

**The preliminary investigation the amidogen
anion using Anion Photoelectron
Spectroscopy and investigation of amidogen
anion complexes through *ab initio*
calculations.**

by Stephen Gregory Dale

Signed Statement

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

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

Abstract

In this research a number of attempts were made to produce the amidogen ion for analysis in the time-of-flight mass-spectrometer coupled with a photoelectron-spectrometer. These attempts lead to modification to the time-of-flight mass-spectrometer when problems were encountered. The amidogen anion was not observed despite an m/z peak of 16 amu however a number of exotic species which show potential for future research were. The photoelectron spectra of O^- was taken to showing the composition of the m/z peak at 16 and additional photoelectron spectra of O_2^- , Cl^- and Br^- were taken for calibration.

High level theoretical calculations were performed and yielded the optimum structures for clusters involving the amidogen species, argon and carbon monoxide. Structures found for clustering of the amidogen species with water were shown to be transition states and give different results than calculations previously performed at different levels of theory. The $NH_2^- \cdots CO$ complex forms a covalent bond where all other minima structures form van der Waals complexes. Perturbation in the amidogen species and completing ligands have been compared in each case and the D_0 and adiabatic detachment energies have been reported where possible.

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List of abbreviations

TOF-MS	Time of Flight Mass Spectrometry
TOF-PES	Time of Flight Mass Spectrometer coupled with a Photoelectron Spectrometer
STP	Standard Temperature and Pressure
MP2	Møller-Plesset Perturbation Theory using second order corrections
CC	Coupled Cluster Theory
CCD	Coupled Cluster with double excitations theory
CCSD(T)	Coupled-Cluster with Single and Double and Perturbative Triple excitations
NBO	Natural Bond Order analysis

1. Introduction

Studies of molecular clusters are undertaken to understand how a single molecule or atom interacts with its surrounding solvents. This interaction can take a number of forms, and is important in furthering our understanding of the solvation of species in the liquid and gas phases. Solvation can then effect reaction pathways available to a particular species, and hence change the chemistry present in a system. Research into solution chemistry stretches back hundreds of years with a gargantuan body of work on the subject due to the complexity of such interactions.

Recently there has been a drive towards understanding solvation in the gas phase fuelled by increasing concerns about the state of the atmosphere and the development of technology which allows for examination of gas phase species and clusters in far more detail than previously possible. Due to these technological advances, it is possible to study specific species as opposed to macroscopic systems (i.e. at a 1:1 molecular level rather than in a large scale bench top experiments) making it possible to develop and improve current theories to describe specific molecular behaviour.

One such technology is Photoelectron Spectroscopy coupled with Time of Flight Mass Spectrometry (TOF-MS). This is the basis of the apparatus currently used in the Wild laboratory in conjunction with *ab initio* calculations to analyse the properties of ion-molecule clusters. This equipment can separate and observe different solvation states of the same base molecule, hence it is ideal for observing changes in properties of a molecule due to solvation.

1.1 Project Aims

The aim of this research was to study the changes in the electronic properties of the amidogen radical as it interacts with Ar, CO and H₂O. This was to be accomplished by generating clusters consisting of an amidogen anion such as $\text{NH}_2^- \cdots (\text{Ar})_n$, $\text{NH}_2^- \cdots (\text{CO})_n$, or $\text{NH}_2^- \cdots (\text{H}_2\text{O})_n$ and ionising these clusters in order to attain vertical detachment energies.

As the apparatus available is capable of separating each cluster according to its solvating species and the number of solvating species around the NH_2^- anion, it is possible to analyse stepwise each new solvated state and observe the change in properties, specifically the vertical detachment energy. From the vertical detachment energy of the amidogen anion and its clusters other chemical properties can be calculated such as the electron affinity, the gas phase basicity, and the adiabatic detachment energy. These data will help us understand how the amidogen radical and anion interact with the stated solvents and potentially help analyse how the amidogen species affects our atmosphere it should also provide accurate energy readings so that these species can be reliably identified in extra-terrestrial research.

1.2 Motivation

The ‘Holy Grail’ of chemistry or indeed any science is to accurately predict and understand what will occur given situation. In chemistry these situations revolve around how atoms, and the electrons around those atoms, interact with each other. If we understand how those atoms and electrons interact we can presumably change the circumstances of those interactions to attain a desired outcome. While this goal has certainly been realised in a few cases there is still much more to learn and develop in the chemical field.

The aim of this research project is to improve our understanding of how the amidogen radical and anion behave, particularly when solvated by certain species. This leads to the question of how exactly will our understanding be improved? This can be as simple as attaining values for physical constants, proposing new theories, and then knowing where this new understanding can be applied. These questions will be addressed by giving an explanation of some of the most important physical observations as well as an outline of the atmospheric and extra-terrestrial research and how this research can aid such endeavours.

2. Background

2.1 Potential Energy Surfaces

A potential energy surface is an attempt to represent the real world in a way that is easier to understand. These surfaces can take a number of forms from representing something as simple as a single proton interacting with an electron, to the possible energies of a progressing reaction which illustrates how the energy of the system changes. The potential energy surfaces can be mapped through the variations in distances and angles between two bonding atoms or molecules. The simplest form of a potential energy surface is the variation of one degree of freedom, which is then called a potential energy curve rather than a surface.

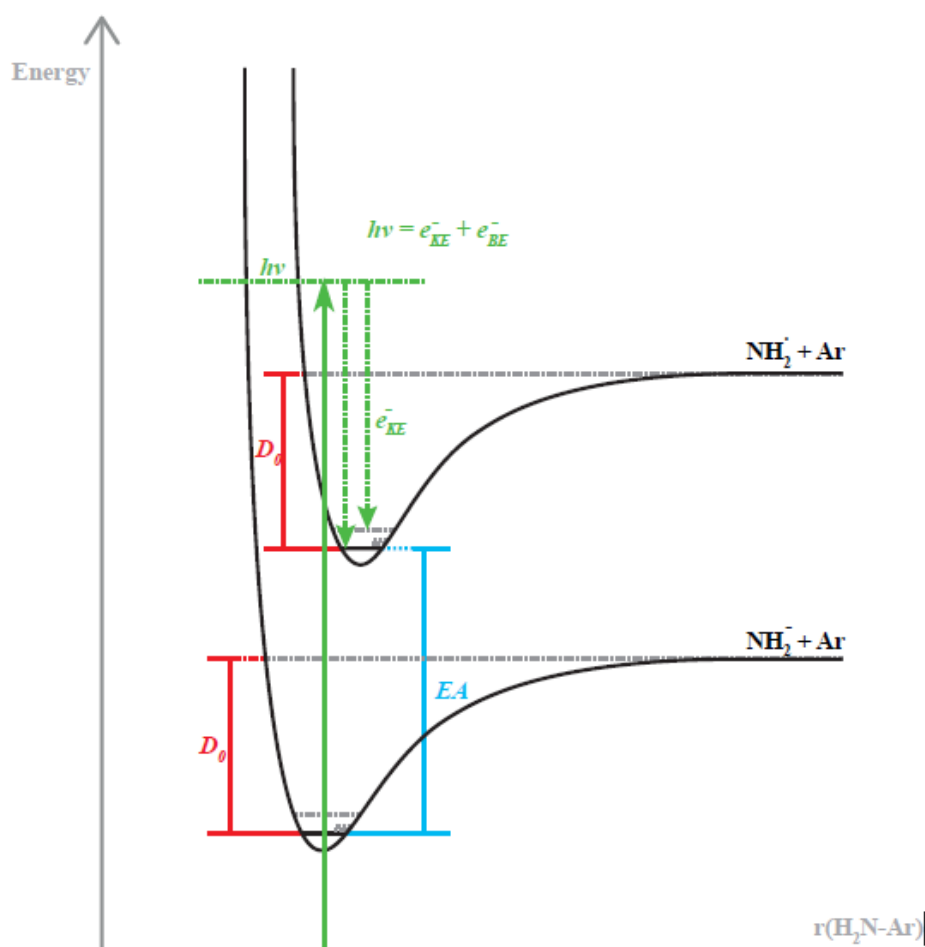


Figure 1 – Potential energy curves of the amidogen anion and amidogen radical co-ordinated with an argon molecule.¹

Figure 1 shows two representations of potential energy curves for the amidogen anion and amidogen radical interacting with an argon atom. The figure shows how the energy of the system changes as a function of the amidogen-argon radial distance. For both curves the interaction is attractive, resulting in a potential well termed a van der Waals minimum. The D_0 for each system is the binding energy of each system taking into account the zero point energy (the small gap between the bottom of the potential energy curve and the first energy level.) EA is the electron affinity which measures the affinity of an electron to the neutral species. The adiabatic detachment energy measures the energy required to remove one electron from the ground state of the anion leaving the molecule in the ground state of the neutral system, this is negative of the electron affinity. Finally the lines in green show $h\nu$ as the laser energy, e_{BE}^- is the electron binding energy and is equal to EA and e_{KE}^- is the Kinetic energy imparted onto the electron. These values will be discussed in greater detail later.

In the proposed work the upper curve, corresponding to the neutral amidogen radical interacting with argon, will be accessed by exciting the amidogen anion-argon van der Waals complex with laser radiation ($h\nu$), thereby detaching an electron. Each detached electron will contain specific information about the potential energy surface of the species from which it originated. This information can be used to map the potential energy surface of any species and better predict and understand its behaviour.¹

2.2 Vertical Detachment Energy

It is important to consider, (in particular for this research) that while a potential energy surface might be continuous, the energy levels supported by the potential energy surfaces are discrete, a consequence of the wave nature of atomic particles. This then affects the molecule, in that modes of vibration of a molecule must also be discrete. Figure 2 shows two different electronic states as potential energy curves and the corresponding discrete vibrational states

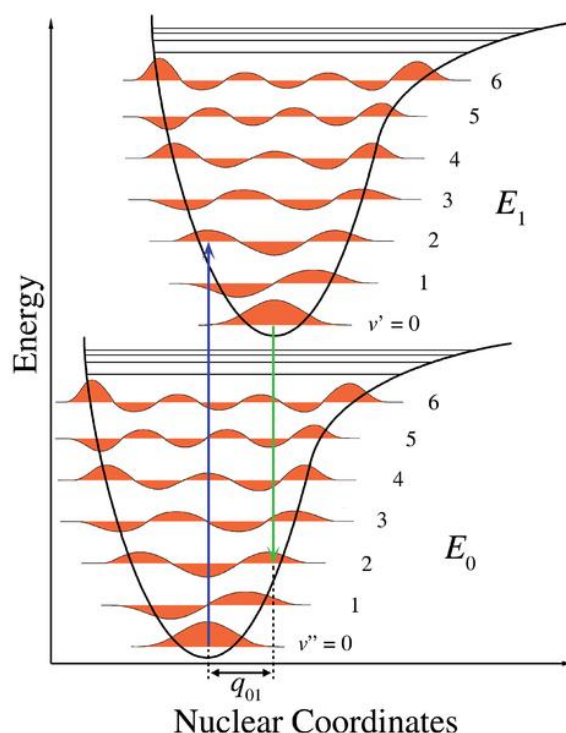


Figure 2 – A diagrammatic representation of the Franck-Condon Effect.²

shown within those curves. Due to these vibrations the nuclear coordinates of the molecule are constantly changing, so the molecule has a probability density for observation of specific nuclear coordinates.

The Born-Oppenheimer approximation states that transitions between energy states such as from E_0 ($v''=0$) to E_1 ($v'=0$) occur so rapidly (on the order of $\sim 10^{-15}$ s) that the nuclear coordinates of the molecule remain the same as the transition occurs (i.e. blue arrow). The most favourable electronic transition between states is determined by the overlap of the wavefunction of each vibrational mode. This means the most favourable electronic transition will have the largest overlap between the wavefunction of its current state and the state it is going to, other transitions will still be observed albeit less intense. The Franck-Condon effect describes the probability of a transition occurring based on the overlap between wavefunctions; the resulting energies of these

transitions determined by the Franck-Condon effect are termed vertical detachment energies.

The adiabatic electron affinity measures the energy difference from the ground state of a given species to the ground state of that same species with one electron removed. In Figure 2, this value would be the energy difference from E_0 ($v''=0$) to E_1 ($v'=0$), provided this energy transition is indeed the loss of one electron. In this case the vertical detachment energy would be E_0 ($v''=0$) to E_1 ($v'=2$). While it is possible that the vertical detachment energy can be the same as the adiabatic electron affinity this is rare and would require the equilibrium nuclear coordinates of the ground state of E_0 to be identical to the equilibrium nuclear coordinates of the ground state of E_1 .

These experiments aim to measure the energy of a transfer from the ground state of the anion potential curve to the ground state of the neutral potential curve in order to attain the adiabatic electron affinity. This is sometimes not possible due to the Franck-Condon effect which prevents observation of direct transitions between these two states. It is still valuable to report the vertical detachment energy of a species.

2.3 NH_2^- in Solution

Students of Chemistry are first introduced to NH_2^- when learning about the behavior of various acids and bases in solution. NH_2^- is the conjugate base to NH_3 as a weak acid.

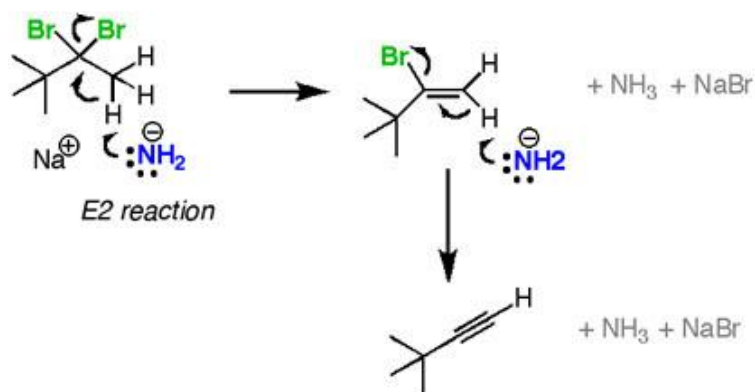


Figure 3 – Example of NH_3 acting as a nucleophile twice in this two-step reaction.⁴

Tack *et al.* noted, “ NH_2^- has long been postulated as a

nucleophilic agent in many chemical reactions.”³ These ideas are heavily supported through the use of substances like NaNH_2 in solution as both a strong base and a strong nucleophile as shown in Figure 3. Properties of these acids and bases are also dependent on their concentration in solution. As such, the properties of any substance in solution are a consequence of both its chemical composition and its solvated state. While it is very well understood what these properties are under standard conditions (STP), it is generally not well understood what will happen to these properties should conditions deviate from STP.

This research aims to provide information on how the properties on $\text{NH}_2^\bullet$ and NH_2^- change when solvated in the gas phase. Ideally this would provide a basis for us to understand how a progressive increase in the solvation number effects the behaviour of the anion or radical species from small clusters such as $\text{NH}_2^- \cdots (\text{H}_2\text{O})_{1-2}$, to the macroscopic scale that is most with in solutions such as $\text{NH}_2^-_{(\text{aq})}$.

2.4 $\text{NH}_2^\bullet$ in the Atmosphere

The atmosphere can be simply described as the layer of gases above the Earth's surface, the composition of this gaseous layer is vital to life on Earth. The atmosphere is divided into a number of regions (according whether the temperature of the atmosphere is increasing or decreasing, measured here as height above sea level) as shown in Figure 4.

