# Halogens and the Carbon-Carbon Double Bond: Spectroscopy and Theory

Damien 't Hart

Supervisor: Duncan Wild

Honours Thesis submitted as part of the B.Sc. (Honours) degree in the School of Chemistry and Biochemistry University of Western Australia

Date of submission: 04/11/16

#### Abstract

This project investigated the halogen carbon-carbon double bond interactions by studying the Bromine-Ethylene and Iodine-Ethylene clusters. These clusters were interrogated using the techniques of coupled Time Of Flight-Mass Spectrometry and Photoelectron Spectroscopy combined with ab initio calculations. The experimental methods determined that the clusters have an electron binding energy of 3.432 eV, 3.904 eV and 3.118 eV, 4.056 eV for Bromine and Iodine respectively caused by the  ${}^{2}P_{3/2} \leftarrow {}^{1}S_{0}$  and  ${}^{2}P_{1/2} \leftarrow {}^{1}S_{0}$  transitions. The experimental results showed a positive stabilisation energy indicating that in the Halogen-Ethylene clusters the electron is more strongly bound than in the Halogens. The computational results predict lower electron binding energies while retaining the relative peak positions and splitting. Computational methods were primarily applied to determine the cluster geometries, finding two possible anion geometries, and one neutral geometry.

I certify that the substance of this thesis has not been previously submitted for any degree or diploma.

I Certify that, to the best of my knowledge, any help received in preparing this thesis, and sources used, have been acknowledged in the thesis,

Damien 't Hart04/11/2016

. . . . . . . . . . . . . . .

# Acknowledgements

It has reached the section of this document where you must inevitably wade through a list of people without whom I would not have completed this thesis, so please bear with me, or skip ahead, it's entirely up to you. First of all I would like to thank my supervisor Duncan Wild, thanks for the opportunity to play with the machine, it was a steep learning curve, but without a doubt worth it. Your can do attitude really helped convince me that I could get some results, even if we cut it a little close, thanks for an interesting and educational year.

Secondly thanks to the Wild group members, Peter and Tim, its been great to see others doing the same things, and the occasional chat.

Thanks to the workshop staff of the Bayliss building, without your skills, readily available, we wouldn't have a machine or results.

Finally I'd like to thank my family and friends, at times I may have been a little preoccupied but you're all stuck around despite it, thanks for all the moral support.

# Contents

1	Inti	itroduction									
	1.1	Atmos	spheric Chemistry	1							
		1.1.1	Halogens	1							
		1.1.2	Ethylene	2							
	1.2	Motiv	ration and Aims	2							
	1.3	Curre	nt Literature	3							
	1.4	Theor	у	4							
		1.4.1	Potential Energy Surfaces	4							
		1.4.2	Time of Flight	5							
		1.4.3	Time of flight-Mass Spectrometry	6							
		1.4.4	Time of Flight-PhotoElectron Spectroscopy	6							
	1.5	Comp	outational Methods	7							
		1.5.1	The Schrödinger equation	7							
		1.5.2	Born-Oppenheimer Approximation	8							
		1.5.3	Hartree-Fock	8							
		1.5.4	Level of Theory	9							
		1.5.5	Møller-Plesset Perturbation Theory	9							
		1.5.6	Coupled Cluster Theory	10							
<b>2</b>	Me	thods		11							
	2.1	Exper	imental	11							
		2.1.1	Gas mixing station	11							
		2.1.2	Gas mixture ratios	13							
		2.1.3	Gas expansion	14							
		2.1.4	Ion production	16							
		2.1.5	Ion selection	17							
		2.1.6	Beam steering	18							
		2.1.7	Photoelectron production	19							

		2.1.8	Photoelectron steering	20
		2.1.9	Timing	20
		2.1.10	Time of Flight Mass Spectroscopy	21
		2.1.11	Optimising Mass Spectra	21
		2.1.12	Photoelectron Spectra	22
		2.1.13	Optimisation the Photoelectron Spectra	23
	2.2	Comp	itational Methods	23
		2.2.1	Potential Surface Scans	23
		2.2.2	Geometry Optimisation	24
		2.2.3	Vibrational Frequencies	25
	2.3	Data t	reatments	25
		2.3.1	TOF conversions	25
		2.3.2	TOF-MS data treatment	25
		2.3.3	TOF-PES data treatment	26
		2.3.4	The Jacobi transformation	27
3	$\operatorname{Res}$	ults an	d Discussion	29
3	<b>Res</b> 3.1	<b>ults an</b> Experi	d Discussion	<b>29</b> 29
3	<b>Res</b> 3.1	ults an Experi 3.1.1	d Discussion mental	<b>29</b> 29 29
3	<b>Res</b> 3.1	ults an Experi 3.1.1 3.1.2	ad Discussion         mental	<ul> <li>29</li> <li>29</li> <li>29</li> <li>29</li> <li>29</li> </ul>
3	<b>Res</b> 3.1	ults an Experi 3.1.1 3.1.2 3.1.3	ad Discussion         mental	<ul> <li>29</li> <li>29</li> <li>29</li> <li>29</li> <li>31</li> </ul>
3	<b>Res</b> 3.1 3.2	ults an Experi 3.1.1 3.1.2 3.1.3 Compu	ad Discussion         mental	<ul> <li>29</li> <li>29</li> <li>29</li> <li>29</li> <li>31</li> <li>34</li> </ul>
3	Res 3.1 3.2	ults an Experi 3.1.1 3.1.2 3.1.3 Compu 3.2.1	ad Discussion         mental	<ol> <li>29</li> <li>29</li> <li>29</li> <li>31</li> <li>34</li> <li>34</li> </ol>
3	Res 3.1 3.2	ults an Experi 3.1.1 3.1.2 3.1.3 Compu 3.2.1 3.2.2	ad Discussion         mental	<ul> <li>29</li> <li>29</li> <li>29</li> <li>29</li> <li>31</li> <li>34</li> <li>34</li> <li>35</li> </ul>
3	Res 3.1 3.2	ults an Experi 3.1.1 3.1.2 3.1.3 Compu 3.2.1 3.2.2 3.2.3	ad Discussion   mental	<ul> <li>29</li> <li>29</li> <li>29</li> <li>31</li> <li>34</li> <li>34</li> <li>35</li> <li>37</li> </ul>
3	<b>Res</b> 3.1 3.2	ults an Experi 3.1.1 3.1.2 3.1.3 Compu 3.2.1 3.2.2 3.2.3 3.2.4	and Discussion         mental	<ul> <li>29</li> <li>29</li> <li>29</li> <li>31</li> <li>34</li> <li>35</li> <li>37</li> <li>40</li> </ul>
3	<b>Res</b> 3.1 3.2	ults an Experi 3.1.1 3.1.2 3.1.3 Compu 3.2.1 3.2.2 3.2.3 3.2.4 3.2.5	and Discussion         mental	<ul> <li>29</li> <li>29</li> <li>29</li> <li>31</li> <li>34</li> <li>34</li> <li>35</li> <li>37</li> <li>40</li> <li>40</li> </ul>

# References

 $\mathbf{47}$ 

# Chapter 1

# Introduction

Clustering occurs when atoms and molecules interact without a chemical reaction taking place. These clusters, not bound by traditional bonds are sometimes called van der Waals clusters,<sup>1</sup> and are clearly bound by intermolecular forces, such as dipole-dipole, dipole-induced dipole, ion-dipole, or dispersion forces. Clusters are widely found in nature both in our atmosphere<sup>2</sup> and in space.<sup>3</sup> Targeted gas phase spectroscopic techniques, such as mass spectrometry and Infrared (IR) spectroscopy,<sup>4</sup> can be used to study clusters<sup>3</sup> and to determine their size and composition.

## **1.1** Atmospheric Chemistry

The atmosphere is an immensely complicated system containing literally thousands of reactive species. As the implications of atmospheric chemistry have been appearing in the media for quite some time now there is a growing public awareness and desire to more accurately model the system.

#### 1.1.1 Halogens

Within the realm of atmospheric chemistry the halogens have received a great deal of attention.<sup>5</sup> Defined as the group 17 elements on the periodic table, from a cursory understanding of the periodic table halogens posses a strongly bound valence shell, resulting in high electro-negativity. Halogens enter our atmosphere by various different paths, from the well known example of CFC's to the less well known marine boundary layer,<sup>5</sup> but irrespective of the source once halogens enter our atmosphere they begin to take part in many reactions. Many of these reactions lead to reservoir species, which can act as something of an atmospheric taxi, carrying the halogen a certain distance before an interaction, often with a photon, releases the halogen

to react again. Ozone destruction by halogens is a simple example of this reservoir system,

$$X + O_3 \to XO + O_2, \tag{1.1}$$

here a reservior species XO is formed, which can be recycled in a number of different ways.

$$XO + XO \to X + X + O_2 \tag{1.2}$$

$$XO + H_2O \to XOH + OH$$
 (1.3)

$$XOH + hv \to X + OH \tag{1.4}$$

Where Equations 1.2-1.4 represent various recycling mechanisms. In order to understand fully how halogens travel through the atmosphere, the way halogens interact with other systems must be understood, including with the carbon-carbon double bond.

#### 1.1.2 Ethylene

Ethylene is unique, it contains the simplest possible carbon-carbon double bond and it is found in our atmosphere,<sup>6</sup> the atmosphere of Titan<sup>7</sup> and in the depths of space. This ubiquitous molecule has a strong effect on plants, cited as a 'potent plant growth hormone' it is also capable of causing changes in plant growth patterns,<sup>8</sup> and documented as an essential part of the ripening of bananas and other fruits.<sup>9</sup> But beyond this as a pollutant of interest, current data shows that ethylene levels in the atmosphere are rising as a result of increased biofuel and biomass burning.<sup>9</sup> With so many sources and increasing concentrations, understanding the interactions between halogens and ethylene is an area of growing importance.

