - www[[Length[www], 1]])}{5} \right\}, \end{bmatrix}$ 

 $\left\{ \sigma, \frac{(www[[1, 1]] - www[[Length[www], 1]])}{5} \right\},$   $\left\{ \mu, mdatavector[x, y, month][[000[[maxno, 1]], 1]] \right\},$   $var, Weights \rightarrow (\#2 \&) ] ]$ 

In[18]= NewApproxR[maxno\_, x\_, y\_, month\_] := Module[{www, ooo},

www = TOFVect[maxno, x, y, month][[
 1 ;; Floor[Length[TOFVect[maxno, x, y, month]] / 3]]];

NonlinearModelFit  $\begin{bmatrix} www, \frac{AA}{\sqrt{(2 \pi) \sigma \sigma}} e^{\frac{-(var-\mu\mu)^2}{2 \sigma \sigma^2}}, \\ \left\{ \left\{ AA, ooo[[maxno, 2]] * \frac{(www[[1, 1]] - www[[Length[www], 1]])}{5} \right\}, \\ \left\{ \sigma \sigma, \frac{(www[[1, 1]] - www[[Length[www], 1]])}{5} \right\}, \\ \left\{ \mu \mu, mdatavector[x, y, month][[ooo[[maxno, 1]], 1]] \right\} \right\}, \\ var, Weights \rightarrow (#2 \&) \end{bmatrix} \end{bmatrix}$ 

In[19]:= NewApproxMid[maxno\_, x\_, y\_, month\_] := Module { {www, ooo} ,

```
www = TOFVect[maxno, x, y, month][[Floor[Length[TOFVect[maxno, x, y, month]] / 3]
;; Floor[Length[TOFVect[maxno, x, y, month]] * 2 / 3]]];
ooo = Maxms[x, y, month];
NonlinearModelFit[www, \frac{AA}{\sqrt{(2 \pi) \sigma \sigma}} e^{\frac{-(vax-\mu\mu)^2}{2 \sigma \sigma^2}},
{{AA, ooo[[maxno, 2]] * \frac{(www[[1, 1]] - www[[Length[www], 1]])}{5},
{\sigma \sigma, \frac{(www[[1, 1]] - www[[Length[www], 1]])}{5}},
{\{\sigma \sigma, \frac{(www[[1, 1]] - www[[Length[www], 1]])}{5}\}},
{\{\mu \mu, mdatavector[x, y, month][[ooo[[maxno, 1]], 1]]\}},
var, Weights \rightarrow (#2 &)]]
```

 $ListPlot[TOFVect[n, x, y, month], PlotRange \rightarrow All]]$ 

4 Untitled-2

```
In[21]:= NewGAppR[n_, x_, y_, month_] :=
       Show[(Plot[#, {z, TOFVect[n, x, y, month][[Length[TOFVect[n, x, y, month]], 1]],
                TOFVect[n, x, y, month][[1, 1]]\}, PlotRange \rightarrow All] & @
            (\{Normal[NewApproxR[n, x, y, month]] /. var \rightarrow z\})),
         ListPlot[TOFVect[n, x, y, month], PlotRange → All]]
ln[22]:= NewGAppMid[n_, x_, y_, month_] :=
       Show[(Plot[#, {z, TOFVect[n, x, y, month][[Length[TOFVect[n, x, y, month]], 1]],
                TOFVect[n, x, y, month][[1, 1]]\}, PlotRange \rightarrow All] \& /@
            (\{Normal[NewApproxMid[n, x, y, month]] /. var \rightarrow z\})),
         ListPlot[TOFVect[n, x, y, month], PlotRange \rightarrow All]]
In[23]:= NewApproxFull[maxno_, x_, y_, month_] := Module {www, ooo},
          www = TOFVect[maxno, x, y, month];
          ooo = Maxms[x, y, month];
          NonlinearModelFit \begin{bmatrix} www, \frac{b}{\sqrt{(2 \pi) \sigma b}} e^{\frac{-(var_{-\mu}b)^2}{2 \sigma b^2}} + \frac{B}{\sqrt{(2 \pi) \sigma B}} e^{\frac{-(var_{-\mu}b)^2}{2 \sigma b^2}}, \end{bmatrix}
            \{\{b, A\}, \{\sigma b, \sigma\}, \{\mu b, \mu\}, \{B, AA\}, \{\sigma B, \sigma\sigma\}, \{\mu B, \mu\mu\}\},\
            var, Weights \rightarrow (#2 &) /.
         Flatten[{NewApproxL[maxno, x, y, month]["BestFitParameters"],
            NewApproxR[maxno, x, y, month]["BestFitParameters"]}]
In[24]:= NewGAppFull[n_, x_, y_, month_] :=
       Show[(Plot[#, {z, TOFVect[n, x, y, month][[Length[TOFVect[n, x, y, month]], 1]],
                TOFVect[n, x, y, month][[1, 1]], PlotRange \rightarrow All] \& /@
            (\{Normal[NewApproxFull[n, x, y, month]] /. var \rightarrow z\})),
         ListPlot[TOFVect[n, x, y, month]], PlotRange → All]
In[25]:= ForcedApprox[maxno_, x_, y_, month_] := Module {www, ooo},
         www = TOFVect[maxno, x, y, month];
         ooo = Maxms[x, y, month];
        NonlinearModelFit \begin{bmatrix} www, \frac{b}{\sqrt{(2 \pi) \sigma b}} e^{\frac{-(var-\mu b)^2}{2 \sigma b^2}} + \frac{B}{\sqrt{(2 \pi) \sigma B}} e^{\frac{-(var-\mu B)^2}{2 \sigma b^2}}, \end{bmatrix}
          \{\{b, ooo[[maxno, 2]] * 5 * 10^{-8}\}, \{\sigma b, 5 * 10^{-8}\}, 
            \{\mu b, mdatavector[x, y, month] [[000[[maxno, 1]], 1]] - .25 * 10^{-7}\},\
            \{B, ooo[[maxno, 2]] * 5 * 10^{-8} / 2\}, \{\sigma B, 5 * 10^{-8}\},\
            \{\mu B, mdatavector[x, y, month][[000[[maxno, 1]], 1]] + .25 * 10^{-7}\}\},\
          var, Weights \rightarrow (#2 &)
In[26]:= ForcedGApp[n_, x_, y_, month_] :=
       Show[(Plot[#, {z, TOFVect[n, x, y, month][[Length[TOFVect[n, x, y, month]], 1]],
                TOFVect[n, x, y, month][[1, 1]], PlotRange \rightarrow All] \& /@
            (\{Normal[ForcedApprox[n, x, y, month]] /. var \rightarrow z\})),
         ListPlot[TOFVect[n, x, y, month]], PlotRange → All]
ln[27]:= backgroundcor[spec_, back_] :=
       Module[{ccc, bbb},
         ccc = back;
         bbb = spec;
         \texttt{ReplaceList[bbb, \{ \_, \{x\_, y\_\}, \_] \rightarrow \{2 x, y\}] - ccc]}
      Not yet finished below
```