One of the beneficial functions of the atmosphere is to filter out the majority of the lethal radiation that approaches Earth. High energy radiation such as X-rays and UV light interact with molecules in the atmosphere (most famously ozone) and is either absorbed or re-

dispersed as lower energy radiation. High energy radiation can also lead to unwanted reactions or break apart stable molecules to form radicals or ions. The formation of radicals and ions usually occurs in the troposphere or stratosphere where the density of the atmosphere is higher and interaction between radiation and these molecules are much more common. In fact this is part of the reason the Aurora Borealis and Aurora Australis occur.

The amidogen radical is formed in the stratosphere through direct photolysis as illustrated in reaction Eq. 1. Another mechanism involves the reaction between the hydroxyl radical and ammonia in the troposphere (reaction Eq. 2), with the hydroxyl radical formed through the photolysis of water.

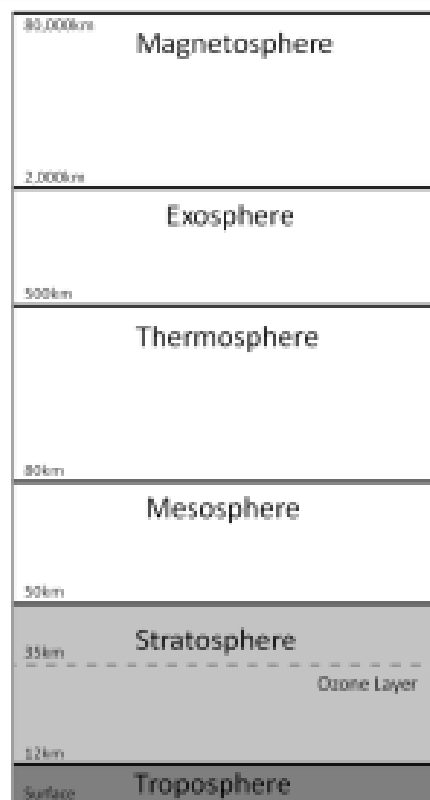
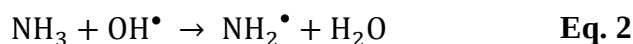
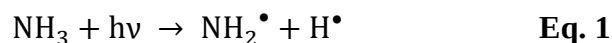
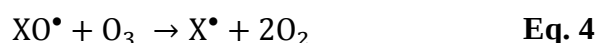
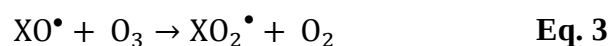


Figure 4 – A diagrammatic representation of the various layers of the atmosphere.⁵

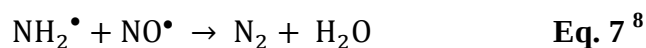
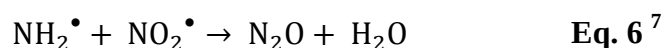


As the $\text{NH}_2^\bullet$ radical it is highly reactive it has a short lifetime in the atmosphere and it is considered to be an intermediate species for a host of reactions. A series of reactions conducted in the 1980s involved the reaction of the amidogen radical with nitrogen oxide gases (NO_x) in the atmosphere. This was around the time the hole in the ozone layer was noticed and potential solutions were being investigated. NO_x species react with ozone in much the same way halogens catalytically destroy ozone:



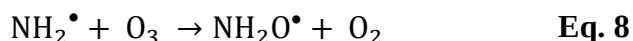
(where X is usually a halogen but can also be an NO_x species) ⁶

NH_2 reacts with the NO_x species forming a stable N-N bond and preventing it from further catalysing the destruction of ozone:



The reason $\text{NH}_2^\bullet$ was chosen for this study was due to the reaction kinetics. Most reactants that will remove NO_x species from a system can potentially themselves also take part in the catalytic destruction of ozone as shown above, as indeed can the amidogen radical. However, the reaction between the amidogen radical and ozone Eq. 8 is very slow with a rate constant of $6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁹ especially compared to

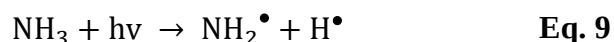
reactions Eq. 6 and Eq. 7, with a rate constant of $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for reaction Eq. 7.



From this research the hypothesized function of $\text{NH}_2^\bullet$ in the atmosphere is two-fold. Firstly, its production and subsequent reaction is the primary mechanism for removing ammonia from the atmosphere and secondly it reacts with and removes NO_x species which actively destroy the ozone in Earth's atmosphere.⁸

2.5 $\text{NH}_2^\bullet$ and NH_2^- in Extra-Terrestrial Environments

Ammonia has been shown to exist on a number of celestial bodies in our solar system including Saturn, Jupiter, Neptune, Uranus,¹⁰ and Halley's Comet¹¹ with evidence showing it could exist on Titan.^{12,13} The relative volume of ammonia on Jupiter and Saturn have been measured to be 0.3% and 0.05-0.2% respectively (compared to Earth at less than 0.00001% ammonia)¹⁰ and the chemistry of ammonia in each respective environment is heavily dependent on the amidogen radical (with some of the ammonia reactions observed of Saturn and Jupiter shown below). The reason that chemistry of the amidogen anion on Jupiter and Saturn does not follow that on Earth, is due to the large difference in composition.



On Earth, ammonia is found in trace concentrations, whereas within the atmosphere of these gas giants, ammonia is the fourth most common compound in the atmosphere.

This means there is potentially a much greater chance of two amidogen radicals interacting.

Neptune and Uranus have also been shown to contain ammonia in the atmosphere,¹⁰ however in much smaller quantities than Jupiter and Saturn. This is because the temperatures of Neptune and Uranus are low enough that ammonia condenses to a liquid. The ammonia that is contained in the atmosphere acts in much the same way as it does on Jupiter and Saturn.

Titan is a moon orbiting the planet Saturn, and is of particular interest to astronomers as it is considered to be the next most likely celestial body in our solar system to harbour life after Earth.¹⁴ As such, it has been the subject of many research papers and space missions. One of the studies of interest here is the analysis of negative ion content in Titan's upper atmosphere. Vuitton *et al.*¹² used data attained from a number of space missions that probed Titan's upper atmosphere in order to identify the negative ions present. The ions identified largely consisted of small carbon-centred species. The authors noted that, "Negative ion chemistry, especially when involving N-bearing species, is extremely poorly known and potentially induces large uncertainties in the ion densities." The research presented here aims to increase the knowledge of how N-bearing species, namely the amidogen radical, interact with the environments they are in.

Halley's Comet also shows evidence for the presence of NH_3 ¹⁰ as well as numerous negative ions.¹¹ In such an environment where ammonia is present and exposed to cosmic rays it is highly likely that the amidogen radical would be formed via equation Eq. 1 and would play a role in the chemistry present on the comet.

3. Past Research

3.1 The Amidogen Radical

The amidogen radical is a well-studied radical with a range of information available on its electronic states and thermodynamic properties. Perhaps the most relevant information to our study is the electron affinity of the amidogen radical which has been reported by a number of research groups^{15–20}. However many of the initial reported values for electron affinity disagreed with each other^{16–20}. A paper by Celotta *et al.*¹⁶ in 1974 collected all research in this field at the time showing that old studies of the electron affinity of the amidogen radical grouped around ~ 1.1 eV^{19,20} and a number of more recent studies a value around ~ 0.77 eV^{16–18}. While Celotta *et al.*¹⁶ offered no explanation for these grouping of values, there has been no published dispute over the electron affinity of the amidogen radical since. The current accepted value for the electron affinity is $0.779^{+0.013}_{-0.017}$ eV¹⁶ with Wickham-Jones *et al.* reporting an adiabatic electron affinity of 0.771 eV¹⁵ in 1989.

There are also a number of studies on the vibrational and electronic states of the amidogen radical which are compiled by the National Institute of Standards and Technology (NIST), see tables below, where the experimentally determined vibrational frequencies for the ground state (X) and excited state (A) are presented. Also presented are term values for the first excited state (A state), and for excited Rydberg states (high principle quantum number “n”).

Table 1 - Known vibrational modes of the X state of the amidogen radical

Vibrational Symbol	No.	Mode	Wavenumber (cm ⁻¹)	Reference
a₁	1	Symmetric Stretch	3219.37	21-25
	2	Bend	1497.32	21,23,26-31
b₂	3	Asymmetric Stretch	3301.11	22,24,25

Table 2 – Known vibrational modes of the A state of the amidogen radical

Vibrational Symbol	No.	Mode	Wavenumber (cm ⁻¹)	Reference
a₁	1	Symmetric Stretch	3325	26
	2	Bend	1157.8	32

Table 3 - A States of the amidogen radical

Energy (cm ⁻¹)	Medium	Transition	$\lambda_{\min}$ (nm)	$\lambda_{\max}$ (nm)	Reference
T ₀ = 11122.23 ± 0.05	gas	A-X	342	2700	21,22,26,27,32-37
	Ne	A-X	344	880	38
	Ar	A-X	344	880	23,38,39
	Kr	A-X	344	880	23,38,39
	Xe	A-X	344	880	23,38,39
	N ₂	A-X	480	620	39
	Ar	A-X	344	790	23,39
	Kr	A-X	344	790	23,39
	Xe	A-X	344	790	23,39

Table 4 - Rydberg States of the amidogen radical

Quantum Number (n)	Energy (cm ⁻¹)*
4	T₀= 98049
5	T₀= 97193
6	T₀= 95753
7	T₀= 93054

Note: The above tables are adapted from the National Institute of Standards and Technology website (US)⁴⁰

*All values from Gibson *et al.*⁴¹

The separation between X and A states of $\text{NH}_2^\bullet$ is 11122.23 cm^{-1} or 1.38 eV. Usually when removing an electron from a species with laser radiation it is only possible to observe the ground electronic state of the radical species. However, if the laser is of high enough frequency it should be possible to remove an electron from the amidogen anion and leave the amidogen radical in first excited electronic state. In this case 1.38 eV extra energy is needed to leave the amidogen radical in its first excited state rather than the ground state. As the setup used in Wild laboratory employs laser radiation at 4.66 eV it should be high enough frequency to observe both the A excited state and the X ground state.

Theoretical studies also exist, giving thermodynamic constants for the amidogen radical.^{42–45} These studies discuss the effectiveness of conducting research by combining theoretical and experimental work⁴⁵ to investigate how the amidogen radical might be solvated in water.⁴⁴ In fact the paper by Merchán *et al.*⁴³ discusses the errors associated with calculating the electron affinity of the amidogen radical particularly when using the geometry of the amidogen anion as the geometry for the amidogen radical. The reason as to why the same geometry was used was because experimental studies start with the amidogen anion in order to measure the electron affinity of the radical. The conclusion was that the difference in geometry of the two amidogen states is so slight it would only introduce an error of 0.001 eV. As this study uses the amidogen anion it is prudent to also investigate its past research.

3.2 The Amidogen Anion

The amidogen anion has been less studied than its neutral radical counterpart. The majority of the research conducted on the amidogen anion is coupled directly with work on the amidogen radical. Typically, this involved finding the electron affinity of the amidogen radical through ionisation of the amidogen anion using photoelectron

spectroscopy. Research groups that did this often attained adequate data to report the vibrational characteristics of the amidogen anion, and in addition identified a low lying excited electronic state at 6220 cm^{-1} above the ground state.^{15–17}

Other research on the vibrational structure of the amidogen radical include matrix infrared spectroscopy⁴⁶ and velocity modulation infrared spectroscopy.⁴⁷ This vibrational data has also been collated by NIST and is shown below:

Table 5 - Known vibrational modes of the X state of the amidogen anion

Vibrational Symbol	No.	Mode	Wavenumber (cm^{-1})	Reference
a₁	1	Symmetric Stretch	3121.93	3,47
	2	Bend	1523	46
b₂	3	Asymmetric Stretch	3190.29	3
	3	Asymmetric Stretch	3152	46

Table 6 – A state of the amidogen anion

Energy (cm^{-1})	Reference
T₀ = 6220 ± 40	15,16,18

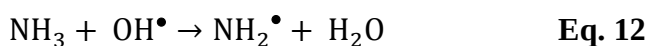
Note: The above tables are adapted from the National Institute of Standards and Technology website (US)⁴⁰

Theoretical studies have also been conducted^{48,49} mostly with the goal of providing data to compare with the experimental results. Calculations using a number of functional methods and basis sets were compared with experimental results allowing conclusions to be made regarding the best functional and basis set to use with Tschumper *et al.*⁴⁹ reporting DFT was the best method to use in this case.

Finally, a small amount of research has been conducted regarding how the amidogen anion interacts with solvents. This is the focus of the proposed study, so research that has already been conducted in this field is of particular interest.

3.2 Amidogen Radical and Anion Solvation

The amidogen radical solvating with water was found to be the most commonly studied cluster. A research paper by Ennis *et al.*⁵⁰ investigated the reaction:



and was particularly concerned with the complex that forms as an intermediate in the reaction. This was done by calculating the vibrational modes of $\text{NH}_2^\bullet \cdots \text{H}_2\text{O}$ and then investigating the observable vibrational modes experimentally. Experimental work showed two vibrational modes of the $\text{NH}_2^\bullet \cdots \text{H}_2\text{O}$ complex corresponding with two predicted vibrational modes from CCSD(T) calculations. It also failed to observe any vibrational modes from $\text{OH}^\bullet \cdots \text{NH}_3$ complex, suggesting that it was reacting to form the $\text{NH}_2^\bullet \cdots \text{H}_2\text{O}$ complex.

This research was preceded by a theoretical study by Yu *et al.*⁴⁴ concerning the thermochemistry and transition energies of the amidogen radical and ammonia radical. It also proposed possible geometries of these species when coordinated to one, two and three water molecules.

The only research that could be found that used photoelectron spectroscopy techniques to investigate the complex formation around an amidogen anion and then probe the change in electrical properties associated with that was by Snodgrass *et al.* in 1994,⁵¹ and this research was recently added to by Sanov *et al.* in 2011.⁵² In this research the amidogen anion once generated, formed complexes with ammonia. Snodgrass *et al.* was able to attain and report on the photoelectron spectra of the two complexes

$\text{NH}_2^- \cdots \text{NH}_3$ and $\text{NH}_2^- \cdots (\text{NH}_3)_2$. These spectra showed an increasing vertical detachment energy starting from 0.78 eV (the electron affinity of $\text{NH}_2^\bullet$) for NH_2^- , increasing to 1.311 eV for $\text{NH}_2^- \cdots \text{NH}_3$ and ending at 1.775 eV for $\text{NH}_2^- \cdots (\text{NH}_3)_2$. This is to be expected considering coordination of the amidogen anion to a solvent will stabilise the species, leading to a larger electron affinity. Gas phase basicities and ion-

solvent dissociation energies were then calculated based on the data acquired.