### **1.2** Motivation and Aims

The motivations behind this project are three fold,

1. Improve our understanding of the field of terrestrial chemistry

- 2. Provide valuable insight into extraterrestrial atmospheric chemistry
- 3. Provide insight into ion interactions and transport in extraterrestrial gas clouds

This project aims to study halogen ethylene clusters using a coupled time of flight mass spectrometry (TOF-MS) and photoelectron spectroscopy (PES) approach. These aims will be achieved by collecting data that will be used to elucidate the structure and intermolecular bonding of these halogen ethylene clusters. The experimental results will be reinforced with computational chemistry allowing the determination of the structures of the anion and neutral clusters.

## **1.3** Current Literature

Previously the  $(Cl^-/Br^-)...C_2H_4$  systems have been studied using a tandem mass spectrometer (MS) coupled with IR, where the first MS selected the ion of interest, while the second detects the products after interaction with IR.<sup>4</sup> This study determined that the anion clusters can take either a bent or T-shaped geometry as seen in Figure 1.1. A similar study examined the  $(Cl^-/Br^-/I^-)...C_2H_2$  systems using



Figure 1.1: The anion cluster geometries (left bent, right T-shaped)<sup>4</sup>

a coupled TOF-MS/PES technique. This study showed acetylene has two neutral structures, due to differences in shape ethylene is predicted assume the T-shaped neutral geometry, in addition it offers carbon-carbon triple bond data for comparisons.<sup>10</sup> A coupled TOF-MS/PES study of the  $(Cl^{-}/Br^{-}/I^{-})...C_{2}H_{4}$  is a natural extension of these studies.

There is also a series of previous Wild group papers examining a range of other halogen-gas systems using the TOF-MS/PES technique that attest to the robustness of the chosen methods.<sup>11–15</sup> Also heavily studied is the halogenation pathway of ethylene<sup>16–22</sup> in an attempt to understand the mechanics of addition to the carbon-carbon

double bond. The geometry of the halogenation intermediate, as seen in Figure 1.2, bears a strong resemblance to the predicted neutral cluster geometry. This similarity implies that the neutral cluster is the halogenation intermediate, expanding the applicability of the results obtained. This study will also provide useful information for modelling solvent-solute systems. Although there are all the mentioned studies there are no records of a TOF-MS/PES study of the halogen ethylene clusters.

## 1.4 Theory



#### 1.4.1 Potential Energy Surfaces

At the heart of physical chemistry lies the laws governing the behaviour of all systems, which if fully exFigure 1.2: The halogenation intermediate of diatomic Iodine<sup>19</sup>

pressed allow for the understanding of all physical systems. One such set are the laws of thermodynamics, from a physical understanding of these laws it is clear that physical systems tend to decrease the free energy in the system. This decrease, while still obeying the law of conservation of energy, tends towards a minimum energy value, every system having its own set of unique minima.

This concept is best explained by considering the simplest example,  $X_2$  (where X is any diatomic molecule). If the  $X_2$  molecule is the system, then the system has one variable that can change, the bond length, thus if the potential energy of the system is plotted against bond length then the plot like Figure 1.3 is produced. A technical note at this point, since potential energy is a dependant variable it is removed from the dimension count, thus Figure 1.3 is a 1D plot and if there were two variables, for example bond length and bond angle of a triatomic molecule, the plot would be 2D and so on. The number of dimensions that a system posses is equal to the number of degrees of freedom which for linear molecules is found using, DOF = 3N - 5, or for non-linear molecules, DOF = 3N - 6, where N is the number of atoms in the system.

Since the system is tending towards minimum energy the preferred conformation



Figure 1.3: Sample potential energy surface

will be at the lowest point on the graph. If a system possesses several minima then the lowest energy value will be at the conditions of the most thermodynamically favoured conformation. In computational chemistry the process of moving towards this conformation is called 'geometry optimisation', which will be used to determine the geometries of the halogen-ethylene clusters.

#### 1.4.2 Time of Flight

The equipment used collects time of flight data, this section outlines the basics needed to understand the applications outlined in the following sections.

Time of flight measurements rely on an elegant manipulation of the fundamental definitions of velocity

$$v = \frac{L}{t},\tag{1.5}$$

and kinetic energy

$$KE = \frac{1}{2}mv^2, \tag{1.6}$$

these can be combined to give

$$KE = \frac{1}{2}m(\frac{L}{t})^2.$$
 (1.7)

TOF systems being of fixed size (L) use detectors to record time of arrival (t), which according to Equation 1.7 defines the velocity as a function of KE and mass (m). Practically this means that two types of TOF systems are possible, systems with fixed KE and system with fixed mass.

#### 1.4.3 Time of flight-Mass Spectrometry

TOF-MS makes KE a fixed value allowing explicit solutions of Equation 1.7 that give the mass of the sample submitted for analysis. A more physical explanation is that since every ion submitted to the TOF-MS is accelerated through the same potential field all ions are given the same KE. From an understanding of Equation 1.7 this means that the heavier a particle the slower it will be, leading to a separation of particles by mass causing t to be directly related to m.

#### 1.4.4 Time of Flight-PhotoElectron Spectroscopy

TOF-PES records the TOF of electrons. Since this method only studies electrons, and all electrons have the same mass (9.10938356  $\times 10^{-31}$ kg) Equation 1.7 can be solved for the *KE* of the electrons. On its own the energy of an electron is a vague value of minimal interest. Yet when considered in light of Einstein's description of the photoelectric effect

$$KE = hv - BE, (1.8)$$

where hv is the photon energy and BE is the electron binding energy, it becomes clear that knowing the kinetic energy can be useful. Equation 1.8 is the mathematical expression of the photoelectric effect, which describes the interactions of an incoming photon with an electron bound to an atom, molecule, clusters of molecules or indeed liquid and solid samples. If the incoming photon has sufficient energy the electron will overcome the BE and be ejected from the atom or molecule with a specific KE. From Equation 1.8 it can be seen that this KE will be the difference between the photon's energy and the BE. In TOF-PES the energy of the incoming photon is a known constant. Combining Equations 1.7 and 1.8 gives

$$\frac{1}{2}m(\frac{L}{t})^2 = hv - BE,$$
(1.9)

which rearranged to make BE the focus gives

$$BE = hv - \frac{1}{2}m(\frac{L}{t})^2.$$
 (1.10)

Thus TOF-PES from electron energy can give the binding energy, a very interesting and important quantity. In terms of this project the BE will be influenced by the states of the neutral halogen-ethylene complex (i.e. rotational, vibrational and electronic states).

## **1.5** Computational Methods

Quantum computational chemistry is the process of solving variations on the Schrödinger equation in order to determine system properties such as the energy, geometry and vibrational frequencies. This section outlines some of the theoretical methods used.

#### 1.5.1 The Schrödinger equation

The starting point for computational quantum chemistry is the Schrödinger equation. The Time Independent Schrödinger Equation (TI-SE) given by

$$\hat{H}\psi = E\psi, \tag{1.11}$$

serves as the equation that computational 'quantum' chemistry aims to solve. Despite the fact that solutions to the TI-SE in principle provide nearly exact information about systems with light-weight nuclei the rapid increase in complexity with the size of system renders it analytically unsolvable for most systems. As a work around it is possible to create an iterative solver that works through the variables and attempts to find a solution by trial and error. There are a variety of approximations used to find approximate solutions to the TI-SE and this body of methods forms the field of computational 'quantum' chemistry.

#### 1.5.2 Born-Oppenheimer Approximation

The idea that electrons and nuclei move at vastly different speeds and thus can be treated separately has a special meaning when applied to the TI-SE. The difference in speed means that electrons can be considered to be travelling through a constant field created by the nuclei, or that electronic interactions do not have a dynamic relationship with the nuclei, rather the nuclei provides a constant force 'field' that can be treated as fixed. This explicit separation of nuclei and electrons serves to simplify the TI-SE and serves as a starting point for the quantum chemical methods considered.<sup>23</sup>

#### 1.5.3 Hartree-Fock

Hartree Fock (HF) methods are briefly introduced here. HF methods operate on the principle that the wavefunction can be approximated by a single Slater determinant and can be used to solve for the HF energy as follows,

$$E_{HF} = \int \Phi_{HF}^* \hat{H} \Phi. \tag{1.12}$$

Where  $\Phi_{HF}^*$  is the approximated wavefunction. An anti-symmetry operator is included in the wavefunction that prevents electrons of the same spin occupying the same orbital. The HF method tends to be less accurate than more sophisticated methods, which take into account electron correlation, in general leading to computational energies higher than the true energy. HF is often used as the reference wavefunction for other methods such as MP2 or CCSD(T).<sup>13,24</sup>

#### 1.5.4 Level of Theory

In computational chemistry tasks are performed at what is called a level of theory, which is composed of a method and a basis set. The methods are sets of approximations that can be used to create approximate solutions to the TI-SE, while the basis sets are sets of mathematical expressions that describe atomic orbitals centred on each atom. The methods used in this project are described as post-Hartree Fock methods, meaning that they are built on the HF wavefunctions. These methods are second order Møller Plesset perturbation theory (MP2) and Coupled Cluster theory with single, double and perturbative inclusion of triplet excitations (CCSD(T)). The basis sets used are Dunning's augmented correlation consistent polarised valence N zeta basis sets where N is Double, Triple and Quadruple (aug-cc-pVNZ, N=D or T).

#### 1.5.5 Møller-Plesset Perturbation Theory

Perturbation theory is an adaptation designed to deal with unsolvable problems. The basic principle is that for every unsolvable version of the TI-SE the Hamiltonian can be broken into two parts, a solvable component and a perturbation,<sup>25</sup>

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}^{(1)},$$
(1.13)

where  $\hat{H}$  is the original Hamiltonian,  $\hat{H}_0$  is the solvable component and  $\hat{H}^{(1)}$  is the perturbation,  $\lambda$  is a number with values between 0 and 1 that varies the effect of the perturbation on the system. When  $\lambda$  is 0 the system contains no perturbation and can be solved exactly, however when  $\lambda$  is not 0 the system contains a perturbation and the solution, i.e. the wavefunction or energy, can be found as a polynomial in powers of  $\lambda$ ; the coefficients of this polynomial are determined by linear equations (involving the solvable part and the 'matrix elements' of the unsolved part,  $\hat{H}^{(1)}$ , in terms of the solved part). Since these linear equations involve many terms an iterative solver is applied.