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In[28]:= backredApprox[maxno\_, bgno\_, x\_, y\_, month\_] := Module[{www, ooo},

www = TOFVect[maxno, x, y, month];  
ooo = Maxms[x, y, month];  
NonlinearModelFit[www, 
$$\frac{A}{\sqrt{(2\pi)\sigma}} e^{\frac{-(var-\mu)^2}{2\sigma^2}}$$
,  
 $\left\{\left\{A, \frac{ooo[[maxno, 2]]}{\frac{(www[[1,1]]-www[[Length[www],1]])}{10}}\right\}, \left\{\sigma, \frac{(www[[1,1]]-www[[Length[www],1]])}{10}\right\}, \left\{\sigma, \frac{(www[[1,1]]-www[[Length[www],1]])}{10}\right\}\right\}$ 

{ $\mu$ , mdatavector[x, y, month][[ooo[[maxno, 1]], 1]]}}, var, Weights  $\rightarrow$  (#2 &)]]

# **Research** proposal

The project deviated from its initial course when the opportunity to investigate the accetylene complexes was presented. Efforts to improve the apparatus and extend is capabilites were hampered by poor performance in the latter half of the research period.

#### M.Sc. Physics Project **Research Proposal** Duncan Beckham School of Physics & School of Chemistry and Biochemistry University of Western Australia April 2013

#### Gas Phase Ion Molecule Photoelectron Spectroscopy

*Keywords:* Photoelectron spectroscopy, Mass spectrometry, anion/cation clusters, quantum chemistry *Supervisors:* Asst Prof Duncan Wild (UWA-Chemistry)

#### 1 Research Plan

#### 1.1 Aims

In this project exotic gas phase ion complexes and clusters will be measured using the state of the art photoelectron spectrometer in the Wild laboratory. The aim of these measurements will be to extract information about the multi-dimensional potential energy surfaces arising from the rotational and vibrational states of the molecular complexes. Additional to the experimental procedures the project will involve extending the current apparatus to include cation mode capabilities; involvement in the continuing maintenance; and improvements to the operational performance of the apparatus, such as upgrading to a pulsed discharge source. In analysing experimental results comparison to advanced computational modeling using a high level of quantum chemical theory will be employed.

#### 1.2 Significance

In measuring ion species the derived results will provide an important model for understanding the chemistry of such species and predictions about their reactivities and conditions of their formations. Of specific importance are the halide complexes which are active in atmospheric chemistry. Measurements of cations will have importance in understanding the chemistry of interstellar bodies. The research relies and will build on a strong understanding in various disciplines related to Chemical Physics, and will provide an excellent opportunity to work towards publication of work in the field.

#### 1.3 Methods

The apparatus used by the Wild research group is the Time Of Flight Mass-Spectrometer coupled to a Photoelectron Spectrometer TOF-PES. The source is able to produce exotic ion species clustered with neutral molecules, while the mass spectrometer allows for

selection of the target cluster before the spectrometer probes the electronic structure with the UV laser. Computational programs such as Gaussian, ORCA and GAMESS along with EasyWave, modeling with high level quantum chemistry, will be employed to accompany results with predicted spectra. Access to iVEC and NCI is available for the group, however as part of the project a dedicated workstation will be constructed to aid in spectrum analysis and computational quantum chemistry.