Sanov *et al.*⁵² extended the work of Snodgrass *et al.*⁵¹ by investigating $\text{NH}_2^- \cdots (\text{NH}_3)_n$, ($n=1-5$). Additionally higher frequency laser radiation was used allowing for observation of the next energy state of the amidogen radical shown in Figure 5. The electron binding energy of these amidogen clusters show good agreement with the work by Snodgrass *et al.*⁵¹ for clusters $n=1,2$ and continued to increase the binding energy of the amidogen clusters for $n=3-5$. Photoelectron spectra taken of the same complex using a wavelength of 532 nm (rather than the 355 nm used in Figure 5) showed the existence of a

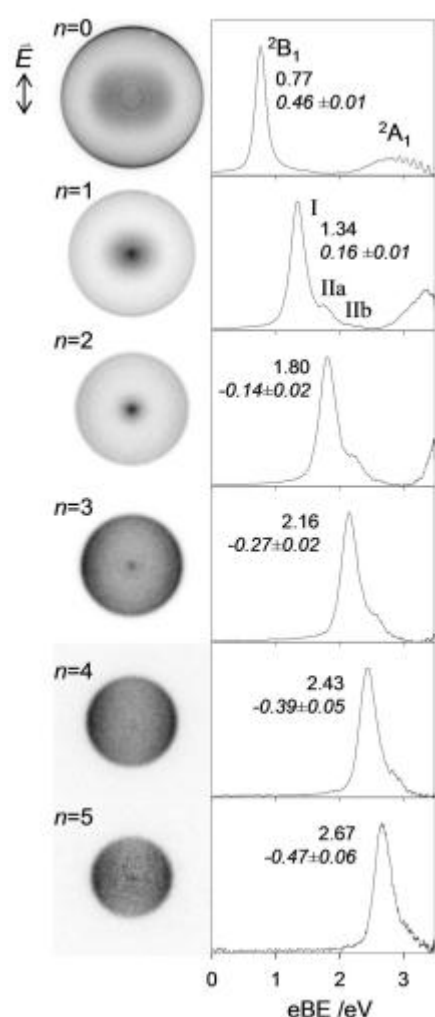


Figure 5 - Photoelectron image and energy spectra for photodetachment from $\text{NH}_2^-(\text{NH}_3)_n$, ($n=0-5$), at 355nm. Taken from Sanov *et al.*⁵⁰

possible charge-transfer-to-solvent precursor state, a phenomenon previously observed using photoelectron spectroscopy by Neumark *et al.* in

2000.⁵³ In this metastable state the extra electron from the parent anion is donated to a solvent molecule after which auto detachment occurs.

This study was then reinforced the next year by Roszak⁵⁴ who performed theoretical calculations on the complexes studied by Snodgrass *et al.* showing, “excellent agreement between experimental and theoretical results”. This ‘excellent agreement’ showed that a new recently proposed basis set for *ab initio* calculations of weak molecular complexes is indeed useful and valid.

4. Theoretical Work

4.1 Theoretical Overview

When conducting theoretical work using computational software it is easy to lose sight of what is happening beneath layers of code and programming. Sometimes termed the ‘black box’ approach in which a problem is answered by an *ab initio* program while the reason for this answer remains unclear. This section aims to increase the clarity of how theoretical solutions are arrived at followed by the process behind theoretical calculations for this research.

4.1.1 The Schrödinger Equation

The time-independent nonrelativistic Schrödinger equation is the basis of all *ab initio* computational chemistry calculations reported in this thesis. Written as:

$$\hat{H}\Psi = E\Psi \qquad \text{Eq. 13}$$

where Ψ is called the wavefunction and describes properties of a quantum system given certain boundary conditions. $\hat{H}$ is an operator called the Hamiltonian and when acting upon a wavefunction will give the energy E of the system described by the wavefunction. However analytical solutions to Schrödinger equation are only possible for the motion of one electron in a potential well and the more complex the system becomes the harder the Schrodinger equation is to solve, eventually becoming impossible.

Consequently a number of approximations have emerged allowing for solutions to many electron systems. Some of the approximations used in this thesis follow below and for a more detailed description of quantum chemistry including these approximations and more please see Levine⁵⁵ and Jensen.⁵⁶

4.1.2 Born-Oppenheimer Approximation

The Born-Oppenheimer approximation states that the wavefunction for a system $\Psi(r_e, r_n)$ (where r_e and r_n are the electronic and nuclear coordinates respectively) can be approximated by separating the wavefunction into two parts, one describing the position of electrons about the nuclei and the other describing the position of the nuclei, shown mathematically below:

$$\Psi(r_e, r_n) = \Psi_e(r_e, r_n)\Psi_n(r_n) \quad \text{Eq. 14}$$

The errors introduced by this approximation are small especially when compared to errors introduced by approximations yet to come, and hence these errors are rarely corrected for.

4.1.3 Variation Theorem

The Variation theorem starts from a base set of parameters for any system and states that any wavefunction that can be written to describe that system will have an energy equal to, or higher than the ground state of that system, described mathematically below:

$$\langle \Psi | \hat{H} | \Psi \rangle = E \geq E_G \quad \text{Eq. 15}$$

where E is the energy of the system described by Ψ and E_G is the lowest possible energy a system can have with the same boundary conditions as Ψ . It is therefore possible to trial a number of wavefunctions for a system until you have an appropriate wavefunction for the ground state by investigating which wavefunctions give the lowest energy. An example trialling three wavefunction is shown in Eq. 16.

$$\langle \Psi_3 | \hat{H} | \Psi_3 \rangle \geq \langle \Psi_2 | \hat{H} | \Psi_2 \rangle \geq \langle \Psi_1 | \hat{H} | \Psi_1 \rangle \geq E_G \quad \text{Eq. 16}$$

4.1.4 Perturbation Theory

Perturbation theory starts with a wavefunction for which the Schrödinger equation cannot be solved and aims to find a solution using a slightly different wavefunction which can be solved. For example, if a system is a one-dimensional anharmonic oscillator giving a Hamiltonian and Schrödinger equation of:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 + cx^3 + dx^4 \quad \text{Eq. 17}$$

$$\hat{H}\Psi_n = E_n\Psi_n \quad \text{Eq. 18}$$

a similar harmonic oscillator giving a similar Hamiltonian and Schrödinger equation to begin approximating a solution to our initial wavefunction can be used (on the condition that c and d are small):

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2}kx^2 \quad \text{Eq. 19}$$

$$\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \quad \text{Eq. 20}$$

This gives us an unperturbed system with Hamiltonian $\hat{H}^{(0)}$, a perturbed system with Hamiltonian $\hat{H}$ and our perturbation $\hat{H}'$:

$$\hat{H}' = \hat{H} - \hat{H}^{(0)} \quad \text{Eq. 21}$$

It is then possible to relate the known eigenvalues and eigenfunctions of the unperturbed system to the eigenvalues and eigenfunctions of the perturbed system through the perturbation. The first order correction for the wavefunction using perturbation theory is:

$$\Psi_n^{(1)} = \sum_{m \neq n} \frac{\langle \Psi_m^{(0)} | \hat{H}' | \Psi_n^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}} \Psi_m^{(0)} \quad \text{Eq. 22}$$

For details on how this correction was attained and further corrections refer to Levine Chapter 9 pg 225⁵⁵.

4.1.5 Hartree Self-Consistent Field

A large portion of the complexity of many electron systems is due to each electron in a system interacting with every other electron in that system. Each interaction changes the wavefunction slightly and will have its own term within the Hamiltonian describing its behaviour mathematically. The number of terms needed to describe interactions as the number of electrons in a system increases grows exponentially.

The Self-Consistent Field method bypasses much of this difficulty by considering each electron individually and ‘smearing’ out the remaining electrons in the system. This simplifies the problem as; first we are averaging the interactions between the electron we have chosen to focus on with all the others, secondly by neglecting the individual repulsion we can write a zeroth order wavefunction:

$$\Psi^{(0)} = f_1(r_1, \theta_1, \Phi_1) f_2(r_2, \theta_2, \Phi_2,) \dots f_n(r_n, \theta_n, \Phi_n) \quad \text{Eq. 23}$$

with each function f describing each individual electron (ordinarily individual electron wavefunctions cannot be separated like this). This wavefunction can then be worked through iteratively, improving each time by modifying each individual electron’s wavefunction while the remaining electrons are ‘smeared’ out as a charge density and trying to minimize the variation integral, $\langle \Psi | \hat{H} | \Psi \rangle$. (Being an iterative method the cycle is finished when the most recent calculation is identical to the previous ones).

The Hartree Self-Consistent Field Method is improved upon by the Hartree-Fock Self Consistent Field Method which uses Slater Determinants to provide proper anti-symmetry found in electron systems, please see Levine pg271⁵⁵ for further explanation of Slater determinants.

4.1.6 Møller-Plesset Perturbation Theory

As the Hartree Fock Self Consistent Field Method averages the electron interactions it fails to take into account individual electron-electron interactions. As electrons repel each other the average treatment of electrons is not indicative of typical electron behaviour and hence methods that do take these interactions into account had to be developed, one such being Møller-Plesset Perturbation Theory. Møller-Plesset Perturbation Theory in essence combines the Hartree Fock Self Consistent Field Method with standard perturbation theory, both of which have been introduced above. Starting from the unperturbed wavefunction the Hartree-Fock energy is calculated giving the first energy approximation of the system:

$$\begin{aligned} E_0^{(0)} + E_1^{(0)} &= \langle \Psi^{(0)} | \hat{H}^0 | \Psi^{(0)} \rangle + \langle \Psi^{(0)} | \hat{H}' | \Psi^{(0)} \rangle \quad \text{Eq. 24} \\ &= \langle \Psi^{(0)} | \hat{H}^0 + \hat{H}' | \Psi^{(0)} \rangle \\ &= \langle \Psi^{(0)} | \hat{H} | \Psi^{(0)} \rangle = E_{\text{HF}} \end{aligned}$$

The above equation simply shows that the perturbative method of attaining first energy correction simplifies down to the energy correction found using the Hartree Fock method. This is followed up by applying perturbation theory to determine second order corrections and higher, giving rise to MP2 as a calculation using second order corrections (MP3 and MP4 including third and fourth order corrections respectively). Using the variation theorem these steps can then be repeated until the approximated energy reaches a limit. Møller-Plesset Perturbation Theory has considerable accuracy and computational efficiency making it a very commonly used level of theory when conducting *ab initio* calculations such as those undertaken in this thesis. As such the MP2 level of theory was used to calculate the geometries of each complex before moving to a higher level of theory such as Coupled-Cluster Theory.

4.1.7 The Coupled-Cluster Method

Another theoretical method that includes effects due to electron-electron interaction is the Coupled Cluster theory. Coupled-Cluster (CC) theory revolves around the equation:

$$\Psi = e^{\check{T}}\Phi_0 \quad \text{Eq. 25}$$

where Ψ is the exact non-relativistic ground-state molecular electronic wavefunction, Φ_0 is the normalized ground-state Hartree-Fock wavefunction and $\check{T}$ is the Cluster Operator such that:

$$\check{T} = \check{T}_1 + \check{T}_2 + \dots + \check{T}_n \quad \text{Eq. 26}$$

with n being the number of electrons in the system and each $\check{T}_i$ being defined individually. The $e^{\check{T}}$ operator can also be expanded through Taylor series:

$$e^{\check{T}} = 1 + \check{T} + \frac{\check{T}^2}{2!} + \frac{\check{T}^3}{3!} + \dots = \sum_{k=0}^{\infty} \frac{\check{T}^k}{k!} \quad \text{Eq. 27}$$

The operator $\check{T}_1$ when acting on Φ_0 will give a linear combination of all possible singly excited states of the system (or more correctly give a linear combination of all single excited Slater determinants of the system, please see Levine pg271⁵⁵ for further explanation of Slater determinants.) Similarly $\check{T}_2, \check{T}_3, \dots \check{T}_n$ will give all the doubly, triply, etc. excited states of the system. Additionally, when an operator acts twice on the wavefunction such as, $\check{T}_1(\check{T}_1\Phi_0)$ this will give a linear combination of doubly-excited states, although not all of them.

It has been shown⁵⁷ that the most important contributor to the $\check{T}$ operator is $\check{T}_2$ giving an approximation to the CC approach called Coupled-Cluster Doubles (CCD) Method. This method, when expanded by the Taylor series above (replace $\check{T}$ with $\check{T}_2$) is still a substantial computational task, however considerably less than that required to amount

for all the components of the cluster operator. The CCD method then also gives an approximation to quadruple excitations as $\frac{1}{2}\check{T}_2^2$ appears in the Taylor expansion (similar to $\check{T}_1(\check{T}_1\Phi_0)$ giving doubly excited states) and this has been shown to be an accurate approximation too.⁵⁵

A further modification to CCD termed Coupled-Cluster with Single and Double and Perturbative Triple excitations (CCSD(T)) has been used in this thesis. This level of theory uses the $\check{T}_1$ and $\check{T}_2$ operators in full and approximates $\check{T}_3$. This is the highest and final level of theory used to determine possible geometries of the clusters analysed in this thesis, with calculations using a pre-optimised geometry from MP2 usually taking 100 or more computational hours to give a result.

4.2 Theoretical Methodology

Ab initio calculations have been carried out in order to predict the optimal structure and respective energy changes of the 1 : 1 complex ions (ion : ligand) that this research is investigating, the computational program suits used include GAMESS⁵⁸ and ORCA.⁵⁹

The first attempts to find an optimised structure for the clusters being investigated involved guessing, using chemical intuition, the structure of these clusters. This usually meant placing the ligand molecules within 2.5 Å to 3.5 Å and changing the position and orientation of these molecules with respect to the amidogen anion or radical that it is bonding to.

It may be that chemical intuition may omit other possible isomeric forms of a complex. In order to test for this, initial geometries for the complexes were produced by constructing a program whereby a ligand is placed at a set radius and angle (using spherical-polar coordinates, see Appendices for source code) from a central species,

with the option to change the orientation of the ligand if necessary (e.g. it is necessary for CO but not Ar). The purpose of this was to have a systematic sweep of all geometries rather than those considered most likely by chemical intuition. These initial structures were then tested using Møller-Plesset 2nd order perturbation theory and aug-cc-pVXZ (X = D,⁶⁰ T^{61,62}) basis sets with either ‘tight’ or ‘very tight’ optimisation constraints.

The optimisation constraints refers to the difference in energy between each optimisation step, for an optimisation calculation converges to an optimum geometry the difference in energy between each step decreases. An optimisation calculation is considered to be finished when the difference in energy between iterations falls below a certain value. ‘Tight’ or ‘very tight’ optimisation constraints refer to an energy change between the penultimate and final step of an optimisation calculation of 1×10^{-5} and 1×10^{-6} hartrees respectively.

Once these calculations had settled upon an optimum structure a vibrational frequency analysis was conducted to test whether it was a minimum or transition state on its potential energy surface. Any structures that show imaginary frequency values are higher order stationary points and hence discarded, all remaining stationary points were assumed to be local minima and were further tested and optimised using Coupled-Cluster with Single and Double and Pertubative Triples excitation. Optimum structures yielded by the Couple Cluster calculations were again tested using a frequency analysis to confirm they were still minima under Coupled Cluster Theory. Finally, a Natural Bond Order analysis (NBO) was carried out to determine the bonding order and location of electrons within the complexes.⁶³ Basis set superposition error (BSSE)⁶⁴ calculations were also performed to determine appropriate binding energies for these complexes.

4.3 Theoretical Results

There has been very little theoretical work reported for the following complexes especially in such a way that can be compared to the work here, however comparisons have been made where possible. All values quoted are taken from calculations at CCSD(T)/aug-cc-pVTZ unless stated otherwise. All relevant molecular and electronic parameters (as well as for the higher order stationary points) have been included in the Appendices.

4.3.1 $\text{NH}_2^{\cdot\cdot}\cdots\text{Ar}$

Attempts to find the optimum structure of the amidogen anion-argon clusters at the MP2/aug-cc-pVTZ level of theory returned a number of geometries of which only one proved to be a minimum after Hessian analysis shown in Figure 6 (for additional structures see Appendices).