In this project the particular type of perturbation theory used is called Møller-Plesset perturbation theory (MP). In MP theory the first component of the Hamiltonian  $\hat{H}_0$  is the HF Hamiltonian while the second component  $\hat{H}^{(1)}$  is the full many-electron Hamiltonian minus the HF Hamiltonian. In MP theory the polynomial order can be increased to improve the accuracy of the method, at the cost of increased computation time, in this study second order polynomials are used defining the method as MP2.

#### 1.5.6 Coupled Cluster Theory

Coupled Cluster (CC) like MP builds on the HF, but unlike MP CC does not use perturbation theory, rather it adds determinants to the wavefunction that describe electronic excitations. These additional determinants allow explicit solutions of the energy in a series of excited states.<sup>26,27</sup> The determinants allow pairs of electrons to 'escape' each other by temporarily occupying another higher energy orbital thus reducing the overall repulsion. While the theory of allowing excitations can technically be extended from singlet to doublet to triplet and so on 'infinitely' most CC tasks stop at single and double excitations, (CCSD) as the computational cost to exceed this are currently prohibitive. An interesting compromise is the combination of CCSD with perturbative approximations of triple excitations, offering a compromise between accuracy and computation time, giving the method used in this study CCSD(T). Currently CCSD(T) is at the forefront of computational chemistry, representing the gold standard in calculating accurate potential energy surfaces.

# Chapter 2

# Methods

This chapter describes the experimental and theoretical set-up and methods used. In particular it will address the make up and use of the coupled TOF-MS/PES, while also explaining the motivations behind the choices made. The rational behind the computational methods applied is also considered. As this project features both theory and experimental methods only a cursory description of the theory used will be given.

## 2.1 Experimental

The Wild group operates a custom built coupled TOF-MS/PES spectrometer as seen in Figure 2.1. The schematic, taken from Dr K. Lapere's thesis,<sup>13</sup> is missing the secondary set of XY deflection plates located between the second einzel lense and the laser interaction chamber.

#### 2.1.1 Gas mixing station

The gas mixtures were prepared using the gas mixing station as seen in Figure 2.2. The carrier and neutral gasses in all species were respectively high purity Argon and industrial grade Ethylene, connected to the mixing station with teflon lines. The halogen sources used were carbon tetrachloride ( $CCl_4$ ), dibromomethane ( $CH_2Br_2$  and iodomethane ( $CH_3I$ ). The halogen sources are delivered into the gas mixing station by the vapour pressure of the liquid in the sample vial.

The steps to create a mixture are as follows

- 1. The gas mixing station is pumped out to a pressure of  $1 2 \times 10^{-2}$  Torr
- 2. The halogen source is subjected to freeze, pump, thaw cycles to remove dis-



Figure 2.1: The Wild group coupled  $TOF-MS/PES^{13}$ 

solved gasses

- 3. The gas mixing station is flushed with Argon and pumped out again, repeat three times, to reduce traces of other mixtures
- 4. The pressure is maintained at  $1 2 \times 10^{-2}$  Torr for about 10 minutes to ensure adsorbed material is removed
- 5. The pure halogen source is opened to the gas mixing station for between one and three minutes
- 6. Approximately 40 kPa of ethylene is added
- 7. The pressure of the gas mixture is made up to 400 kPa with Argon

The freeze, pump, thaw cycle mentioned above is a process used to purify liquid samples. The source is added to the sample vial and attached to the gas mixing



Figure 2.2: Schematic representation of the gas mixing station<sup>13</sup>

station, then frozen with liquid nitrogen. The liquid nitrogen is then removed and the sample exposed to vacuum, in this manner any nitrogen and oxygen in the mixture should evaporate and be removed. This process is repeated three times or until there is no pressure spike in the system when exposing the sample to vacuum. In order to control the amount delivered the sample vial was cooled with ice water slurry and opened for a timed interval.

#### 2.1.2 Gas mixture ratios

While the approximate mixing ratios presented may appear to be arbitrary there is an underlying logic. Clearly if there is too little of the halogen source clusters will not form in sufficient quantities and on the other hand if too much of the halogen source is added then the ion production is dominated by larger halogen source clusters. An example of this is seen in Figure 2.3. In this case the source is iodomethane and the partial pressure, while not known explicitly, is approximately 5%. The clusters forming here are numerous iodomethane molecules clustered around a single iodide atom. Where the cluster size can be seen to range from 1 to 28 Iodomethane molecules per Iodine molecule.



Figure 2.3: Time of Flight spectrum of clusters produced from a gas mixture rich in iodomethane. Note the long progression of clusters of the form  $I^{-} \dots [CH_3I]_n$ 

#### 2.1.3 Gas expansion

The gas mixture is released into the source chamber by a pulsed solenoid valve (General Valve Series 9, Parker Hannifin), in a supersonic expansion. The nozzle used contains a magnetic armature, a pair of springs, a sealing poppet and the casing. Built into the casing is a coil of wire that acts as an electromagnet and draws the armature and sealing poppet back against a spring when pulsed on, allowing gas to flow into the chamber. The springs return the armature and sealing poppet to the closed position when the coil is off. The nozzle is pulsed at 10 Hz, and the relative pulse timing of the nozzle can be found in Figure 2.8.

Supersonic expansions reliably produce a narrow range of velocities based on the mass of the carrier gas. When the mixture expands the majority of the collisions the source and neutral species undergo are with carrier gas molecules, this leads to a form of energy averaging amongst the molecules in the mixture where the majority of molecules have a similar velocity. An example of this energy averaging can be found in Figure 2.4 where the velocity profile of an expanding ammonia mixture seeded with Xenon is compared to both a pure ammonia mixtures velocity profile and the Boltzmann distribution. The Boltzmann distribution is included here as the velocity profile of a gas mixture not undergoing an expansion. The narrow velocity profile, compared to the Boltzmann distribution, can significantly increase spectroscopic resolution.



Figure 2.4: Velocity profiles for different gas mixtures undergoing expansion compared to the Boltzmann distribution<sup>28</sup>

For spectroscopic experiments it is beneficial to have a large proportion of the population in the ground state. The thermodynamics of a gas expansion requires energy, given an expansion into a vacuum this energy must come from the expanding gas. The energy consumed will be drawn from the most readily available source first, in this case depopulating the higher energy levels and causing a reduction in temperature. Supersonic expansions can in this way produce a gas mixture that largely populates the ground state, offering resolution improvements for subsequent spectra.<sup>23</sup>

Following the expansion ion formation occurs, as outlined in the next section. Once

ion formation is complete the expansion reaches a skimmer that only allows passage of the centre of the expansion, creating a molecular beam with a uniform velocity profile and a large ground state population.

#### 2.1.4 Ion production

In the source chamber there is a rhenium filament with a concave shield, the shield is pulsed to a bias voltage to promote the ejection of electrons. Typically the shield is pulsed from 0 V to -500 V. These electrons are focussed by a small einzel lens assembly and intersect the expansion. As a result of the intersection soft ionisation of the buffer gas occurs, as outlined in Equations 2.1 to 2.4.

$$Ar + e_{fast}^- \to Ar^+ + e_{slow}^- + e_{fast}^- \tag{2.1}$$

$$e_{slow}^- + CH_2Br_2 \to [CH_2Br_2^-]^* \tag{2.2}$$

$$[CH_2Br_2^-]^* \to [CH_2Br]^* + Br^-$$
 (2.3)

$$Br^- + C_2 H_4 \to Br^- \dots C_2 H_4 \tag{2.4}$$

Alternatively cluster formation may occur as outlined in Equations 2.5 and 2.6.

$$CH_2Br_2 + nC_2H_4 \to CH_2Br_2\dots(C_2H_4)_n \tag{2.5}$$

$$e_{slow}^- + CH_2Br_2\dots(C_2H_4)_n \to [CH_2Br]^* + Br^-\dots(C_2H_4)_{(n-m)} + mC_2H_4$$
 (2.6)

It is also possible for larger clusters to form at this stage. Equations 2.7 and 2.8 show a potential path for the formation of the clusters seen in Figure 2.3.

$$e_{slow}^- + CH_3I \to [CH_3]^* + I^-$$
 (2.7)

$$I^{-} + n[CH_3I] \to I^{-} \dots [CH_3I]_n \tag{2.8}$$

Cluster formation is believed to be due to the mechanism outlined in Equations

2.1 to 2.4 as the large number of collisions during the expansion are assumed to destroy clusters formed earlier. The source chamber is thus believed to be where formation of clusters occurs and formation is dependent on the variables present here, being nozzle pulse timing, electron pulse width, timing and energy and the level of vacuum.

#### 2.1.5 Ion selection

The extraction chamber contains two components of note, the TOF plates and the first set of XY deflection plates, this section focuses on the purpose and operation of the TOF plates while XY deflection plates will be addressed in a later section. The two TOF plates are set such that the voltage across one plate is greater than the other, creating a field that directs negatively charged species towards the plate with the lower voltage. Figure 2.5 shows how this is used to selectively discard neutral and positively charged species



Figure 2.5: Schematic representation of Ion passage through the TOF plate assembly<sup>13</sup>

Given that the voltages on the two plates can be explicitly controlled the energy per unit charge transferred is a controlled variable, this is one of the primary criteria for performing ion based TOF-MS. This particular method of ion acceleration has a unique benefit, space focussing. Space focussing effectively allows one to modify the point of maximum beam density, for example when taking mass spectra this intensity is focussed at the detector.

The TOF plates are pulsed at 10Hz with a suitable delay relative to the nozzle pulse, as seen in Figure 2.8.

#### 2.1.6 Beam steering

Beam steering is achieved by the use of two sets of XY deflection plates and two einzel lenses. The XY deflection plates used contain two X plates and two Y plates where each plate is set at a voltage from -100 V to 100 V. The plates are kept at this voltage and create a constant field that modifies the path direction in the XY plane (direction of travel is assumed to be along the Z axis) allowing the beam to be moved up or down and from side to side.