Figure 1: Schematics of the TOF-PES

#### 1.4 Status

The research group completed construction of the alpha configuration of the apparatus in 2009 and have been obtaining data of various species such as chloride-carbon monoxide complexes [4], bromide-carbon monoxide complexes [2] and iodide-carbon monoxide clusters [3]. There is also research focusing on ab initio calculation in the group that aims to compliment experimental results. Currently the group has seven members, three of whom are PhD students, one chemistry honours and two masters of physical sciences students. In the past the research group has had three honours in chemistry students.

#### 1.5 Problems

Problems lie mainly in the reliance on the apparatus. In initially extending the machine for cation capabilities there may lie some unforeseen nuances that will cause delay. As the research group is of a substantially larger size this year there will be some problems with scheduling usage times. The increased usage also increases the risk of chronic machine failure and the general need for maintenance.

#### 2 Benefits

This project provides an opportunity to measure fundamental interactions on the molecular scale. These interactions are useful both in the comparison to existing theory and the potential to make predictions for the behaviour of the molecules. Such behaviours have vital implications in atmospheric chemistry, a field critical to the understanding of climate behaviour. The research also provides an insight into the behaviour of stellar bodies and how they might be observed in a laboratory environment

#### 3 Publications

The Wild group currently has a strong base of publications studying anionic species [4] [2] [3]. There is a research group from Melbourne university that is using a similar set-up to measure cationic species [6] [5] [1] this also opens up the potential for collaboration in this field.

#### 4 Costs

All changes to equipment have already been budgeted or are of minor functional difference. All manpower costs are already accounted for. There is the potential cost of new computing equipment for the honours/masters students of approximately 1100 dollars. There will be a conference in December 2013 that will require 400 dollars airfare and 500 dollars for conference fees.

#### References

- V. Dryza, E. J. Bieske, A. A. Buchachenko, and J. Kłos. Potential energy surface and rovibrational calculations for the mg[sup +]-h[sub 2] and mg[sup +]-d[sub 2] complexes. *The Journal of Chemical Physics*, 134(4):044310, 2011.
- [2] Lin Hian Quak Marcus Kettner Stephen G. Dale Allan J. McKinley Duncan A. Wild Kim M. Lapere, Rob J. LaMacchia. The bromide-carbon monoxide gas phase complex: Anion photoelectron spectroscopy and ab initio calculations. *Australian Jour*nal of Chemistry, 457(65), 2012.
- [3] Kim M. Lapere, Robert J. LaMacchia, Lin H. Quak, Marcus Kettner, Stephen G. Dale, Allan J. McKinley, and Duncan A. Wild. Anion photoelectron spectra and ab initio calculations of the iodide–carbon monoxide clusters: I–…(co)n, n = 1–4. The Journal of Physical Chemistry A, 116(14):3577–3584, 2012.

- [4] K.M. Lapere, R.J. LaMacchia, L.H. Quak, A.J. McKinley, and D.A. Wild. Anion photoelectron spectroscopy and ab initio calculations of the gas phase chloride-carbon monoxide complex: Cl-...co. *Chemical Physics Letters*, 504(13):13 – 19, 2011.
- [5] B. L. J. Poad, V. Dryza, A. A. Buchachenko, J. Kłos, and E. J. Bieske. Properties of the b[sup + ]-h[sub 2] and b[sup + ]-d[sub 2] complexes: A theoretical and spectroscopic study. *The Journal of Chemical Physics*, 137(12):124312, 2012.
- [6] B. L. J. Poad, V. Dryza, J. Kłos, A. A. Buchachenko, and E. J. Bieske. Rotationally resolved infrared spectrum of the na[sup + ]-d[sub 2] complex: An experimental and theoretical study. *The Journal of Chemical Physics*, 134(21):214302, 2011.

# Summary of work

At the beginning of the project I undertook the laser saftey course and was learnt how to opperate the laboratory aparatus. While a few experiments of colleagues were concluding I assisted in the production and debugging of some circuit boards. When the machine had suffered a serious malfunction we disassembled, cleaned and reassembled parts of it. I learnt how to produce gas mixes and started experimental work on the chloride acetylene complexes. I recorded several days worth of Chloride spectra before machine conditions deteriorated at which point more machine maintainance was required. I help in the implementation of a new voltage source and testing for a new pulse discriminator. I finished recording the bromide and Iodide spectra. In the rest of the research period experimental work was focused on trying to fix problems occuring in the machine as well as testing the setup for the SEVI. Work on coding for the fitting began. I implimented a shceme to collect and analyse the data, though it is not entirely finished to collate the results and has many manual inputs needed. The data I have collected and analysed has been used in conjuction with a paper being written by Duncan Wild soon to be submitted to Chemical Physics Letters on which I will appear as a co-author.