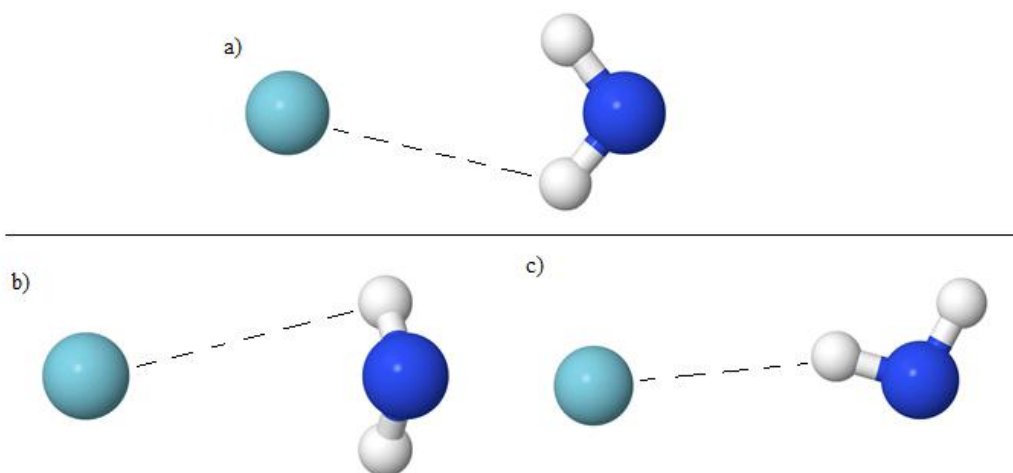


Figure 6 - Geometries predicted from *ab initio* calculations of (a) the $\text{NH}_2^{\cdot\cdot}\cdots\text{Ar}$ anion complex and (b), (c) the $\text{NH}_2^{\cdot\cdot}\cdots\text{Ar}$ radical complexes where complex b) shows argon equidistant to each hydrogen atom and complex c) shows argon in the same plane as the amidogen species.

In each complex the argon ligand is always closest to a hydrogen atom which could be due to a dipole induced dipole interaction arising from a slight positive charge on the hydrogens of 0.26 e shown by the NBO Analysis. The NBO analysis shows only -0.87 me (milli electrons) on argon as part of the amidogen anion-argon complex. Such a small deviation from the expected zero charge on argon suggests a very small electronic change due to coordination to the amidogen species. This in turn suggests very small geometric changes in the amidogen anion.

This is indeed the case and can be shown by examining the perturbation of the amidogen anion and radical respectively when bonded to Argon. Using CCSD(T)/aug-cc-pVTZ level of theory and ‘very tight’ constraints the amidogen anion is predicted to have a nitrogen-hydrogen bond length of 1.032 Å and bond angle of 101.9°. For the amidogen anion-argon complex shown in Figure 6 the nitrogen-hydrogen bond length decreases to 1.031 Å and bond angle of the amidogen anion remains 101.9°. The amidogen anion-argon cluster symmetry displays close to C_{2v} , however the distance between the argon atom and each hydrogen atom is 3.204 Å and 3.231 Å, meaning C_s symmetry is observed instead.

The D_0 value of the amidogen anion-argon species is 1.4 kJmol⁻¹, this is consistent with the small contribution from argon to the electronic state of the amidogen anion and the negligible changes to the geometry of the amidogen anion.

4.3.2 $NH_2^{\bullet} \cdots Ar$

Two minimum geometries were found for the neutral amidogen radical-argon complex, both are shown in Figure 6 (other transition state geometries are available in Appendix). Attempts to calculate a minimum starting from the structure of the amidogen anion-argon complex returned transition state geometries.

Similar to the anion species the change in the electronic state of the argon is negligible with 0.81 me on argon for neutral species b) and 0.39 me for neutral species c) (Figure 6). The structural change in the amidogen anion is also negligible with a change of only 0.001 Å for complex b) with nitrogen-hydrogen bond closest to argon (there were no other bond length changes for either species). The bond angle of the amidogen radical does not change for complex a) and only by 0.1° for complex b).

Compared to the amidogen anion the argon ligand has moved to the top of the neutral radical for complex b) and such that it is closest to one of the hydrogen atoms for complex c). For complex b) this increases the distance between hydrogen and argon to 3.380 Å for both hydrogen atoms however brings it closer to nitrogen with a separation of 3.438 Å rather than 3.766 Å as is seen for the anion species. For complex c) argon is now 2.888 Å away from the closest hydrogen. Finally amidogen radical-argon complex b) displays C_s symmetry while c) has C_1 symmetry.

As for the anion species the small effect on the electronic and geometric structure the amidogen radical is reflected by a small D_0 with 0.3 kJmol⁻¹ and 1.2 kJmol⁻¹ for the amidogen radical-argon complexes b) and c) respectively. The D_0 of complex b) is so low that for MP2/aug-cc-pVTZ calculations the Basis Set Superposition Error correction causes the D_0 to become negative.

The predicted adiabatic detachment energy based on the above calculation is 0.866 eV and 0.862 eV when detaching into complex b) and c) respectively using MP2/aug-cc-pVTZ level theory. The predicted adiabatic detachment energy of the amidogen anion is 0.852 eV when the experimental value is 0.779 eV. The respective increase in adiabatic detachment energy for these complexes appears reasonable and in line with other observed changes in adiabatic detachment energies such as the shift observed between I^- and $I^- \cdots CO$.⁶⁵ In the case of $I^- \cdots CO$ the observed change in energy was

0.04 eV, in this case it is 0.010 eV and 0.014 eV and considering argon is a weaker ligand this seems reasonable. Using CCSD(T)/aug-cc-pVTZ level theory the predicted adiabatic detachment energy is slightly worse at 0.650 eV and 0.641 eV for b) and c) respectively however the adiabatic detachment energy for the bare amidogen anion in this case is 0.638 eV and so these comments still hold.

4.3.3 $\text{NH}_2^- \cdots \text{CO}$

Attempts to find structures for the amidogen anion-carbon monoxide species returned only two geometries and only one of these was a minimum. This optimum minimum structure showed a covalent bond formed between nitrogen and carbon, resulting in the formamide anion and consequently changing the structures of the amidogen anion and carbon monoxide monomers significantly.

The formamide anion has been previously studied including work based on its basicity,^{66–68} the reactivity of formamide with carbon chain substituents⁶⁹ and a photodetachment study of formamide.⁷⁰ The reason these studies cannot be compared with the work done here is that the focus is different, the structure of the formamide anion is shown in Figure 7, the work mentioned above focusses on the reactivity of the formamide anion in various systems. Work that does look into the structure of the formamide anion⁶⁸ removes a hydrogen from nitrogen rather than hydrogen from carbon to form the amidogen anion, bond lengths have been compared with this work regardless. The formamide molecule has also been previously studied⁷¹ and bond lengths and angles can be compared (See Table 7).

The NBO analysis shows a considerable change in the electronic structure of both molecules. A charge of 0.61 e and -0.61 e on carbon and oxygen respectively when bonded together as carbon monoxide, this changes to 0.24 e and -0.89 e when part of the formamide anion. Similar analysis for the amidogen anion shows a charge of -1.5 e

on nitrogen with the a positive charge of 0.53 e being shared by each hydrogen before bonding with carbon monoxide. After bonding with carbon monoxide this decreases to -0.99 e on the nitrogen with 0.31 e and 0.33 e on each hydrogen. Clearly the excess charge is further stabilized by the addition of carbon monoxide to the molecule and the electron withdrawing effect should be expected as oxygen is the most electronegative species present. The NBO analysis also shows the carbon monoxide triple bond becomes a double bond, allowing for the formation of a new single bond between carbon and nitrogen.

These considerable electronic changes are reflected by the structural changes each monomer undertakes. The carbon-oxygen bond length increases from 1.138 Å to 1.245 Å, the nitrogen-hydrogen lengths decrease to 1.029 Å and 1.014 Å, with a much larger amidogen bond angle of 112.3°.

The electronic change and geometric changes of the amidogen anion-carbon monoxide cluster are reflected by a very large D_0 at 126.5 kJ·mol⁻¹.

The bond angle and lengths found here have been compared to those found by Csizmadia *et al.*⁶⁸ who studied de-protonation of formamide to form the formamide anion (although Csizmadia *et al.*⁶⁸ removes one hydrogen from nitrogen rather than carbon) and those found by Chong.⁷¹ Csizmadia *et al.*⁶⁸ conducted calculations at 3-21G SCF level theory and Chong conducted a number of calculations the highest level of theory he used was CCSD(T)/6-311+(p,d).

Comparisons have been made in Table 7 and it can be seen that all the values are similar. The largest differences being in the carbon-nitrogen bond length and oxygen-carbon-nitrogen bond angle. Furthermore the formamide molecule is predicted to be planar by Chong while the anion species shown in this work features the nitrogen-hydrogen bonds angled away from the plane of the central molecules.

A paper published by Ning *et al.*⁷² refers to the ‘wagging angle’ of the nitrogen-hydrogen bonds in the formamide molecule, the ‘wagging angle’ refers to the tendency of the nitrogen-hydrogen bonds to move out of the planar conformation of the formamide molecule, with the probability of these bonds being within 10° of the molecular plane being 29%.⁶⁸ As the formamide anion optimal structure found here shows a large deviation from this plane perhaps comparing the anion and neutral formamide molecules would be a good method for investigating this ‘wagging angle’.

Table 7 - Comparison of Formamide bond lengths and angles across research papers

Formula of Formamide	r(N-H)ave* (Å)	r(C-N) (Å)	r(C-O) (Å)	θ(N-C-O) (°)	θ(H-N-H) (°)	References
OCNH ₂ ⁻	1.0215	1.466	1.245	113	112.3	This work
OCHNH ₂	1.0106	1.3753	1.2154	124.64	117.09	Chong ⁷¹
OCHNH ⁻	1.0253	1.304	1.264	131.84		Csizmadia ⁶⁸
OCHNH ⁻	1.0204	1.3071	1.2559	129.07		Csizmadia ⁶⁸

* average of all N-H bond lengths

4.3.4 NH₂•···CO

Attempts to find an optimised geometry for the amidogen radical-carbon monoxide cluster proved difficult. Initial calculations using MP2/aug-cc-pVDZ level theory yielded seven optimum geometries only three of which converged when the basis set was increased in size from aug-cc-pVDZ to aug-cc-pVTZ and of which only one proved to be a minimum structure after Hessian analysis. The reason so few optimum geometries were returned when investigating the amidogen radical-carbon monoxide cluster was due to a failure of the SCF to converge. This is due to the initial structure

for optimisation being very different from any possible optimal geometries for example carbon monoxide being too close or far away from the amidogen radical. Despite attempts to improve these initial structures finding optimum structures were particularly difficult for this system.

When the optimal structure from MP2/aug-cc-pVTZ level theory was analysed CCSD(T)/aug-cc-pVTZ level theory it converged to a much different geometry as shown in Figure 7 (which is yet to be tested with Hessian analysis). Furthermore the program used to attain the initial stationary point of the amidogen radical-carbon monoxide complex was GAMESS at MP2/aug-cc-pVTZ level theory Figure 7 a) and it was found that the equivalent structure using the same level theory in ORCA is a transition state. This prompted a double check of all MP2 geometries in ORCA and all other geometries with the exception of this one are consistent. Unfortunately this came to light late in the conducted research and a search for an optimum structure of this system using ORCA could not be conducted even though it seems different results could be found.

As can be seen the optimal geometries found using MP2 and CCSD(T) level theory are very different. This is very odd but makes more sense now we know the MP2 optimised geometry is a transition state from ORCA rather than a minima from GAMESS. Hessian analysis shows the geometry calculated using ORCA with CCSD(T)/aug-cc-pVTZ level theory is a minima.

The optimal geometry from CCSD(T)/aug-cc-pVTZ level theory shows a very small change in the electronic structure of the carbon monoxide and amidogen radical monomers. The largest change is an increase in atomic charge of nitrogen from -0.55 e to -0.56 e matched by a slight decrease in the atomic charge of oxygen from -0.61 e to -0.60 e. Intuition suggests a polar bond between these two molecules however the

positive part of each molecule are closest to each other with carbon closest to hydrogen both of which have a charge of 0.60 e and 0.27 e respectively instead suggesting repulsion.

The structure of each monomer has changed very little due to coordination with the bond length of carbon monoxides bond length decreasing by 0.001 Å and the bond length of each nitrogen hydrogen bond increasing and decreasing by 0.001 Å when closer and further away from the carbon monoxide molecule respectively. The bond angle of the amidogen radical increases by 0.2°. The distance between the carbon atom and the closest hydrogen atom is 2.680 Å.

Unexpectedly the D_0 for this complex is large at 52.8 kJ·mol⁻¹ even though the geometric changes are small. Double checking the NBO analysis reveals no new formation or destruction of bonds that might explain this large value.

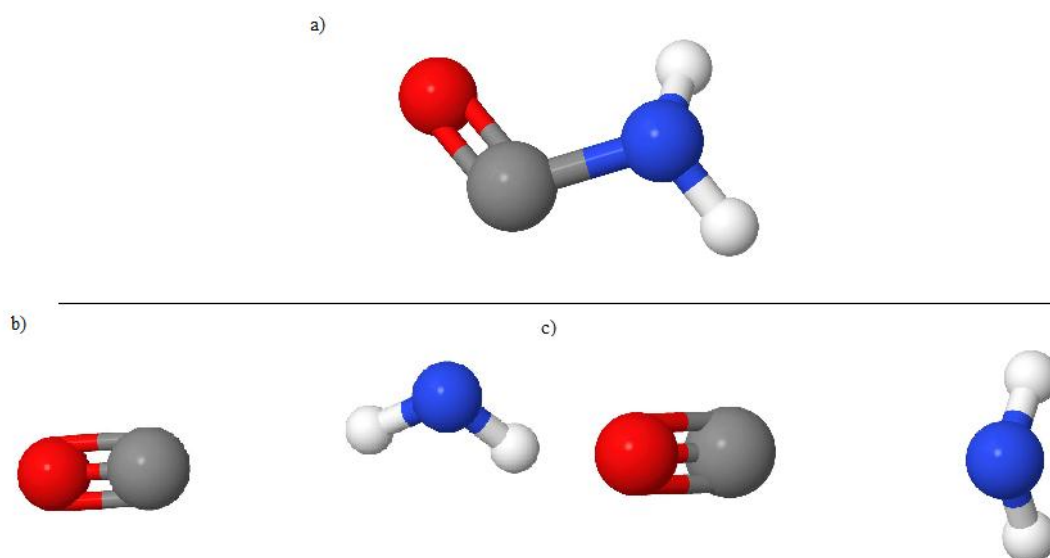


Figure 7 - Geometries predicted from *ab initio* calculations of (a) the NH₂⁻...CO anion complex and (b), (c) the NH₂...CO radical complexes. Complexes (a) and (b) are predicted from CCSD(T)/aug-cc-pVTZ level theory and c) from MP2/aug-cc-pVTZ for (c) level theory.

The predicted adiabatic detachment energy for this species is 1.391 eV. However with the breaking of a covalent bond in addition to the loss of an electron this seems like a gross underestimate especially considering the mean bond enthalpy of C-O is 3.73 eV.⁷³ As this system does not change from one van der Waals minima to another it seems unreasonable to make predictions on the adiabatic detachment energy.