Since the beam only contains the negatively charged species there is a repulsive spreading of the ions during their transit through the TOF spectrometer. The einzel lense as seen in Figure 2.6 is used to reduce the beam radius. It is made of three cylinders, the outer two at ground potential while the central cylinder is set at a negative voltage, which creates the electrical field seen in Figure 2.6. Since the beam contains only negatively charged species they are repelled by the electrical field and form a narrower beam, compensating for the repulsive beam spreading.



Figure 2.6: Schematic representation of an einzel lenses operation<sup>23</sup>

The XY deflection plates and einzel lenses are used together to direct the beam from

the extraction chamber to the ion detector and adjust the beam path such that laser overlap in the laser interaction chamber is possible.

#### 2.1.7 Photoelectron production

In order to take photoelectron spectra the laser radiation needs to overlap both temporally and spatially with the ion of interest, this overlap takes place in the laser interaction chamber as seen in Figures 2.1 and 2.7. Photodetatchment is achieved by use of a 266 nm (4.66 eV) laser beam, produced by a Spectra-Physics Quanta-Ray<sup>®</sup> laser and a series of optics that produce the fourth harmonic of the Nd:YAG (Neodynium:Yttrium Aluminium Garnate  $Y_3Al_5O_{15}$ ) laser which is pulsed at 10 Hz.



Figure 2.7: Schematic representation the laser interaction and of a magnetic bottle directing photoelectrons<sup>13</sup>

#### 2.1.8 Photoelectron steering

Photoelectrons are directed into the photoelectron tube by a magnetic bottle, as seen in Figure 2.7. The magnetic bottle is effective as electrons as moving charges have a magnetic field and can be acted upon by external magnetic fields, small magnetic fields are able to induce a large change in direction as electrons are very light. The magnetic bottle used in this project is a fixed magnet, rather than a pulsed solenoid magnet, but the same theory can be applied.

To avoid any other magnetic fileds playing a role the photoelectron tube is covered with a  $\mu$  metal shield that reduces the effects of external magnetic fields.

#### 2.1.9 Timing

The machine is designed for several components to be pulsed at 10 Hz, allowing the collection of 10 spectra per second. The pulse timing diagram found in Figure 2.8 is an idealised pulse diagram and several comments need to be made.

First the machine is operated by firing channel A, and all pulses are relative to this initial pulse, as depicted by the dotted line on the left hand side of the pulse diagram. However electrical current, and even laser beams have travel times, while the system technically operates with the delays as depicted in the timing diagram, and indeed for the human observer it appears to, there are several delays in the system that have been compensated for.

Second, the flash lamp and Q-switch are two independent pulses, where the Q-switch can be pulsed after 173 µs which is the time required for the flash lamp to build the excited state population of the  $Nd^{3+}$  cations in the Nd:YAG rod to the point where the Q-switch is fired. Not shown here is that the Q-switch pulse length is 5 ns. As in the first point, the laser does not instantaneously reach the laser interaction chamber.

Third, the laser beam appears to generate a peak in the PE spectrum. This peak is included here as the arrival of the laser pulse starts the timer for the photoelectron time of flight, or in other words the photoelectron time of flight is relative to the arrival of the laser pulse.

## 2.1.10 Time of Flight Mass Spectroscopy

The theory of a TOF-MS has already been covered in the introduction. The particular operation of the Wild group TOF-MS is as follows



Figure 2.8: Timing Diagram showing the relative timeing of all pulsed components

#### 2.1.11 Optimising Mass Spectra

The procedure for finding and optimising a mass spectrum from unknown conditions is as follows

#### 1. Set the

- XY deflection plates to 0 V
- Einzel lenses to -35 V and -90 V
- Nozzle to 220 V-240 V and  $190 \,\mu\text{s}$
- Electron current and voltage respectively to  $3.90 \,\mathrm{A}$  and  $-500 \,\mathrm{V}$
- TOF timing to 700 µs
- 2. Scan the electron timing
  - If the mass spectrum is found skip ahead to step 3
  - If the mass spectrum is not found increase the timing by 5 µs and repeat step 2
- 3. Modify the conditions in step 1 till the conditions giving a maximum signal are found

Some typical conditions are given in Table 2.1.

Apparatus	Setting	Units
Nozzle Voltage	285	V
Nozzle Width	180	$\mu s$
Electron Current	3.80	А
Electron Voltage	-461	V
Electron Einzel Lense	-285	V
TOF Plates	-1000, -900	V
TOF Timing	904	$\mu s$
Set one		
X1, X2	-33, -76	V
Y1, Y2	-67, 54	V
Set two		
X1, X2	14, -74	V
Y1, Y2	-54, 0	V
Einzel 1	-30	V
Einzel 2	-94	V

Table 2.1: Typical TOF-PES operating conditions

#### 2.1.12 Photoelectron Spectra

With the mass spectrum optimised, and a cluster of interest with a minimum intensity of at least 20 mV, photoelectron spectra can be recorded. To produce PES the laser overlap needs to be set to the ion of interest. Figure 2.8 shows how effectively the laser pulse timing is managed by controlling when the flash lamp is triggered. By adjusting this timing the cluster of interest can be overlapped. The laser pulse width is 5 ns, while ion widths are typically about 100 ns, allowing the accurate selection of a single ion or cluster.

#### 2.1.13 Optimisation the Photoelectron Spectra

When recording the PES one typically uses the same settings for generating mass spectra, with the exception of the TOF Plates, where the space focussing is adjusted by reducing the second voltage by 20-30 V, which increase the number of ions arriving at the laser interaction point at the same time, thereby increasing the yield, or signal strength.

## 2.2 Computational Methods

Computational work for this project has been carried out using Wild group computers and the Pople super computing facilities, housed in the Physics department at UWA. The Wild group computers are set up with Intel i7 processors, 32 GB of RAM, with Linux operating system, and with the Gaussian 09 software installed. The Pople super computer has several nodes dedicated for School of Chemistry and Biochemistry staff and students which has per node 24 cores, 24 GB of RAM with the Gaussian 09 software available through use of a PBS queuing system.

#### 2.2.1 Potential Surface Scans

In the introduction the theory behind generating a potential surface was outlined, and linked to geometry optimisation. The project focus being the determination of cluster structures there needs to be a way to generate 1D or 2D segments of the potential surface for analysis. The Gaussian 09 keyword Scan and a custom script, found here,<sup>\*</sup> were used to generate 1D segments of the potential surfaces.

<sup>\*</sup>http://laser.scb.uwa.edu.au/code.html

The ethylene molecule posses  $D_{2h}$  symmetry, thus any single scan that covers the appropriate 90° segment will provide data that is representative of a complete 360° scan. A series of scans were employed to characterise the potential energy surface and determine how many possible cluster geometries might exist. These scans used a Z-matrix similar to the one found in figure 2.9 where A3 and D1 were the variables of interest.

Х						
Х	1	0.5				
С	1	R1	2	90.0		
$\mathbf{C}$	1	R1	2	90.0	3	180.0
Η	3	R2	1	A1	2	- 90.0
Η	3	R3	1	A2	2	90.0
Η	4	R2	1	A1	2	-90.0
Η	4	R3	1	A2	2	90.0
$\operatorname{Cl}$	1	$\mathbf{R4}$	2	A3	4	D1

Figure 2.9: Z-matrix employed for scanning the geometry to produce the potential surface of the chlorine-ethylene neutral complex. X are dummy atoms, used to better define the geometry

#### 2.2.2 Geometry Optimisation

Using the information from the potential energy scans, the approximate geometries of the two anion clusters and single neutral cluster were optimised at the MP2/augcc-pVTZ level. As time was always marked as a critical factor, effective core potential (ECP) basis sets were employed to reduce the computation time. These basis sets were taken from the EMSL basis set exchange,<sup>31</sup> and are as follows,

- Cl:aug-cc- $pV(N+d)^{33}$
- Br:aug-cc-pVNZ PP<sup>34</sup>
- I:aug-cc-pVNZ PP<sup>35</sup>

in all cases N = D or T

The geometries from the MP2/TZ optimisations were used as starting point for CCSD(T)/TZ optimisations which were run on the Pople super computing cluster, due to time constraints only two of these jobs reached completion.

As the potential wells found in the surface scans were very shallow the convergence criteria were tightened for the geometry optimisations, such that the maximum gradient was  $2 \times 10^{-6}$  hartree/bohr. This was achieved by using the vtight keyword in Gaussian 09. The inclusion of vtight necessitated also the inclusion of Maxcy-cles=N, where N was set to 50, as the additional steps required to reach very tight convergence criteria often exceeded the Gaussian 09 default of 20 steps.

#### 2.2.3 Vibrational Frequencies

To ensure that the stationary points found from the geometry optimisations were minima, vibrational frequency calculations were undertaken, with the presence of one or more imaginary frequencies indicative of a transition state or higher order saddle point. The frequencies were all calculated at the MP2 level with the Gaussian 09 keyword noraman. This keyword was chosen as the raman spectra was not desired.

#### 2.3 Data treatments

This section outlines how the experimental data was treated before being presented in Chapter 3.