4.3.5 $\text{NH}_2^{\cdot-} \cdots \text{H}_2\text{O}$

Attempts to optimise the geometry of the amidogen anion-water complex resulted in the hydroxide-ammonia complex shown in Figure 10 in nineteen cases from twenty starting geometries with the twentieth starting geometry converging to a transition state. This was predicted by a previous study concerning hydroxide by

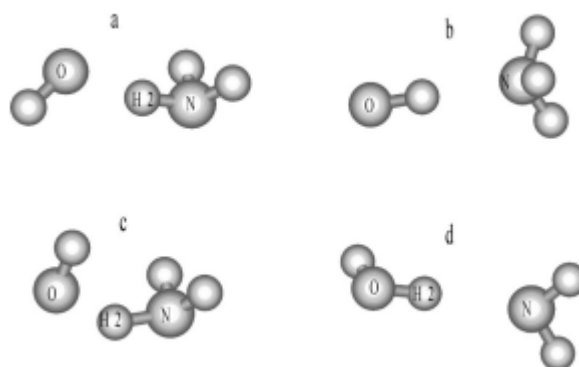


Figure 8 - Geometries of stationary points found along the anion and neutral surfaces found by Schwartz *et al.* a) shows $\text{OH}^-(\text{NH}_3)$ while complexes b), c) and d) are neutral.

Schwartz *et al.*⁷⁴ where calculations were conducted to investigate the hydroxide radical ammonia reaction and attained very similar results to those shown here. Figure 8 shows the optimised geometries attained by Schwartz *et al.*⁷⁴ with structure a) in Figure 10 matching structure a) in Figure 8 from this work. It should be noted that when attempting to optimise 1 : 2, amidogen anion-water complexes geometries were found that retained the amidogen as the anion of the system. Unfortunately these calculations were not completed due to the time consuming nature and cost of such jobs.

The frequency analysis of this optimal geometry using CCSD(T)/aug-cc-pVTZ level theory suggest this is actually a transition state. This is counter to the results from this research using MP2/aug-cc-pVTZ level theory and those of Schwartz *et al.*

MP2(FULL)/6-311++G** level theory. It appears that this difference is due to the level of theory used in each respective frequency calculation. No alternative minimum energy geometry was found.

The change in the electronic state of the system shown by the NBO Analysis is large as would be expected due to the breaking and formation of old and new covalent bonds respectively. The charge on nitrogen decreases from -1.5 e to -1.2 e while the charge on oxygen increases from -0.93 e to -1.3 e, this would be expected as oxygen is more electronegative than nitrogen and will increase the stability of the excess charge. Looking at each new molecule individually it can be seen that a charge of -0.95 e on hydroxide with the remaining -0.052 e on ammonia. This confirms what is already apparent, that hydroxide is indeed the anionic species present.

The structural change is also dramatic as the nitrogen-hydrogen bond lengths have contracted by 0.013 Å with the newly formed nitrogen-hydrogen bond length at 1.064 Å. The remaining hydrogen oxygen bond length changes very little with a slight expansion of 0.004 Å.

A valid D_0 value could not be returned as the system has changed from amidogen anion and water to hydroxide and ammonia. Calculations must be performed on hydroxide and ammonia to attain a valid D_0 value.

4.3.6 $\text{NH}_2^\bullet \cdots \text{H}_2\text{O}$

Attempts to optimise the amidogen radical-water complex returned only two optimum geometries both of which retained the amidogen species, only one of these geometries was determined to a minimum after Hessian analysis using MP2/aug-cc-pVTZ level theory, both structures are shown Figure 10. Investigation by Schwatz *et al.* of the hydroxide radical and ammonia also found a stationary point at MP2(FULL)/6-311++G** level theory shown in Figure 8 d). Ennis *et al.*⁵⁰ also investigated the

hydroxyl radical and ammonia reaction and found a stationary point matching that found by Schwartz *et al.*⁷⁴ in Figure 8 d) using CCSD(T)/aug-cc-pVTZ level theory. Comparison between this research and that conducted by Schwartz *et al.*⁷⁴ and Ennis *et al.*⁵⁰ show nitrogen and oxygen have switched places. The structure in Figure 10 b) was predicted to be a minimum by GAMESS at MP2/aug-cc-pVTZ level theory however when analysed using Oera was shown to be a higher order stationary point. Frequency analysis of this geometry at CCSD(T)/aug-cc-pVTZ level of theory showed this structure to be a higher order stationary point and is hence consistent with work done by Schwartz *et al.*⁷⁴ and Ennis *et al.*⁵⁰

The amidogen radical-water complex shows very little charge movement upon the formation of the complex compared to the amidogen and water monomers. The initial atomic charge on nitrogen increases from -0.55 e to -0.58 e and the charge on oxygen changes from -0.93 e to -0.95 e. The largest change in charge on the hydrogen atoms occurs for the hydrogen between oxygen and nitrogen increasing from 0.28 e to 0.31 e with charge differences on other hydrogen atoms being on the order of milli electrons.

The structure of the amidogen radical and water monomers have not changed significantly with only a 0.1° decrease in the bond angle seen for water. The changes seen for the amidogen radical are slightly larger with the nitrogen-hydrogen bond lengths contracting by 0.002 Å and 0.004 Å each and the bond angle increasing to 103.1° . The amidogen radical-water complex also shows C_s symmetry.

The small change in the electronic and geometric structure is reflected by a small D_o value of 11.3 kJ mol^{-1} at MP2/aug-cc-pVTZ level theory. This binding energy is consistent with the $\sim 3 \text{ kcal mol}^{-1}$ (12.5 kJ mol^{-1}) binding energy between the amidogen radical and water shown by Ennis *et al.*⁵⁰ shown in Figure 9 suggesting these two structures are closely related. The binding energy here has been calculated using

MP2/aug-cc-pVTZ level theory as it is the only level theory this complex was determined to be a minima in this research.

An adiabatic detachment energy has not been predicted for these complexes as they both show imaginary frequencies and the prediction will be both inaccurate and unobservable. Furthermore a covalent bond is broken and formed presenting a similar problem to that seen for the amidogen-carbon monoxide complex.

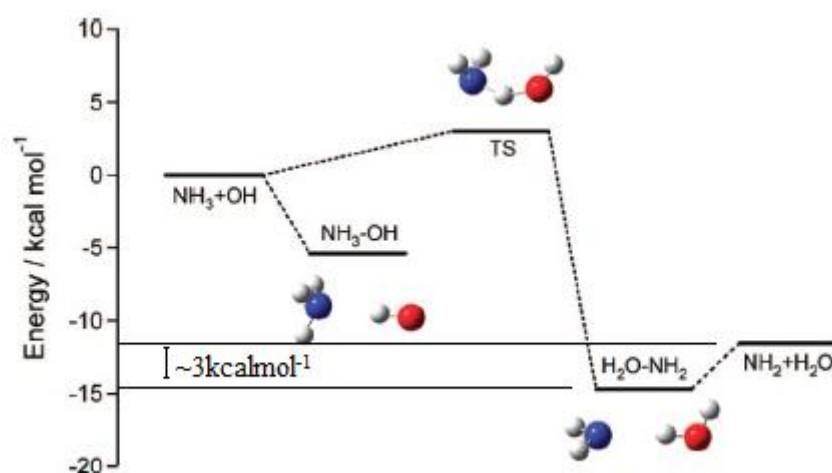


Figure 9 - The reaction path investigated by Ennis *et al.* showing a binding energy of close to 3 kcal mol⁻¹ and the minimum energy geometry of the amidogen radical-water complex.⁴⁸

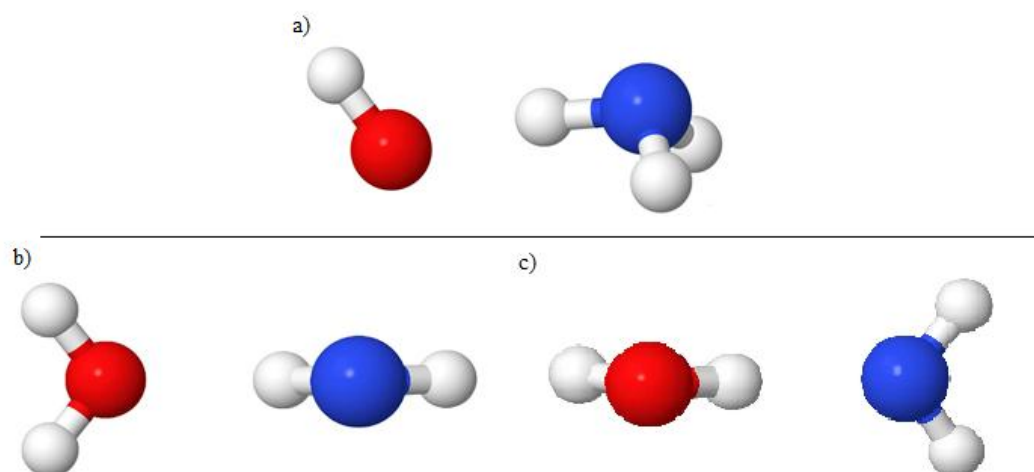


Figure 10 - Geometries predicted from *ab initio* calculations of (a) the NH₂⁻...H₂O anion complex and (b), (c) the NH₂...H₂O complexes. Geometries of complexes (a) and (b) are from CCSD(T)/aug-cc-pVTZ level theory and complex c) from MP2/aug-cc-pVTZ level theory.

5. Experimental Work

5.1 TOFPES (Quick overview)

As previously mentioned the experimental apparatus consists of a Time of Flight Mass Spectrometer coupled with a Photoelectron Spectrometer (TOF-PES). Figure 11 shows a top down schematic of the major components of the TOF-PES. The mass spectrometer for this apparatus follows the design of Wiley and McLaren,⁷⁵ while the design of the photoelectron spectrometer follows that proposed by Cheshnovsky *et al.*⁷⁶ Construction and initial testing of the TOF-PES was conducted by LaMacchia and is detailed in his Honours thesis.⁷⁷ Further modifications to the TOF-PES and its subsequent testing as well as previous work with the apparatus is detailed by Quak⁷⁸ and Lapere⁷⁹ in their respective Honours theses and further modifications are detailed below [Modifications 6.2.5].

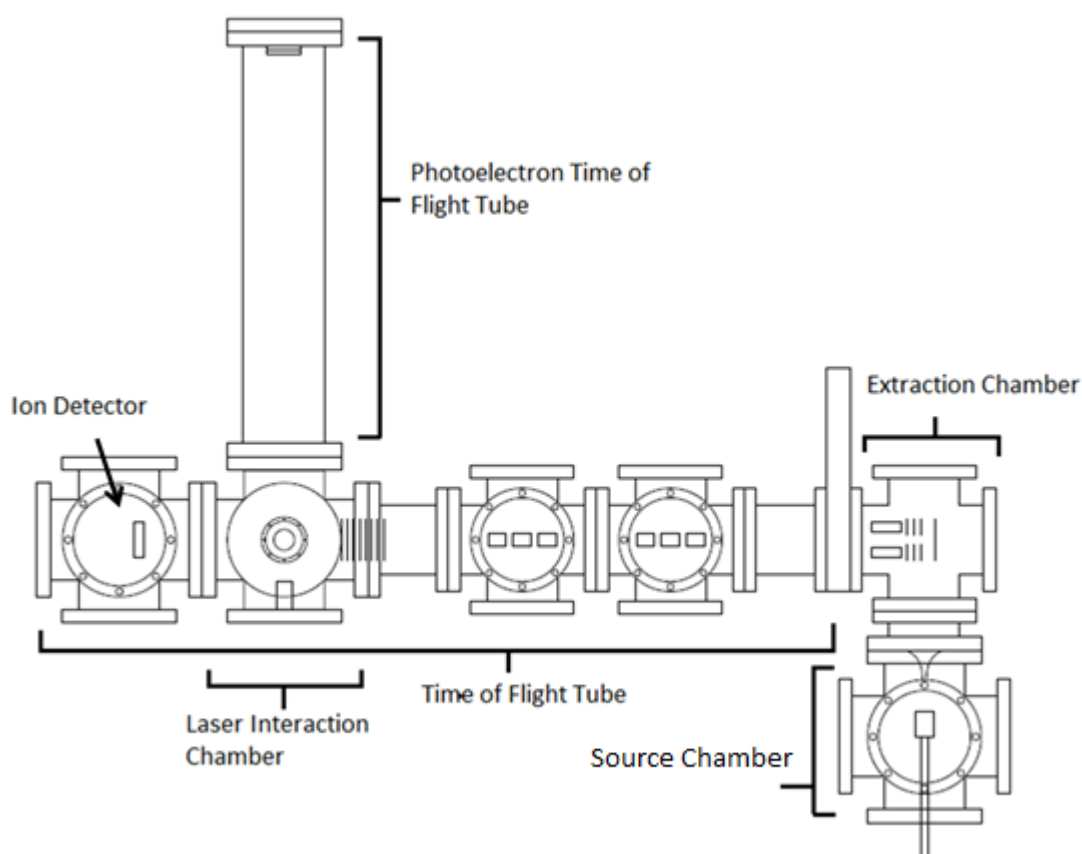


Figure 11 - A top down schematic of the TOF-PES apparatus detailing all the major components¹

Experiments conducted using the TOF-PES involve producing anion-molecule clusters in the source chamber (Figure 11), using mass spectrometry to separate the various cluster sizes, and subsequently intersecting the ion beam with a pulsed laser at 266nm. The laser-ion interaction serves to detach an electron, the energy of which is determined through measuring its time of flight along the photoelectron flight tube. The process described briefly here, and in detailed below, is constantly repeated at a rate of 10 Hz. Data from ten thousand cycles are collected and averaged improving consistency and accuracy.

5.2 Experimental Method

5.2.1 Gas Mixing Chamber

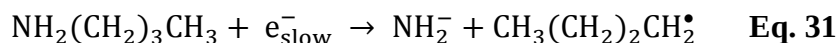
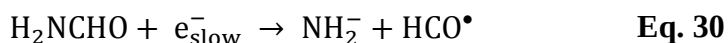
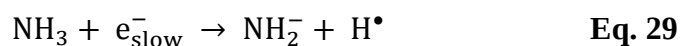
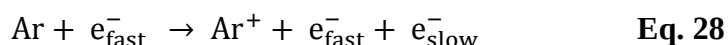
The aim of this research was to produce the amidogen anion NH_2^- , a process which starts in the gas mixing chamber. As with Quak, Lapere and LaMacchia⁷⁷⁻⁷⁹ argon was used as a buffer gas as it has been shown to improve spectral resolution through vibrational cooling.⁸⁰ Ammonia, hydrazine, formamide and n-butylamine were used as precursor gases to produce the amidogen anion when exposed to electrons. If desired, a complexant gas can be added to the gas mixture when aiming to produce anion clusters; carbon monoxide was used as the complexant gas for this research.

Repeated attempts were made to produce the amidogen anion and observe its mass peak using different gas mixtures. The ratio of each gas mixture of NH_3 : Ar attempted was 1 : 99, 6 : 94, 10 : 90, 12 : 88, 30 : 70, 50 : 50 and 100 : 0. Additionally hydrazine was used in a 1:99 ratio of N_2H_4 : Ar. Formamide was then used in a ratio of 0.08 : 99.92, H_2NCHO : Ar and was the only gas mixture to successfully yield a mass of 16. Unfortunately due to the vapour pressure of formamide being only 0.08 Torr more formamide could not be added to the gas mixture using the current setup. This meant that only very small amounts of formamide were available in the source chamber

making it difficult to analyse the impact of formamide. A gas mixture of 0.08 : 7 : 99.92, $\text{H}_2\text{NCHO} : \text{CO} : \text{Ar}$ was used to try and produce $\text{NH}_2^- \cdots (\text{CO})_n$ clusters unsuccessfully. N-butylamine was used as an alternative NH_2^- precursor to formamide as it had a higher vapour pressure than formamide in gas mixtures of 0.5 : 99.95, $\text{NH}_2(\text{CH}_2)_3\text{CH}_3 : \text{Ar}$ and 1 : 7 : 92, 0.5 : 7 : 92.5 of $\text{NH}_2(\text{CH}_2)_3\text{CH}_3 : \text{CO} : \text{Ar}$, these attempts were unsuccessful. Previous research groups have used a gas mixture of 30 : 70 to produce $\text{NH}_2^- \cdots (\text{NH}_3)_n$ clusters⁵² and hydrazine has been used in the past with hydrogen atoms acting as a stimulant for $\text{NH}_2^\bullet$ production.^{41,81}

5.2.2 Making Anion Clusters

Once an appropriate gas mixture has been made it is pulsed through the gas nozzle into a vacuum and intersected with energetic electrons ejected from rhenium filaments. Typically 3.7 A is passed through the filaments and biased at 220 V with ranges between 0-5 A and 0-300 V. These electrons then interact with the gas mixture forming a plasma with a number of reactions occurring and exotic species being produced. In this instance the exotic species of interest is NH_2^- , through the following reactions:



To try and improve the production of plasma and anions in our experiment the filament plate and voltage supply have both been modified (See Modifications).

5.2.3 Separation and Selection of Anion Clusters

After exposure to the electron source the gas expansion then travels through a 3 mm skimmer into the extraction chamber. The extraction chamber's function is to accelerate anions (or cations for other experiments) down the Time-of-Flight (TOF) tube towards the ion detector. This is achieved using three metal plates; The back plate, usually at -1000 V, provides the desired acceleration down the Time-of-Flight tube by repulsion. The second plate usually between -800 to -950 V ensures that ions with the same mass arrive at the detector at the same time. This is termed space-focusing and occurs as ions have slight lateral components to their velocities as they pass into the extraction chamber. This brings some ions close to the back TOF plate and some further away, when the TOF plates are pulsed at -1000V in order to accelerate there ions those closer to the TOF plate will receive more energy than those further away giving ions of the same mass different velocities. As shown in Figure 12 ions of the same mass will then arrive at the 'focal point' at the same time and then spread out past that point. By having a second plate with an adjustable voltage it is possible change this 'focal' point to the ion detector or laser interaction region decreasing the spread of ions as they reach these locations and increasing the resolution achievable.



Figure 12 – An exaggerated example of spatial focussing with ions of the same mass starting at different distances from the back plate. After receiving different velocities they slowly group up until a ‘focal point’ (single point) is reached after which they spread out. The X deflection plates have been included and Y deflection plates are not in the same plane as the image. This diagram is not to scale.

The third plate is grounded at 0 V and acts like a Faraday cage ensuring anions in the TOF tube do not experience additional forces due to voltages present inside the extraction chamber which might influence their flight times and hence effect the resolution of the mass spectrum.

Past the final TOF plate there are pairs of X-Y deflection plates. By altering the voltages on these plates the ion beam can be deflected or aimed along the desired path in the TOF tube. Typically the target is the ion detector or laser beam.

As discussed all ions leave the extraction chamber with the same kinetic energy imparted by the TOF plates. As these ion have the same kinetic energy yet different masses they will have different velocities as they travel down the TOF tube. Differing velocities means the ions will spread out along the TOF tube and arrive at the ion detector at different times allowing for accurate determination of the mass of each ion. This can be described by the following equations:

$$\mathbf{F} = \mathbf{Eq} \quad \text{Eq. 32}$$

$$\mathbf{F} = \mathbf{ma} \quad \text{Eq. 33}$$

$$\mathbf{v} = \mathbf{at} \quad \text{Eq. 34}$$

These equations combine to give:

$$v = \frac{Eq t}{m} \quad \text{Eq. 35}$$

These equations describe what is happening to each individual ion when undergoing acceleration due to the TOF plates where F is the applied force, E is the electrostatic field, q the charge of the ion experiencing the force, m is the mass of the ion, a the acceleration of the ion, t the time the ion is accelerating for and v the final velocity of the ion.

As all particles are exposed to the same electric field for the same period of time and have the same charge, the only variable that changes in the above equation, and hence the only variable that can cause a change in velocity, is the mass. This is shown to be an inverse relationship, so a heavier particle will have a lower its velocity and will hence take longer to reach the detector and vice versa.

It should be noted that any cationic species entering the extraction chamber are deflected towards the back TOF plate and any neutral species are unaffected by the charged plates and strike wall of the chamber opposite the skimmer. These species therefore are not seen and do not interfere with the mass spectrum past this point.

As anions of the same mass travel together, Coulombic repulsion will cause them to diverge from the direct flight path. This is countered using two electrostatic Einzel lenses which allow the ion beam to be refocused before they arrive at the ion detector or laser interaction chamber as shown in Figure 13.

Depending on the time it takes between pulsing of the TOF plates and the arrival of anions at the detector it is possible to determine the mass and thus the composition of each anion that arrives at the detector, knowing the velocity and distance of the anions and flight path. If desired, a mass gate can be turned on

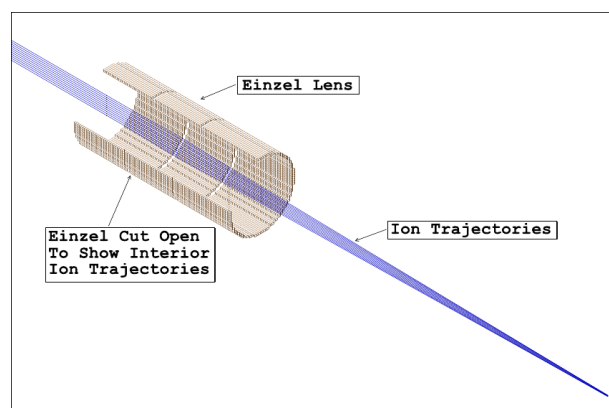


Figure 13 – An example of how an Einzel Lens refocusses and ion beam to a point. Taken from SIMION manual.⁷⁵

and timed to only let a species with a certain time of flight (and hence mass) to pass through to the laser interaction chamber and detector. This is best used if other species are interfering when trying to obtain a photoelectron spectrum.⁸²

5.2.4 Laser Interaction and Photoelectron Spectroscopy

Once enough of the desired species is being produced a laser pulse is fired such that it intersects with the ion beam as it is passing through the Laser Interaction Chamber, this is the ionization area in Figure 14. The laser pulse has a wavelength of 266 nm (4.66 eV) which is sufficient to excite an electron from the anion species (i.e. overcoming the electron binding energy). The excess energy from the laser is then imparted to this now-free electron as kinetic energy. These photoelectrons are then redirected down a second TOF tube to the photoelectron detector using a bottle magnetic field⁷⁶ generated by a constant magnetic field within the TOF tube in combination with a pulsed magnetic field around the laser interaction point when in the inset in Figure 14. Based on the arrival of the electrons at the photoelectron detector it is possible to work out the electron binding energy of the analysed species.

$$E_{BE} = 4.66 - E_{\text{electron}} \quad \text{Eq. 36}$$

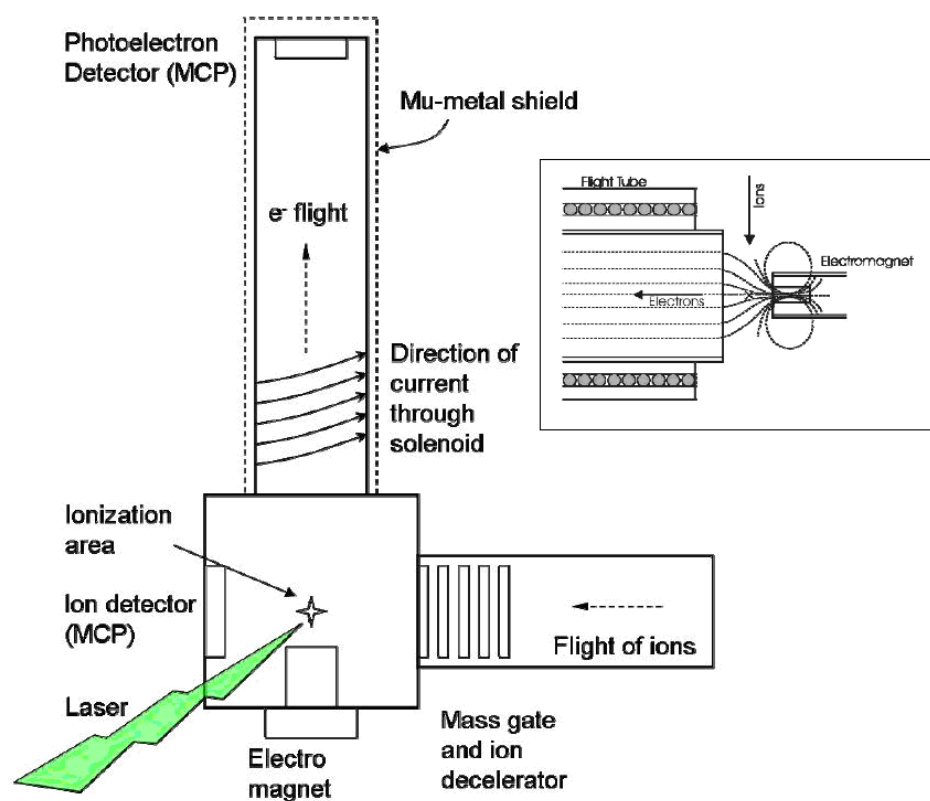


Figure 14 – Schematic showing the path of ions and photoelectrons with the oriented to come out of the page from the ionisation area (or star). The inset is a detailed view of the bottle magnetic field around the Ionisation area produced to trap photoelectrons, it is oriented at 90° CCW to the main figure. Courtesy of Quak and Wild.⁷⁸

5.2.5 TOF-PES Settings

For the TOF-PES to be functioning correctly a number of components have to work in union with the correct settings. Of all of the components in the apparatus, the variables that the operator has direct control over include; the nozzle pulse voltage, the nozzle pulse width, the filament current, the filament voltage, the filament voltage pulse width, the position of the gas nozzle with respect to electron filaments, the voltages across all four X-Y deflection plates, the timing of the TOF-plates with respect to the nozzle pulse, the voltages across the TOF-plates, the voltages across the Einzel lenses, and the positioning and intensity of the laser.

Being a highly sensitive apparatus the correct setting for the TOF-PES vary from day to day or from gas mixture to gas mixture. The small differences in settings are often enough as to be unable to observe the mass spectrum at all and this makes finding a

mass spectrum with a new gas mixture difficult and time consuming. An example of typical TOF-PES settings as well as changes within a week with the same gas mixture are shown below in Table 8.

Table 8 - Typical TOF-PES Operating conditions and changes in those conditions over a week.

Date:	19 th March 2012	23 rd March 2012
Nozzle Pulse Voltage	225 V	187 V
Electron Filaments	3.63 A / -220 V	3.76 A / -220 V
X Deflection Plates	-60 V / -60 V	-8 V / -8 V
Y Deflection Plates	27 V / -20 V	54 V / 90 V
Einzel Lenses	-22 V / -97 V	-23 V / -89 V
TOF plates	-1000 V / -904 V	-1000 V / -912 V
TOP plate timings	887 μ s	868 μ s

5.2.6 Modifications

Modifications to the machine have been proposed and started due to complications encountered while conducting the research proposed in this thesis. However these modifications have not yet been implemented due to time constraints. These should make a difference in future experiments and warrant a revisit of this research in the Wild Lab when these modifications have been completed. These modifications include; a new filament setup aimed at increasing the electron density within the gas mixture and also improving running costs of the TOF-PES, modifying the filament voltage source to provide a higher voltage aimed at accessing more anions within the gas expansion and moving the location of the gas mixing chamber and replacing Teflon hose with stainless steel aimed at increase the efficiency with which the gas mixture can be replaced.

5.2.6.1 New Filament Setup

The new filament setup involves a single, shorter filament used as the electron source and an added Einzel lens that will be used to focus the electrons ejected from the filament to a point in front of the nozzle where it intersects with the gas expansion. While the number of electrons in our source chamber decreases considerably using this setup the concentration of ions at a point within our gas mixture should be higher. As a result it is hoped that more exotic ions would be produced for analysis within our gas mixture. The overall reduction of electrons in the gas mixing chamber should also decrease the noise seen within the TOF-PES (see Complications). Additionally the filament usage of the machine with this setup should decrease considerably as a much smaller length of rhenium wire is required each filament replacement. This will also decrease the longterm running cost of the machine as rhenium is ~\$70 per gram.