#### 2.3.1 TOF conversions

Time of flighte techniques require data treatment to produce standardised data, in particular the recorded TOF must be converted into a usable value, in this project TOF needed to be converted to mass to charge ratio (m/z) and electron binding energy. These conversions were carried out in a series of steps, outlined as follows:

#### 2.3.2 TOF-MS data treatment

- 1. Acquire TOF for peaks of known mass
- 2. Plot mass against TOF to create the calibration curve (see Figure 2.10 for example)

- 3. Extract calibration curve coefficients
- 4. Use calibration coefficients to convert TOF to m/z
- 5. Plot intensity against m/z



Figure 2.10: Calibration curve for TOF to m/z conversion

#### 2.3.3 TOF-PES data treatment

- 1. Acquire TOF of known electron kinetic energies
- 2. Plot electron kinetic energy against  $1/\text{TOF}^2$  to create the calibration curve
- 3. Extract calibration curve coefficients
- 4. Use calibration coefficients to convert TOF to electron kinetic energy
- 5. Subtract the electron kinetic energy from 4.66 eV to get the electron binding energy
- 6. Average PES data

- 7. Smooth PES data using 10 point adjacent-averaging
- 8. Subtract a smoothed background
- 9. Apply the Jacobi transformation
- 10. Plot intensity against electron binding energy

#### 2.3.4 The Jacobi transformation

The raw data collected is in the form of time based intensity against TOF, when TOF is converted to electron binding energy if the intensity is not also converted by some means peak asymmetry is introduced. So a conversion must be found, if the intensity is collected is considered to be time dependant intensity I(t) in the time interval with width dt, transforming the data to a function, lets say, Y(E), requires creating energy intervals for it with width dE, so

$$I(t)dt = Y(E)dE.$$
(2.9)

Since for this system,

$$E(t) = \frac{m_e}{2} \frac{l^2}{t^2},$$
(2.10)

then

$$\frac{dE}{dt} = \frac{A}{t^3},\tag{2.11}$$

where

$$A = m_e l^2. (2.12)$$

Rearranging Equation 2.9 gives

$$Y(E) = \frac{I(t)dt}{dE},$$
(2.13)

and combining Equation 2.13 with Equation 2.11 gives

$$Y(E) = \frac{I(t)}{A}t^3 \tag{2.14}$$

And since A is a constant relating to the mass of an electron and the length of the flight tube it leaves a factor of  $t^3$  as the applicable conversion factor. Or in other words multiply all intensity values by TOF<sup>3</sup> to re-match the data to the electron binding energy values.

# Chapter 3

# **Results and Discussion**

This chapter presents the core results of experimental and computational methods and comments on how these results lead to the completion of the project aims.

### 3.1 Experimental

The results for the experiments are composed of mass spectra that show the clusters formed and photoelectron spectra that provide the electron binding energy.

#### 3.1.1 Ethylene or Nitrogen

A concern during this project was how to differentiate between ethylene and nitrogen. While high resolution mass spectroscopy can differentiate the two species, the four decimal point masses of ethylene and nitrogen are 28.0313 u and 28.0062 u respectively, the TOF-MS used does not posses sufficient resolution to differentiate these two masses. Rather, the TOF-MS simply confirmed the presence of clusters that could be due to ethylene or nitrogen. Instead of relying on the mass spectrum the experimental electron binding energies were compared to the electron binding energies for halogen-nitrogen systems.<sup>11</sup> The experimental electron binding energies were found to be significantly different to the literature values for the halogen-nitrogen clusters.

#### 3.1.2 Mass Spectrum

While TOF-MS were recorded every day PE spectra were collected, and presented here is the spectrum from the  $20^{\text{th}}$  September when both bromide and iodide clusters formed in sufficient quantities to collect mass and photoelectron spectra. This spectrum was collected from a gas mixture with partial pressures of <1% iodomethane, 40 kPa Ethylene and made up to 400 kPa with argon as the backing gas. Though iodmethane was the only halogen source added residual dibromomethane was also present. The peak assignment for the major peaks in Figure 3.1 is located in table



Figure 3.1: Mass Spectrum of the Bromine and Iodine Ethylene clusters

3.1. The calibration curve for converting from TOF to m/z, using the peak positions of the two isotopes of bromide, i.e. <sup>79</sup>Br and <sup>81</sup>Br, and <sup>127</sup>I, has a Pearson's regression coefficient of 0.99998.

m/z	Assignment		m/z	Assignment
78.91	Bromide-79	1	18.80	Dromido Argon
80.96	Bromide-81	1	20.70	Dronnde-Argon
96.85	Durani la Watan	1	26.90	Iodide
98.85	Bronnide-water	1	44.80	Iodide-Water
106.80			154.7	Iodide-Ethylene
108.90	Bromide-Ethylene		166.7	Iodide-Argon

Table 3.1: Major peak assignment for Figure 3.1

The spectrum reveals evidence of halide-water, halide-ethylene and halide-argon clusters, given the system design it is expected that the target cluster forms, and that the carrier gas also forms some clusters, though with a lower clustering rate than the target species. The presence of water was not entirely unexpected, the hydrogen bonding that makes water a liquid at room temperature also makes it exceptionally good at adsorbing to surfaces, even while under vacuum, and possessing such a strong dipole moment if it is present in the gas mixture it tends to form clusters.

#### 3.1.3 Photoelectron spectra

The spectra for bromide and iodide-ethylene anion clusters are presented in Figures 3.2 and 3.3. The spectra have been recorded and treated with the methods outlined in Chapter 2. The two peaks displayed in the spectra are due to ejection of an electron. The ejected electron leaves the system in the  ${}^{2}P_{3/2}$  and  ${}^{2}P_{1/2}$  states of the halogen, corresponding to a p<sup>5</sup> configuration. The  ${}^{2}P$  state has two corresponding J values, J = 1/2 and 3/2, the degeneracy of these states can be calculated when the J values are substitued into the following equation,

$$2J + 1,$$
 (3.1)

which gives  ${}^{2}P_{3/2}$  a degeneracy of 4 and  ${}^{2}P_{1/2}$  a degeneracy of 2, which can be simplified to a ratio of 2:1. Given this the peak ratio should be 2:1 as well, where the peak ratio is based on the area under the curve, however it can be approximated by peak height.

The  ${}^{2}P_{3/2}$  energy level lies below the  ${}^{2}P_{1/2}{}^{29,30}$  therefore the  ${}^{2}P_{3/2} \leftarrow {}^{1}S_{0}$  transition has a lower electron binding energy compared with the  ${}^{2}P_{1/2} \leftarrow {}^{1}S_{0}$  transition resulting in the ejected electron having more energy. This high KE means that TOF data shows the  ${}^{2}P_{3/2}$  at a shorter time than the  ${}^{2}P_{1/2}$  electrons. Recalling Equation 1.8, which is presented here, re-arranged with *BE* as the subject,

$$BE = hv - KE, (3.2)$$

we know that if  ${}^{2}P_{3/2}$  electrons have higher KE they have a correspondingly lower BE. Following on the peak assignment is quite simple, the lower eBE peak corresponds to the  ${}^{2}P_{3/2}$  energy level and the higher eBE peak corresponds to the  ${}^{2}P_{1/2}$  energy level.

Given all ejections occur from a P orbital, which has an orbital angular momentum (l) of 1 and the selection rules state that  $\Delta l = \pm 1$ , the ejected electrons will have l=0 or 2, giving them mixed s and d wave character.



Figure 3.2: The bromide-ethylene cluster Photoelectron spectrum, plotted as a function of the electron binding energy

In a idealised system all electrons would be ejected pointing towards the detector and would fly in a perfectly straight line, in reality the electrons are forced towards the detector by a magnetic bottle, as described in Chapter 2. More importantly in some ways are the electron-electron interactions, as two regions of negative charge they repel each other, which to varying degrees causes a spread of electron of arrival times. Functionally this results in spectral broadening. The application of the Jacobi transformation while accounting for the non-linear transformation of the TOF values can cause a small shift in the position of the eBE peak.

The bromine ethylene spectrum shows the two peaks with a small overlap, this is because the gap between the energy levels is only slightly larger than the resolving power of the spectrometer, but the two peaks are clearly distinguishable from each other and the peak positions are not affected by the overlap.

The iodine ethylene spectra has a better separation of the peaks, with no visible overlap between the two peaks, though the spectra does have some noise between the two peaks, while it is possible that this is not noise, but rather caused by vibrational progressions, there is insufficient resolution to make any solid conclusions. The peaks show the expected 2:1 ratio, confirming the earlier peak assignment.



Figure 3.3: The iodide-ethylene cluster Photoelectron spectrum, plotted as a function of the electron binding energy

The eBE values for the bare halide and complexes as experimentally determined are given in Table 3.2 as well as the stabilisation energy  $(E_{stab})$ , which is the difference between the electron binding energies of the halogen-ethylene clusters and the bare halides. The cluster energies were found to all be higher than the values for the bare halides, with approximate stabilisation energies of 0.16 and  $0.13 \,\mathrm{eV}$  for bromide and iodide respectively.

The stabilisation energies were all positive values which indicates that clustering provides a stabilising effect to the electron attached to the halogen. These values will be compared with the computationally determined difference between the dissociation energies  $(D_0)$  of the anion and neutral clusters in another section.

	B	$r^{-}$	I-		
	$P_{3/2}$	$P_{1/2}$	$P_{3/2}$	$P_{1/2}$	
Bare	Bare 3.43		3.04	4.05	
Cluster	3.59	4.06	3.17	4.17	
$\mathbf{E}_{stab}$	0.16	0.15	0.13	0.12	

Table 3.2: Experimental binding energies (eV)

### **3.2** Computational Results

A series of calculations optimising the geometries and calculating frequencies was carried out at the MP2 level on the halogen ethylene clusters using the aug-ccpVNZ basis sets (N = D and T). Single point energy CCSD(T) calculations were also carried out using the aug-cc-pVNZ basis sets (N = D and T). From these calculations relevant values such as the Adiabatic Detachment Energy (ADE) and Vertical Detachment Energy (VDE) were calculated. The full set of computational results can be found in Appendix A, however important results are reported here.

#### 3.2.1 Comparison of MP2 to CCSD(T)

The geometry of ethylene was optimised at several levels of theory, offering the opportunity to perform a comparison of the methods used. The results of the geometry optimisations are presented here in Table 3.3. This comparison implies a 100% agreement between the methods.

	C-C	C-H	∠H-C-C
MP2	1.34	1.03	120.0
$\operatorname{CCSD}(T)$	1.34	1.03	120.0

Table 3.3: Ethylene geometries at MP2 and CCSD(T)

As well as ethylene, the T-shaped bromine anion cluster and bent chlorine anion cluster optimisation tasks were completed and offer the opportunity for a deeper investigation of the correlation between the methods. The full analysis of these clusters is found in Appendix A, the results of this imply at worst a 98.9% correlation and at best a greater than 99% correlation.

#### 3.2.2 Halide-Ethylene Anion Complexes

An was mentioned in the introduction two anion cluster geometries were previously reported, in order to present a thorough investigation un-relaxed scans of the anion geometries were carried out at the MP2/aug-cc-pVDZ level, as seen in Figure 3.4 there are two clearly defined minima, corresponding to the two reported anion geometries. While this results backs up the literature it is mildly mis-leading as it implies that there is a T-shaped geometry at a sharp right angle to the C=C, this was found to not be the case when geometries were extracted from a triple zeta basis calculation. In order to be able to explicitly confirm or deny the nature of this geometry a constrained geometry Z-matrix was made that forced the halogen to take the implied 90° geometry (see Figure 3.5). Using the constrained geometry in all cases generated negative frequencies corresponding to the halogen moving towards an off centre position. The conclusion that should be drawn from this is that the minimum presented in the scan is missing a feature, where it has a slight increase in energy at 90° and there are two identical well next to it where the halogen is slightly offset towards one carbon or the other.

When considering the anion clusters to be pre-cursors to the halogenation of the C=C then the off centre T-shaped geometry implies that the halogen is approaching the carbon in order to from a bond, or more chemically, the highly electronegative halogen approaches the relatively electropositive carbon atom.

The second minima represents the halogen forming a bent cluster where it forms an approximate angle of  $125^{\circ}$  with respect to the C=C. While this geometry might on face value appear to imply hydrogen bonding the relative electronegativity of carbon compared to hydrogen is quite small, leading to an effectively zero dipole moment.



Figure 3.4: Potential energy surface scan of the Chlorine Ethylene anion system

From the point of view of a halogenation precursor this geometry is less favourable than the T-shaped geometry, which matches the scan data where the bent geometry is found at at higher energy.

1	Х						
2	C	1	R1				
3	С	1	R1	2	180.0		
4	Η	2	R2	1	A1	3	0.0
5	Η	2	R3	1	A2	3	180.0
6	Η	3	$\mathbf{R4}$	1	A3	2	0.0
7	Η	3	R5	1	A4	2	180.0
8	Cl	1	R6	2	90.0	3	0.0

Figure 3.5: Z-matrix, showing atom numbering, used to carry out the constrained scans, X is a dummy atom added to allow the system forcing

The results of the geometry optimisations showed that the ethylene molecule retained its geometry, with only minor (less than 1%) changes in geometry, the halogens though showed a strong periodic trend of increasing bond length with molecular mass, these bond lengths and angles are presented in table 3.4 (complete geometries are reported in Appendix A).

		X-C	∠X-C-C
Cl	Tee	3.61	82.0
	Bent	3.61	124.3
Br	Tee	3.69	81.9
	Bent	3.82	125.0
Ι	Tee	4.06	80.7
	Bent	4.05	124.8

Table 3.4: Anion cluster halogen positions

#### 3.2.3 Halide-Ethylene Neutral Complexes

There was no neutral structure in the literature, so using the scan techniques described in Chapter 2 a series of scans were run. First to compare with the anion an in plane scan was carried out, the results of which are presented in Figure 3.6. While the potential surface generated this way had the same form as the anion scan (Figure 3.4) the energy was noted to be higher for the neutral. The lowest minima was found to be when the halogen was set perpendicular to the C=C.



Figure 3.6: In plane scan

A second scan was run starting from the minima of the first scan it rotated the halogen out of the plane while keeping it perpendicular to the C=C, the results of this scan are presented in Figure 3.7, The minima of this scan was found to be when

the halogen is perpendicular to the C=C bond and the plane.



Figure 3.7: Scanning out of plane from the in plane scan minima

A third scan was run from the minima of the second scan, keeping the halogen in line with the C=C double bond it was moved from perpendicular to the C=C to into the plane in a series of steps, the results of this scan are presented in Figure 3.8.

This third scan encountered shows some unexpected gradient changes, there is the appearance of a small minima somewhere between 80° and 85° however this section which would have benefited from more study was proved to be impossible to optimise geometries within. This is believed to be due to the minima not being a true minima, rather it has a zero barrier as the angle tends towards 90° explaining why no geometry can be optimised here.

	X-C	∠X-C-C
	(Angstrom)	(degrees)
Cl	3.09	77.5
$\operatorname{Br}$	2.69	75.4
Ι	3.53	80.5

Table 3.5: Bond lengths and angles for the neutral clusters



Figure 3.8: Scan across the double bond starting from the out of plane minima

The three scans are linked, the first scan supplies the starting point for the second scan, which supplies the starting point for the third scan which ends at the starting point of the first scan. The implication of this is that there is a single low energy neutral cluster geometry and all other point on the potential surface (assuming contributions can only come from the halogen bond length and angle) have a negative barrier pathway to this cluster geometry. This single cluster, even more so than the anion clusters does not change the ethylene geometry, all anions are found out of plane and perpendicular to the C=C double bond. The only major difference between the different halogen systems is the distance at which the halogen sat, these values are reported in Table 3.5.

#### 3.2.4 Comparison with Experimental results

Associated energies for the anion and neutral clusters and bare ethylene and halogens were collected at the CCSD(T)/aug-cc-pVTZ level. These values were used to determine electron binding energies for comparison with experimental values. Though chlorine data was collected as there are no experimental chlorine values thus the chlorine data was not included here, instead it is presented in Appendix A. The results were treated using experimentally determined splitting constants and an experimental shift, found as the difference between the computational value of the  ${}^{2}P_{3/2}$  electron and the corresponding electron binding energies from the experimental section, this shift acts as a correction for the computational results at this particular level of theory.

The corrected electron binding energies were found to be for bromine clusters to be 3.25 and 3.70eV for the  ${}^{2}P_{3/2} \leftarrow {}^{1}S_{0}$  and  ${}^{2}P_{1/2} \leftarrow {}^{1}S_{0}$  transitions respectively, while Iodine was found to have energies of 2.90 and 3.85 eV respectively for the same transitions. While these values are consistently lower than the experimental values they do present a similar magnitude of peak splitting, suggesting that the calculated shift is off by some factor. The position of the peaks with respect for one cluster to the other also predicts the same spectral arrangement.

#### 3.2.5 Comparison to the acetylene system

A was mentioned in the introduction the halogen-acetylene clusters<sup>10</sup> values can be compared to the results of this study. The stabilisation energy and cluster geometries are compared as a way of comparing the halogen c-c double and triple bond interactions. The acetylene clusters were found to have two neutral geometries, a T-shape and linear geometry, compared to the single T-shaped geometry of the ethylene system. The T-shaped geometries do appear to present the same way, while ethylene has no linear geometry to compare.

The presence of this complementary neutral geometry supports the hypothesis that halogens interact with the electrons in the  $\pi$  bond.

The stabilisation energies for ethylene were found to be 0.16 and 0.13 for bromine

and iodine respectively, while acetylene was found to have stabilisation energies of 0.5, 0.41 and 0.38 for chlorine, bromine and iodine clusters respectively. The stabilisation energies for acetylene are much higher than for ethylene, which again supports the hypothesis that the electrons in the  $\pi$  bond are the attractive site for the halogen, as acetylene has a triple bond, doubling the number of  $\pi$  electrons.

# Chapter 4

# **Conclusion and Future Work**

This project aimed to investigated the halogen ethylene clusters with a view to understanding how halogens interact with a carbon-carbon double bond. To this end the technique of coupled time of flight mass spectrometry and photoelectron spectroscopy were applied to the Bromine-Ethylene and Iodine-Ethylene clusters, an attempt was made to also study the Chlorine-Ethylene cluster, however this final investigation was unable to be completed due to an mechanical failure of the apparatus. The experiment was supported by a wide range of computational data that predicted the energies, cluster geometries and vibrational frequencies.

The Halide-Ethylene complex spectra were recorded and calibrated against the halide  ${}^{2}P_{3/2} \leftarrow {}^{1}S_{0}$  and  ${}^{2}P_{1/2} \leftarrow {}^{1}S_{0}$  transition energies, given as 3.432 eV, 3.904 eV and 3.118 eV, 4.056 eV for Bromide and Iodide respectively. The calibrated spectra gave electron binding energies of 3.59 eV, 4.06 eV and 3.17 eV, 4.17 eV and stabilisation energies of 0.16 eV and 0.13 eV for the Bromine and Iodine clusters respectively. The data implies that the halogen clusters are more stable than free halogens, though not excessively so and could in some way contribute to halogen transport in atmospheric conditions.

The computational data collected using Møller Plesset second order perturbation theory (MP2) and Coupled Cluster theory with single, double and perturbative inclusion of triple excitations (CCSD(T)), using triple zeta Dunning's augmented correlation consistent basis sets (aug-cc-pVTZ). The geometry optimisations determined that there are two anion structures, one being a T-shaped geometry and of  $C_s$  symmetry and the second being of a bent geometry and  $C_s$  symmetry. The neutral cluster was found to be T-shaped where the halogen was found in the out of plane position and of  $C_{2v}$  symmetry. The predicted electron binding energies were consistently of lower energy than the experimentally recorded results. When the computationally determined neutral structure was analysed there was found to be a strong link to the halogenation intermediate for the diatomic halogens. This along with the shape of the anion geometries all implies that halogen carbon-carbon double bonds structures investigated have a significant link to the halogenation of double bonds. This opens the door to an interesting new study where the clusters studied could be used as the starting point in computationally determining the energy barriers of halogenation reactions which could be readily compared to experimentally determined values in the literature.

There remains several areas where this project could be directly extended, first of all chlorine spectra and computational data would offer the opportunity to examine possible periodic trends. Currently the data is insufficient to predict a true periodic trend as while a straight line may be drawn between any two points it will rarely be representative of the whole set.