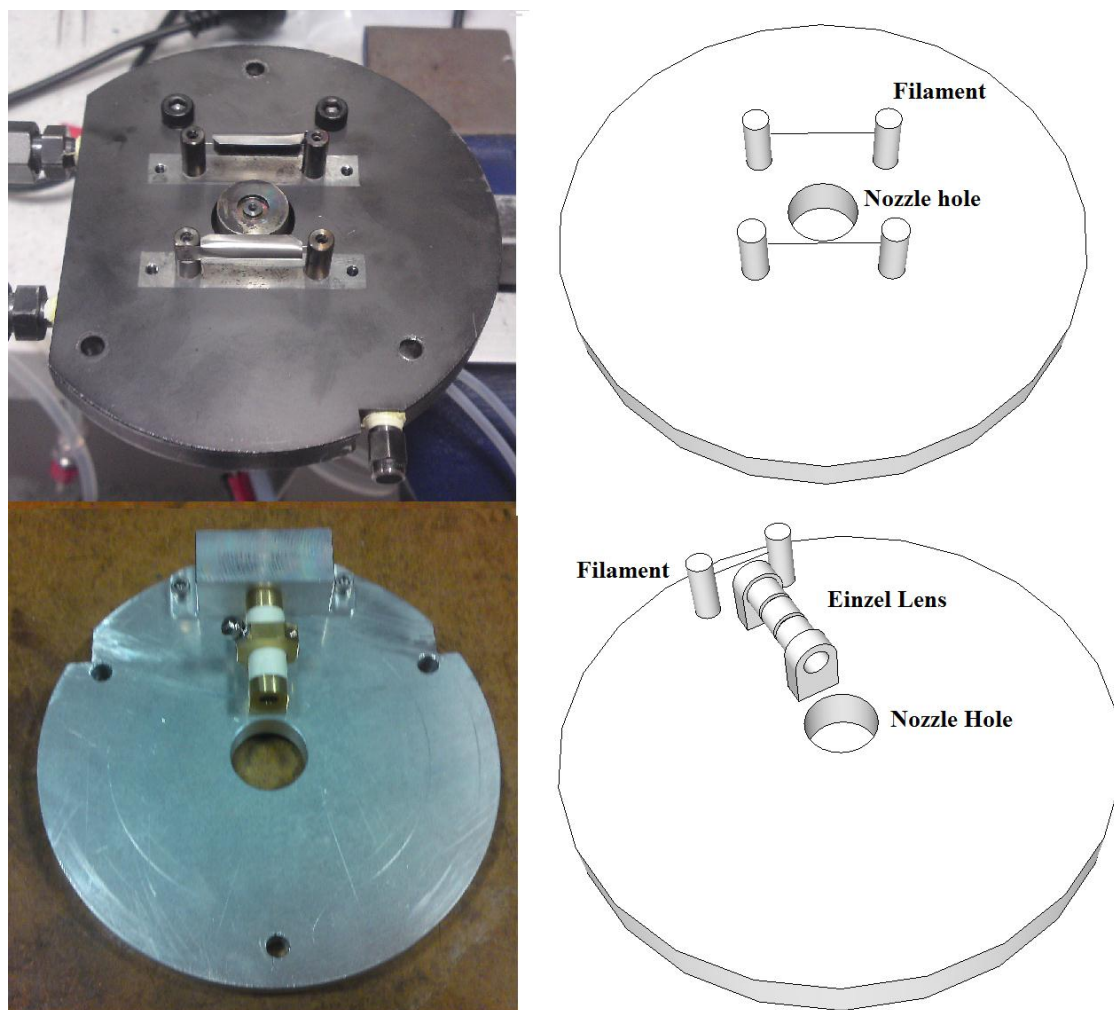


Figure 15 – The top right and left images show the current filament base plate being used. The bottom right and left show the images show the new filament base plate that is yet to be tested.⁵ (The top left image, has been coated in graphite to remove surface charge and decrease noise, hence it's black colour see LaMacchia⁷⁷)

5.2.6.2 New Filament Voltage Source

Our modified voltage source will increase the maximum bias voltage of the filament from ~300 V to ~500 V. This will provide higher energy electrons to the gas expansion, increasing the probability of (relatively) strong intramolecular bonds breaking (such as those found in ammonia). This expands upon the operating range of the TOF-PES as more species can be produced and hence analysed due to the higher impact energies of the electrons. The specific aim of increasing the voltage of the filament voltage source was to break the N-H bond in ammonia to produce NH_2^- which was proving problematic.

5.2.6.3 Relocated gas mixing chamber

The gas mixing chamber has been moved next to the source chamber and any Teflon hosing that connected the two has been replaced with stainless steel hosing. Teflon hosing is known for adsorbing substances onto the surface of the hose and slowly leaking it back into the environment over time. This is a major factor in why the Cl^- anions in the TOF-PES can still be seen despite not having its precursor in a gas mixture for months. While gases will still adhere to stainless steel and the same effect will still be seen it will not be to nearly the same extent and will allow flushing and replacing of a gas mixture to be much faster and more effective. Moving the gas mixing chamber next to the source chamber decreases the hose length required to connect the two components and hence decreases the surface area available for gas to adhere to. This will also increase the efficiency of changing and flushing gas mixtures and hopefully reduce the chance of any possible contamination due to excess unintended species present in the gas mixture from previous experiments. The total length of the hose has decreased from 2.5m of Teflon to 40 cm of stainless steel.

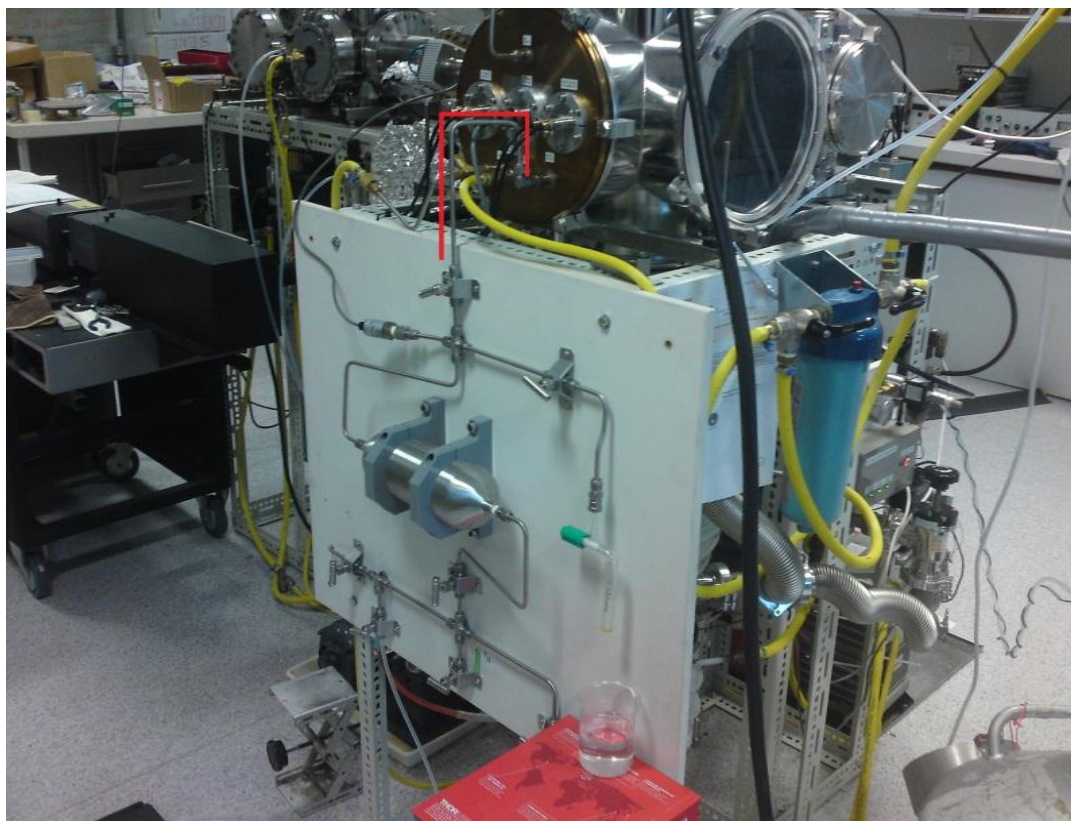


Figure 16 - The gas mixing chamber in its new position with significantly decreased hose length connecting to the machine highlighted in red.

5.3 Complications

5.3.1 Electron Noise

When conducting experiments in the TOF-PES the first problem to overcome is the production of the desired species for analysis. Up until now the species that have been produced within the Wild TOF-PES have been halides. These halides are generated from halide-methyl precursors such as dibromomethane and the largest barrier to the production of the halogen anion from such species is breaking the carbon-halide bond. In this thesis the proposed precursor of ammonia to the amidogen anion (as discussed previously) requires the breaking of a nitrogen-hydrogen bond. This nitrogen-hydrogen bond has considerably higher energy than a carbon-halide bond. Despite initial

expectations that it was possible to produce electrons with sufficient energy to break this bond, it proved beyond the electron energy our machine is currently capable of.

Having never encountered this problem before it took considerably time to realize this was indeed why the amidogen anion was not being observed. Initial analysis on the mass spectrum led us to believe that the amidogen anion was indeed present. Consistently four ion peaks would appear on the mass spectrum whenever ammonia was present within the system and these ion peaks would occur close to the expected time for the amidogen anion, this is shown in Figure 17.

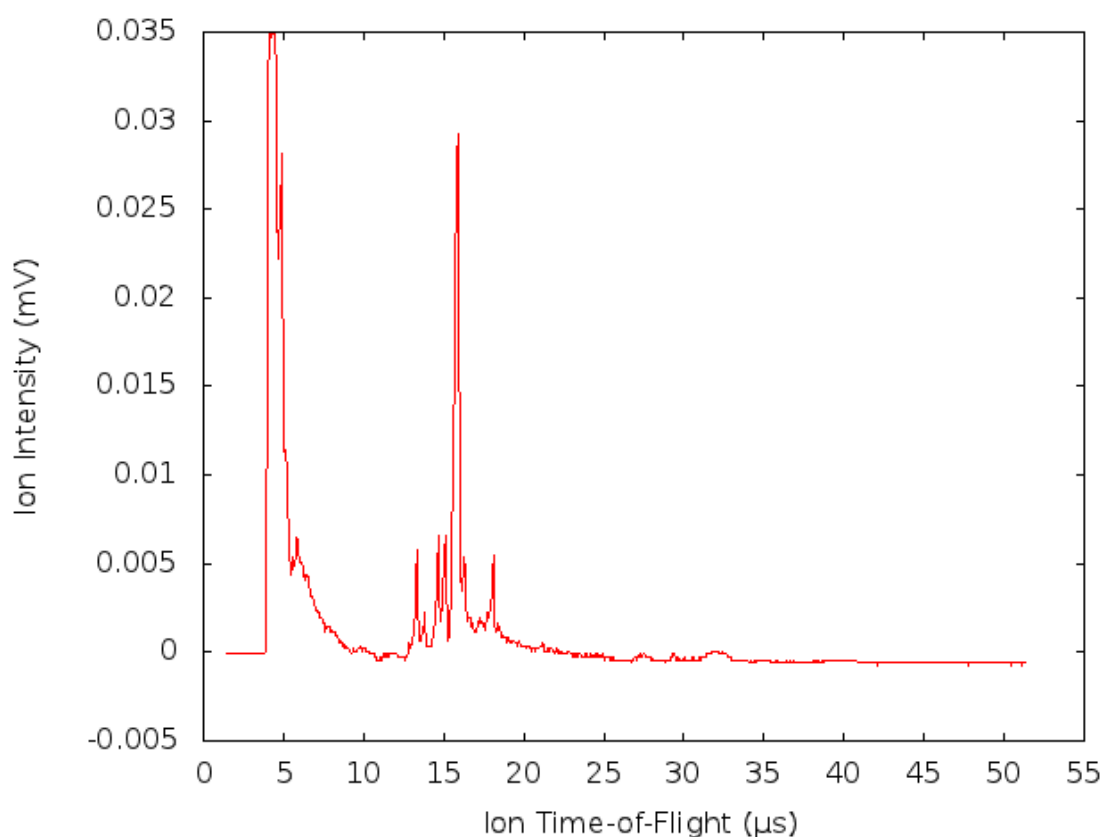


Figure 17 - An example of the four peak noise observed at ~15 us when first trying to produce the amidogen anion.

After considerable time, and attempts with a number of different gas mixtures to attain a photoelectron spectrum with the laser, it became apparent that these four peaks were just electron noise. Adjusting the settings of the TOF-PES this noise became very intense and reasonably well defined. The final proof that this was indeed noise was

when an actual mass spectrum was found with trace amounts of chloride, bromide and iodide observable, and at much higher masses clusters of ammonia containing a solvated electron averaging 850 amu (Figure 21). Under these conditions the aforementioned noise was very small or not present at all yet there was now no observable peak where the amidogen anion should be present.

5.3.2 Dissociative Excitation

It is possible this observed noise is being caused by long-lived high Rydberg states produced by the dissociative excitation of any molecules in the TOF-PES although particularly NH_3 and CO . Through this process high energy electrons collide with these molecules forming a metastable state that is negatively charged. This metastable state has a certain lifetime before it decays into its component parts imparting some of the energy from the electron to each fragment as kinetic energy. This would allow the metastable state to pass into the extraction chamber, be accelerated towards the ion detector plate and then ‘fall apart’ in the TOF tube. The arrival of these dissociative excitation products will be consistent with the arrival of the parent anion as they will have the same velocity as the parent anion. The dissociation products will also be imparted with a slight extra velocity component due to dissociation and hence will have a wider peak than a normal mass peak due to slight increases and decreases in its initial velocity.

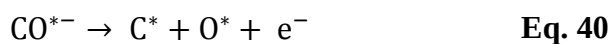


Figure 18 from Christophorou⁸³ shows the dissociative excitation of CO. Peaks of similar structure have been observed previously in the TOF-PES however were unfortunately passed off as noise and hence no spectrum of such structures have been recorded. Figure 19 also from Christophorou,⁸³ shows four different dissociation reactions of NH₃ and may explain the four different peaks observed when ammonia is present in the TOF-PES. It should be noted that the ion detector can detect particles of any charge so, provided a neutral or positively charged species could make its way into the TOF tube (say through dissociative excitation) the ion detector would 'see' it.

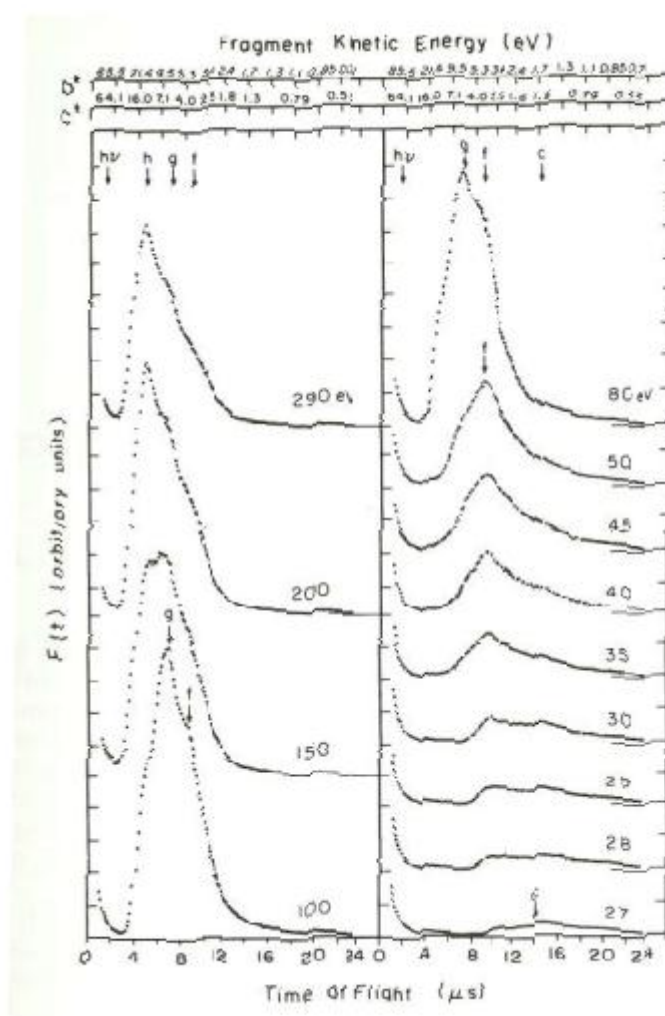


Figure 18 - The time of flight spectra of long-lived high-Rydberg carbon and oxygen atoms produced through dissociative excitation of CO by electron impact. From Wells *et al.*⁸⁴

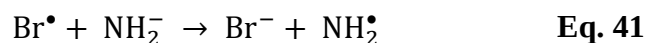
H* fragment	Onset energy (eV)	Approximate range of fragment kinetic energy (eV)	Dissociation products
2s-1	17.8 ± 0.8	0.1–2.3	NH ₂ ($\tilde{X}^2B_1$) + H(3p)
2s-2	21.8 ± 0.8	2.0–8.0	NH ₂ ($\tilde{X}^2B_1$) + H(2s)
2s-3	27.9 ± 1.4	1.0–3.8	
2s-4	35.4 ± 1.0	3.4–6.9	
2s-5	39.3 ± 1.5	6.0–19.0	
R-1	23.2 ± 0.7	0.4–10.0	NH ₂ ($\tilde{X}^2B_1$) + H(Ryd)
R-2	31.0 ± 2.0	1.3–4.5	N(⁴ S ⁰) + 2H(1s) + H(Ryd)
R-3	33.8 ± 0.9	3.5–8.2	
R-4	41.7 ± 1.0	8.0–23.5	

Figure 19 - A table of all the possible products of ammonia when experiencing dissociative excitation.⁸³

There is however a flaw with this proposed source of noise, the lifetime of these metastable states is usually in the order of ps⁸⁵ for initial metastable states and ~100 μs⁸⁶ for secondary metastable products. The usual time difference between allowing gas into the TOF-PES and firing the TOF plates is 850 μs. Comparatively the time the noise is detected at the ion detector is 14 μs after the TOF plates are fired. The only way for dissociative excitation product to be observed using the current TOF-PES setup is if they are constantly being produced and this seems unlikely. However dissociative excitation is a potential avenue for research as well as further investigation into the source of this noise.