The project could also be the starting point for higher order computational tasks, it was mentioned in the discussion that time constraints prevented the completion of CCSD(T) geometry optimisations, these optimisations could be used to refine the predicted geometries and vibrational frequencies. An additional area where the computational data could be extended is completing a basis set extrapolation, Appendix B outlines the basic principles of a two point basis extrapolation and there exists a set of QZ data, however time constraints prevented the completion of a full set of 5Z values and the fitting values for a T-Q extrapolation required an exponential curve be fitted to data not collected.

Finally this study stands as the starting point for studying larger systems containing carbon-carbon double bonds as it offers the benchmark values for pure carboncarbon double bond interactions.

# References

- [1] Klaus Müller-Dethlefs and Pavel Hobza, Chem. Rev., 100:143–168, 2000.
- [2] Leigh R Crilley, E Rohan Jayaratne, Godwin A Ayoko, Branka Miljevic, Zoran Ristovski, and Lidia Morawska, *Environ. Sci. Technol.*, 48:6588–6596, 2014.
- [3] M Larsson, W D Geppert, and G Nyman, *Rep. Prog. Phys.*, 75, 2012.
- [4] R L Wilson, Z M Loh, D A Wild, C D Thompson, E J Bieske, M D Schuder, and J M Lisy, Phys. Chem. Chem. Phys., 7:3419–3425, 2005.
- [5] William R. Simpson, Steven S. Brown, Alfonso Saiz-Lopez, Joel A. Thornton, and Roland Von Glasow, *Chem. Rev.*, 115:4035–4062, 2015.
- [6] Shinichi Sawada and Tsumugu Totsuka, Atmos. Environ., 20:821–832, 1986.
- [7] Athena Coustenis, Richard K. Achterberg, Barney J. Conrath, Donald E. Jennings, André Marten, Daniel Gautier, Conor A. Nixon, F. Michael Flasar, Nick A. Teanby, Bruno Bézard, Robert E. Samuelson, Ronald C. Carlson, Emmanuel Lellouch, Gordon L. Bjoraker, Paul N. Romani, Fred W. Taylor, Patrick G J Irwin, Thierry Fouchet, Augustin Hubert, Glenn S. Orton, Virgil G. Kunde, Sandrine Vinatier, Jacqueline Mondellini, Mian M. Abbas, and Regis Courtin, *Icarus*, 189:35–62, 2007.
- [8] Arkadipta Bakshi, Jennifer M. Shemansky, Caren Chang, and Brad M. Binder, J. Plant. Biochem. Biotechnol., 34:809–827, 2015.
- [9] Jeffrey S. Gaffney, Nancy A. Marley, and Donald R. Blake, Atmos. Environ., 56:161–168, 2012.
- [10] D. A R Beckham, S. Conran, K. M. Lapere, M. Kettner, A. J. McKinley, and D. A. Wild, *Chem. Phys. Lett.*, 619:241–246, 2015.

- [11] Peter D. Watson, Hai-wang Yong, Kim M.L. Lapere, Marcus Kettner, Allan J. McKinley, and Duncan A. Wild, *Chem. Phys. Lett.*, 654:119–124, 2016.
- [12] K. M. Lapere, R. J. Lamacchia, L. H. Quak, A. J. McKinley, and D. A. Wild, *Chem. Phys. Lett.*, 504:13–19, 2011.
- [13] K. M. Lapere, PhD thesis, UWA, 2015.
- [14] Kim M. Lapere, Rob J. LaMacchia, Lin Hian Quak, Marcus Kettner, Stephen G. Dale, Allan J. McKinley, and Duncan A. Wild, Aust. J. Chem., 65:457, 2012.
- [15] Kim M. Lapere, Robert J. LaMacchia, Lin H. Quak, Marcus Kettner, Stephen G. Dale, Allan J. McKinley, and Duncan A. Wild, J. Phys. Chem. A, 116:3577–3584, 2012.
- [16] Roberto Cammi, Benedetta Mennucci, Christian Pomelli, Chiara Cappelli, Stefano Corni, Luca Frediani, Gary W Trucks, and Michael J Frisch, *Theor. Chem.* Acc., 111:66–77, 2004.
- [17] S Coquet and P A Ariya, Int. J. Chem. Kinet., 41:612–612, 2009.
- [18] Willard H. Janneck and Edwin O. Wilg, J. Phys. Chem. B, 62:1877–1878, 1940.
- [19] Aimable Kalume, Lisa George, Andrew D. Powell, Richard Dawes, and Scott A. Reid, J. Phys. Chem. A, 118:6838–6845, 2014.
- [20] Terry Koerner, R. S. Brown, J. L. Gainsforth, and M. Klobukowski, J. Am. Chem. Soc., 120:5628–5636, 1998.
- [21] Yuzuru Kurosaki, Theo. Chem. 545:11080–11087, 2001.
- [22] Susanna L. Stephens, Wataru Mizukami, David P. Tew, Nicholas R. Walker, and Anthony C. Legon, J. Mol. Spectrosc., 280:47–53, 2012.
- [23] Marcus Kettner, PhD thesis, UWA, 2015.
- [24] J. C. Slater, *Phys. Rev.*, 34:1293–1322, 1929.

- [25] Alan Hinchliffe, Computational Quantum Chemistry. Chichester; New York; John Wiley & Sons, 1988.
- [26] Lewars E. G, Computational Chemistry: Introduction to the theory and applications of molecular and quantum mechanics. Springer US, second edition, 2011.
- [27] Ahmed A. Hasanein and Myron W Evans, Computational Methods In Quantum Chemistry. Singapore; River Edge, NJ: World Scientific Publishing, 1996.
- [28] Sebastiaan Y. T. van de Meerakker, Hendrick L. Bethlem, and Gerard Meijer, Nat. Phys., 4:595–602, 2008.
- [29] NIST, http://physics.nist.gov/PhysRefData/Handbook/Tables/iodinetable5.htm; (accessed 03/11/2016).
- [30] NIST, http://physics.nist.gov/PhysRefData/Handbook/Tables/brominetable5.htm (accessed 03/11/2016).
- [31] EMSL Basis Set Exchange, https://bse.pnl.gov/bse/portal (accessed 03/11/2016)
- [32] Gaussian 09, Revision E.01 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D.

Daniels, . Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

- [33] T.H. Dunning, Jr., K.A. Peterson and A.K. Wilson, J. Chem. Phys. 114, 9244 (2001)
- [34] K.A. Peterson, D. Figgen, E. Goll, H. Stoll, and M. Dolg, J. Chem. Phys. 119, 11113 (2003).
- [35] K. A. Peterson, B. C. Shepler, D. Figgen, H. Stoll, J. Phys. Chem. A 110, 13877 (2006).

# Appendix A Tables and Figures

# **Reference Image**

The following sections use this image as a reference for which Carbon the Halogen bonds to and the C-H bond being reported



Reference figure

## Geometries

The data presented here is taken from MP2/aug-cc-pVTZ output files

_			C-C	∠X-C-C	C-H(1)	∠H-C-C(1)	)
_	$Cl^C_2H_4$	3.61	1.34	82.0	1.09	121.0	
	$\mathrm{Br}^{-}\mathrm{C}_{2}\mathrm{H}_{4}$	3.69	1.34	81.9	1.09	118.7	
	$\mathrm{I}^\mathrm{C}_2\mathrm{H}_4$	4.06	1.35	80.7	1.10	119.6	
	C-H(2)	∠H-C-C	(2) C	C-H(3) ∠	4H-C-C(3)	C-H(4)	∠H-C-C(4)
$Cl^C_2H$	$H_4$ 1.09	122.3		1.09	118.7	1.11	121.8
$\mathrm{Br}^{-}\mathrm{C}_{2}\mathrm{H}$	$H_4$ 1.09	121.8		1.09	118.8	1.09	122.0
$I^- \dots C_2 H$	4 1.10	121.7		1.10	119.6	1.10	121.7

Geometries of the T-shaped anion clusters (All lengths in Angstroms, all angles in degrees)

		$X.\ldots C$	C-C	∠Х-С-С	C-H(1)	)	
	$Cl^C_2$	H <sub>4</sub> 3.61	1.33	124.3	1.09	122.7	
	$Br^C_2$	$H_4 = 3.82$	1.35	125.0	1.10	122.6	
	$I^- \dots C_2 H$	I <sub>4</sub> 4.05	1.35	124.8	1.10	122.5	
	C-H(2)	$\angle H$ -C-C(2)	C-H	(3) ∠H-C	C-C(3)	C-H(4)	$\angle \text{H-C-C}(4)$
$Cl^{-}C_2H_4$	1.09	120.0	1.0	8 12	0.8	1.08	122.1
$\mathrm{Br}^{-}\mathrm{C}_{2}\mathrm{H}_{4}$	1.10	120.1	1.1	0 12	0.9	1.10	122.1
$I^C_2H_4$	1.10	120.3	1.1	0 12	0.9	1.10	122.0

Geometries of the bent anion clusters (All lengths in Angstroms, all angles in degrees)

## Vibrational Frequencies

The data in this section is taken from MP2/aug-cc-pVTZ optimisations, all spectra and values were generated using Avogadro.



Predicted spectra for T-shaped Chlorine Ethylene cluster

Position	Intensity				
$\mathrm{cm}^{-1}$					
31.04	0.315				
106.80	18.547				
237.75	1.024				
827.62	7.970				
952.03	0.000				
982.18	74.501				
1068.55	74.501				
1251.39	0.584				
1366.81	9.519				
1437.09	12.341				
1655.73	15.551				
3130.77	26.452				
3148.94	89.474				
3237.27	5.533				
3261.38	0.915				

Vibrational Frequencies for Chlorine Ethylene T-shaped anion



Predicted spectra for the Bent Chlorine Ethylene cluster

Position	Intensity				
$\mathrm{cm}^{-1}$					
53.67	1.698				
131.41	10.550				
189.18	0.070				
838.25	0.076				
932.70	15.579				
1020.72	16.393				
1095.26	3.182				
1246.97	1.313				
1378.43	1.113				
1483.77	1.942				
1667.67	2.604				
3080.98	100.000				
3154.38	22.215				
3210.93	16.758				
3251.13	7.267				

Vibrational Frequencies for Chlorine Ethylene Bent anion



Predicted spectra for Neutral Chlorine Ethylene cluster

Position	Intensity
$\mathrm{cm}^{-1}$	
256.80	0.015
368.45	0.025
608.00	3.580
852.37	0.023
984.99	0.000
999.84	5.834
1241.64	0.000
1354.91	0.858
1453.07	8.945
1621.59	1.696
1798.36	100.000
3195.25	1.992
3203.18	0.247
3289.61	0.000
3313.88	0.004

Vibrational Frequencies for Chlorine Ethylene neutral



Predicted spectra for T-shaped Bromine Ethylene cluster

Position	Intensity				
$\mathrm{cm}^{-1}$					
42.94	0.001				
94.45	5.982				
237.02	2.190				
826.38	9.383				
949.43	0.000				
982.64	79.164				
1068.20	0.000				
1250.11	0.982				
1367.64	12.286				
1437.90	14.846				
1656.52	19.719				
3132.83	28.547				
3150.30	100.000				
3238.01	5.937				
3261.85	1.681				

Vibrational Frequencies for Bromine Ethylene T-shaped geometry



Predicted spectra for Bent Bromine Ethylene cluster

Position	Intensity		
$\mathrm{cm}^{-1}$			
35.45	0.390		
122.10	4.620		
201.62	0.363		
837.36	0.215		
926.08	16.874		
1016.75	19.957		
1094.57	2.847		
1247.64	1.315		
1378.86	0.540		
1479.96	1.498		
1667.97	3.977		
3098.80	100.000		
3156.70	226.741		
3218.01	19.516		
3254.83	6.718		

Vibrational Frequencies for Bromine Ethylene Bent geometry



Predicted spectra for Neutral Bromine Ethylene cluster

Position	Intensity
$\mathrm{cm}^{-1}$	
186.65	0.378
320.30	0.014
584.21	22.006
823.42	0.015
991.54	7.578
1004.55	0.000
1241.40	0.000
1355.20	1.005
1456.30	5.085
1626.05	2.245
1931.27	100.000
3191.90	2.434
3198.27	0.000
3306.48	0.001

Vibrational Frequencies for Bromine Ethylene Neutral geometry



Predicted spectra for Neutral Bromine Ethylene cluster

Position	Intensity				
$\mathrm{cm}^{-1}$					
186.65	0.378				
320.30	0.014				
584.21	22.006				
823.42	0.015				
991.54	7.578				
1004.55	0.000				
1241.40	0.000				
1355.20	1.005				
1456.30	5.085				
1626.05	2.245				
1931.27	100.000				
3191.90	2.434				
3198.27	0.000				
3306.48	0.001				

Vibrational Frequencies for Bromine Ethylene Neutral geometry



Predicted spectra for T-shaped Iodine Ethylene cluster

Position	Intensity				
$\mathrm{cm}^{-1}$					
54.84	0.018				
77.22	2.835				
217.70	2.825				
827.63	9.139				
958.70	0.024				
987.29	95.778				
1063.96	0.000				
1236.63	1.314				
1365.99	14.081				
1440.11	16.367				
1651.74	22.256				
3142.50	33.654				
3159.89	100.000				
3254.68	5.994				
3277.59	6.791				

Vibrational Frequencies for Iodine Ethylene T-shaped geometry



Predicted spectra for Bent iodine Ethylene cluster

Position	Intensity
$\mathrm{cm}^{-1}$	
32.28	0.287
95.01	3.907
172.88	0.713
829.23	0.337
937.39	35.072
1018.71	36.667
1079.99	4.480
1232.31	3.390
1369.47	1.527
1469.02	2.905
1659.85	5.109
3129.48	100.000
3163.60	53.399
3239.13	41.187
3270.10	14.492

Vibrational Frequencies for Iodine Ethylene Bent geometry



Predicted spectra for Neutral iodine Ethylene cluster

Position	Intensity				
$\mathrm{cm}^{-1}$					
186.65	0.386				
318.50	0.016				
579.84	2.183				
823.60	0.015				
991.37	7.795				
1002.00	0.000				
1241.45	0.000				
1355.91	1.055				
1456.00	5.604				
1627.04	2.323				
1902.15	100.000				
3191.40	2.323				
3281.14	0.000				
3306.38	0.001				

Vibrational Frequencies for Iodine Ethylene Neutral geometry

# **Comparison of Methods**

	-	XC	C-C	∠X-C-C	C-H(1)	$\angle$ H-C-C(1)	
		Br	omine	T-shaped	geometry		
M	P2	3.69	1.34	81.9	1.09	118.7	1.09
CCSI	D(T)	3.69	1.34	81.9	1.09	118.7	1.09
% sim	ilarity	100	100	100	100	100	100
		Chl	orine b	ent geome	etry values		
M	P2	3.61	1.33	124.3	1.09	122.7	1.09
CCS	D(T)	3.57	1.34	122.5	1.09	122.5	1.09
$\% \sin$	ilarity	98.9	99.3	98.5	100	99.8	100
	C-H(2)	∠H-O	C-C(2)	C-H(3)	∠H-C-C(	B) C-H(4)	∠H-C-C(4
		Br	omine	T-shaped	geometry		
MP2	1.09	12	1.8	1.09	118.8	1.09	122.0
$\operatorname{CCSD}(T)$	1.09	12	1.8	1.09	118.8	1.09	122.0
% similarity	100	1	00	100	100	100	100
Chlorine bent geometry values							
MP2	1.09	12	0.0	1.08	120.8	1.08	122.1
$\operatorname{CCSD}(T)$	1.09	11	9.9	1.09	120.7	1.09	122.1
% similarity	100	99	9.9	99.1	99.9	99.1	100

MP2 and CCSD(T) geometries and energy of the clusters being compared

# **Computational Values**

This section reports several core values extracted from computational jobs as well as the previously unreported Chlorine data.

		Cl	Br	Ι
	T-Anion	20.741975	75.864610	17.391837
$D_0$ (Hartree)	Bent-Anion	21.894832	21.363431	17.897508
	Neutral	-3.482201	17.665939	10.068793
$E_{stab}$	(eV)	0.263008	0.320746	0.078516
	${}^{2}\mathrm{P}_{3/2}$	3.51	3.25	2.90
EBE (eV)	${}^{2}\mathrm{P}_{1/2}$	3.62	3.70	3.85

Computational values for Cl, Br and I-Ethylene clusters

Clearly here the  $D_0$  value for the chlorine neutral is incorrect, the exact reason for this error is unknown.

# Appendix B: Basis set extrapolation

A common technique to enhance theoretical results is a two point basis set extrapolation, where two consecutive basis sets are used to extrapolate the complete basis set (CBS) limit. In order to calculate the CBS limit first the following equations must be solved,

$$E_{inf,L+1}^{CCSD(T)} = E_{L+1}^{corr} + \frac{E_{L+1}^{corr} - E_{L}^{corr}}{c^{\alpha} - 1},$$
(4.1)

and

$$E_{SCF}^{HF} = E_{L+1}^{HF} + \frac{E_{L+1}^{HF} - E_{L}^{HF}}{c^{\beta} - 1},$$
(4.2)

where

$$c = \frac{L+1}{L},\tag{4.3}$$

and

$$E_L^{corr} = E_L^{CCSDT} - E_L^{CCSD} \tag{4.4}$$

and so CCSD correlation is found by CCSD-HF. Where L is the highest angular momentum quantum number of the basis set and  $\alpha$  and  $\beta$  depend on the basis sets used for the extrapolation, for a T-Q extrapolation the coefficients are 3.05 and 5.79 for  $\alpha$  and  $\beta$  respectively. Equation 4.1 must also be solved for the CCSD value. The CBS limit is found as follows,

$$E_{CBS} = E_{SCF}^{HF} + E_{inf,L+1}^{CCSD} + E_{inf,L+1}^{CCSD(T)}$$
(4.5)

# Appendix C: Distillation of the Polyphenol-ether, Santovac 5

## Introduction

During routine maintenance on a Diffstak 250/2000P diffusion pump it was noted that the oil had suffered degradation leading to the formation of tar like impurities. These impurities were producing a notable change in the physical properties of the oil, namely darkening and increased viscosity. As the price of new oil is approximately \$1500-\$1900 AUD/500mL it was decided to attempt recovery of a pure fraction from the contaminated oil. Using FT-IR comparisons to a pure sample it was determined that the distilled fraction was pure Santovac 5.

## Methods

A classical vacuum distillation setup was used as seen in the following figure, was used for the distillation, with the single difference being a crows foot was used on the receiver end to allow collection of fractions during the distillation. Standard procedure for distillations was followed with the exception that the distilling flask was heated with a Bunsen burner rather than a heating mantle. The distillation was done at approximately  $10^{-3}$  Torr, it was found to be necessary to slowly bring the pressure down before heating to allow for a preliminary degassing of the oil. During the heating the oil temperature stalled at values between 40-60 °C as the oil degassed a second time. Boiling of the oil occurred between 230-240 °C. There was found to be only one fraction recoverable, this entire fraction was removed and collected in a single run. Upon completion of collecting the fraction the temperature was found to rise again but as only a thick black tar remained in the distilling flask the distillation was terminated at this point in time.



Vacuum distillation setup

## Results

From the initial approximate 700-750mL of contaminated oil 600mL of pure Santovac 5 was extracted, this purity was determined by FT-IR, presented following, as compared to a pure sample. An additional approximately 100mL fraction was recovered that while not pure was significantly cleaner than the original oil.

# Discussion

There are only two things to really be considered here, first degassing and second the fact that degassing occurred at twice. The fact that the oil had to degas makes a great deal of sense, as a vacuum oil trapping gas is a design feature, rather than a flaw, and as the external pressure is decreased some of the trapped gas is released. Clearly as seen by the existence of a second degassing region only the weakly trapped gasses were released under low pressure conditions while it required the addition of a notable amount of kinetic energy to release the other trapped gasses.



FT-IR of the various distillation runs