5.3.3 Interference from other species

The initial hypothesis as to why the amidogen anion was not being produced revolved mainly around either electrons in our setup not having enough energy to break the hydrogen-nitrogen bond or the chloride, bromide and iodide precursors were ionized in preference to the amidogen radical or even ‘stealing’ the electrons from the amidogen radical through charge transfer, for example:



Reviewing the previous two papers by Snodgrass *et al.*⁵¹ and Sanov *et al.*⁵² it was concluded that it is more likely that the halides were interfering with the gas expansion. While Sanov *et al.*⁵² used an electron gun to produce electrons at 1000 V (which is higher than we are able to achieve). Snodgrass *et al.*⁵¹ used a filament to produce electrons at 70 V in a similar fashion to that used in our labs. As the TOF-PES is capable of producing electrons at 300 V this was not considered to be a barrier and work began regarding the prevention of halide species interfering with the gas expansion.

A number of tests were conducted to try and remedy the interference of the halide species with the gas expansion, including combinations of modifying the gas mixture and the machine. First by increasingly higher ratios of ammonia to argon gas mixtures were trialled to saturate the halide interference and start producing excess of the amidogen radical. These gas mixtures were 30 : 70, 50 : 50 and 100 : 0 ammonia to argon mixtures. It was found that while the halide species were still observed as expected, the amidogen anion was not. Additionally, when using the 100 : 0 gas mixture the noise increased considerably, presumably due to the lack of vibrational cooling provided by argon.

After this modifications were made to the TOF-PES by removing as much Teflon tubing as possible and replacing it with steel tubing. The reasoning behind this is because Teflon is very good at adsorbing gases onto its surface and hence will hold a gas in our gas mixture in trace amounts long after the gas mixing chamber has been vacuumed out and the majority of the gas removed. Steel, while it will still adsorb some gasses onto its surface, will not adsorb nearly as much as Teflon, hence the trace amounts held within the system will decrease.

The logical extension from changing the material so that less gas will adhere to the hose is to decrease the length of the hose such that there is less hose for the gas to adhere to. Consequently the gas mixing station has been moved much closer to the TOF-PES, specifically decreasing the hose length from gas mixing station to machine length from 2.5 m of Teflon to 40 cm of steel. [See Figure 16 in Modifications]

Throughout these modifications to both the gas mixture and TOF-PES all gas from the gas mixing station was removed. This involved purging the gas mixing station with argon achieved by bringing the gas mixing station to vacuum, filling it with argon and subsequently removing the argon again hopefully taking the remaining gases with it, this process can be repeated numerous times. Additionally, the gas mixing station was left under vacuum for up to 24 hours, again hoping to remove the unwanted gases. Another possible option available for purging the gas mixing station was to use heating tape to increase the temperature of the gas mixing station and then apply the vacuum, however this was not attempted due to cost and difficulty of implementation.

Finally a new electron source that uses Einzel lens to focus electrons to a point in the gas expansion has been proposed and constructed. This differs from our current ionization setup which uses two electron filaments on either side of the gas expansion as point sources for electrons (see Figure 15). While this indeed produces many of the desired ions, stray and excess electrons are an ongoing problem causing much of the noise observed in the TOF-PES and electron density can only be changed by changing the current otherwise it is uniform. Focusing of the electrons from the electron source will be achieved using an Einzel lens just past the point source of electrons (much like the electron filaments currently used). This will generate ions which will then pass through the skimmer into the TOF-PES. (For a more detailed description and figures

please see [Modifications 6.2.5.1]). This modification is still under construction and is yet to be tested.

5.3.4 High energy electrons

After attempting all of these methods to improve the purity of the gas mixture being introduced into the TOF-PES and not seeing any significant results the electron energy problem was revisited. As a filament is being used as the source of high energy electrons there is a distribution of energies with a maximum possible energy set on the filament voltage source. The maximum energy will be increased by increasing the voltage the filament source is capable of supplying. This involves replacing many components of the filament source not rated for these new higher voltages as well as making modifications to the electronic circuit itself. The final result of this is our filament source can now reach ~500V rather than the current 300V. This has not yet been tested in the TOF-PES due to time restrictions.

5.3.5 Mass peak of 16

While modifications were being completed there was continued use of the current setup in hopes of yielding the desired species. After numerous attempts with ammonia : argon gas mixture it was proposed to use a ammonia : carbon monoxide : argon gas mixture. This was due to the predicted structure of the amidogen-carbon monoxide complex forming a covalent bond rather than the usual van der Waals interaction observed in gas clustering (Figure 7). It was observed that the amidogen anion-carbon monoxide complex was of a very similar structure to formamide and hence formamide should be used in the gas mixture instead.⁸⁷ The logic behind this was that the carbon-hydrogen bond would break as, shown in Figure 20, within the gas expansion due to excitation by electrons, leaving the anion shown in Figure 7.

When formamide was added to the gas mixture a mass peak of 16 amu was observed. What was potentially happening when formamide was added to the gas mixture was breaking of the carbon-nitrogen bond with subsequent formation of the amidogen anion, shown in Figure 20.

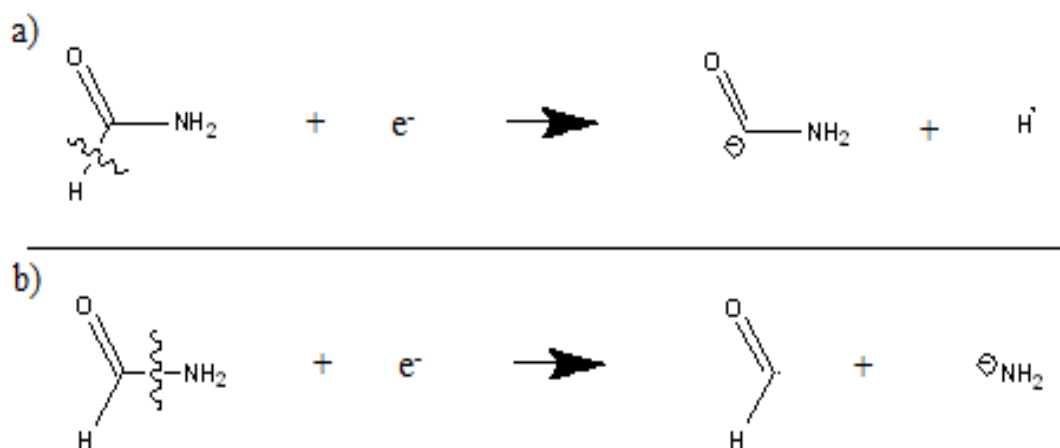


Figure 20 – Represented here are two different possible decomposition reactions of formamide within the gas expansion. Reaction a) was the expected reaction upon addition of formamide to the gas mixture. Reaction b) is the ideal reaction leading to the production of the amidogen anion within the gas mixture.

Initially, as a mass peak of 16 was unexpected it was hypothesised that the formation of a m/z peak of 16 was due to the now trace amounts of ammonia in the gas mixture forming the amidogen anion, however a quick test with a new 0.5 : 99.5, NH_3 : Ar proved this was incorrect (no mass peak of 16 amu was observed). Replacing this gas mixture with formamide again produced a mass of 16 amu lending to the conclusion that reaction b) in Figure 20 was occurring.

This lead to an analysis of the mean bond enthalpies of the different types of bond within the gas expansion shown in Table 9. Of the bonds shown in the table those labelled with (*) have been successfully broken in the current setup of the TOF-PES.^{65,79} Previously it has been observed that the chloride anion has been difficult to produce in the source of the TOF-PES.⁸⁸ Clearly the limit of the machine when breaking bonds is approaching ~ 3.50 eV, hence why it has not been possible to produce the amidogen anion from ammonia due to such a high H-N bond enthalpy (4.27 eV). Similarly this is why it should be easier to produce the amidogen anion from formamide rather than the formamide anion.

Table 9 – Mean Bond Enthalpies

	H-C	H-N	C-N	C-Cl*	C-Br*	C-I*	C-F	C-O	N-F
kJ mol^{-1}	412	388	305	338	276	238	484	360	270
eV	4.27	4.02	3.16	3.50	2.86	2.47	5.02	3.73	2.80

Adapted from Atkins⁷³

Unfortunately I have been unable to find any information mathematically linking electron kinetic energy to the breaking of a covalent bond. This is particularly confusing when the electron kinetic energy in the TOF-PES is 300 eV while the bond

enthalpy on 3.5 eV. (the impression given from most PES papers is in the electron energies are high enough it doesn't really matter).

As will be shown later this mass peak of 16 amu was not actually NH_2^- but O^-

5.4 Experimental Results

5.4.1 Mass Spectra

A number of mass spectra have been recorded throughout this research and while not all of them show production of the amidogen anion and its respective clusters they do show production of other exotic species within the TOF-PES which could serve as potential avenues for future research.

5.4.2 Solvated electrons

Figure 21 shows the mass spectrum recorded from an ammonia : argon 30 : 70 gas mixture. The mass spectrum shows familiar features from past research^{65,77-79} with the TOF-PES with Cl^- , Br^- and I^- ions all present. (The scale of this mass spectrum is such that any the separate isotopes of Cl^- and Br^- not resolved.) It also shows a single $\text{Cl}^- \cdots (\text{NH}_3)$ cluster and five $\text{I}^- \cdots (\text{NH}_3)_n$ ($n=1-5$) clusters. The most interesting feature of this mass spectrum are the clusters of mass 748 amu and higher. Upon analysing this mass spectrum it was found that each of these peaks are separated by 17 amu, corresponding to the mass of ammonia. This suggests that each successive cluster is adding an ammonia molecule. Additionally the mass of each respective peak is divisible by 17 to within reasonable certainty (never more than 0.1 from a round number), suggesting the clusters are made up entirely of ammonia. This led to the conclusion that what is being observed are single electrons solvated in ammonia and are exotic systems.

Previous research has been conducted on all of these systems with $\text{Cl}^- \cdots (\text{NH}_3)_n$ ($n=1-4$) investigated by Tschurl *et al.*⁸⁹ $\text{I}^- \cdots (\text{NH}_3)_n$ ($n=1$) by Bowen *et al.*⁹⁰ $\text{I}^- \cdots (\text{NH}_3)_n$ ($n=4-15$) by Neumark *et al.*⁵³ and solvated ammonia clusters $\text{e}^-(\text{NH}_3)_n$ ($n=41-1100$) by Sarkas *et al.*⁹¹

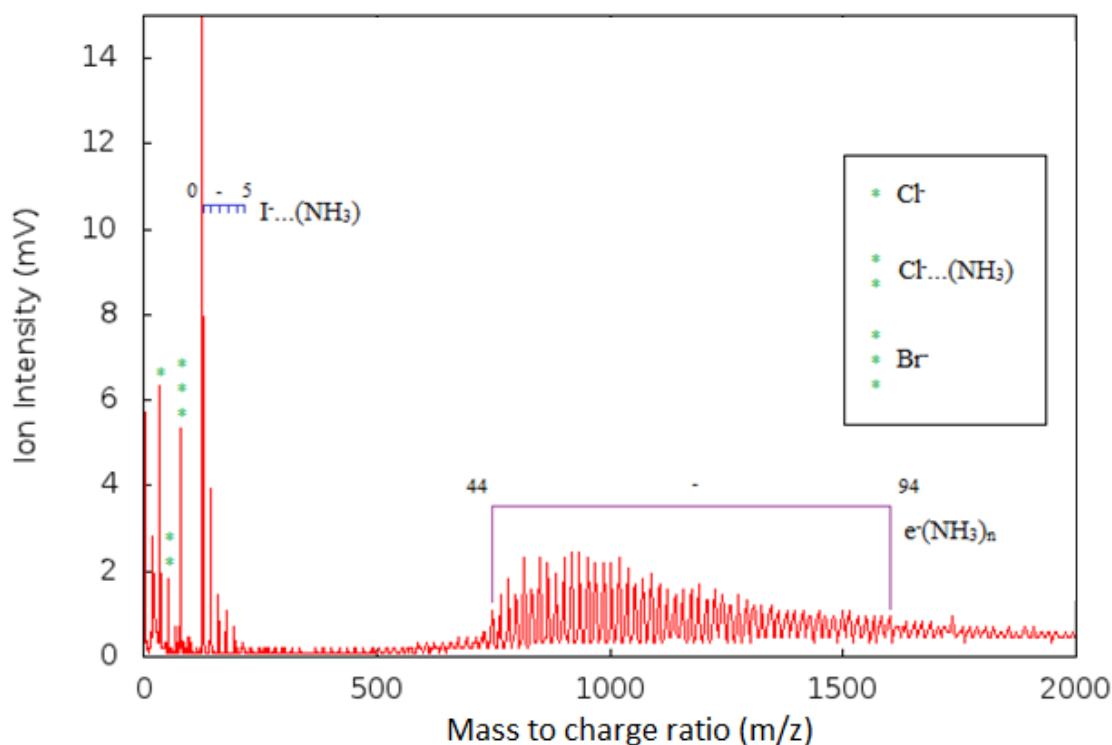


Figure 21 - Mass spectrum recorded using a 30:70 gas mixture of, ammonia:argon. Peaks that are excessively small or unknown are unlabelled.

5.4.3 Smaller Ammonia Clusters

The second mass spectrum shown Figure 22 was attained using a 12:88 gas mixture of, ammonia:argon and shows familiar peaks of Br^- and I^- with Cl^- off the scale to the left and the intensities of Br^- and I^- increasing above the 140 mV scale shown. The extra peaks observed are again separated by 17 amu, each cluster of peaks is then separated by 1 amu suggesting slight variations in the composition of the cluster. As ammonia and water both have atomic masses of 17 and 18 amu respectively the change in the atomic mass of 1 could be due to interchanging of water for ammonia on the

formation of the cluster. As to the composition of the cluster itself there are a number of possibilities; firstly it is possible that these are solvated electron clusters as seen above, although this is unlikely as they are very small clusters compared to those known solvate an electron. A more likely possibility is that there is a central anion such as hydroxide or amidogen anion to which these ligands are clustering around. As the TOF-PES was not yet producing the amidogen anion it is highly unlikely that the clusters being produced are amidogen based. The most likely base anion would be hydroxide which has been present in all of the spectra, if only in trace amounts. The resulting clusters would therefore be $\text{OH}^- \cdots (\text{H}_2\text{O})_n(\text{NH}_3)_m$ (where $n=1-k$, $m=0-(k-1)$ and $k=5-12$). (n is always 1 or more as the mass of each cluster was always 1 amu off being divisible by 17).

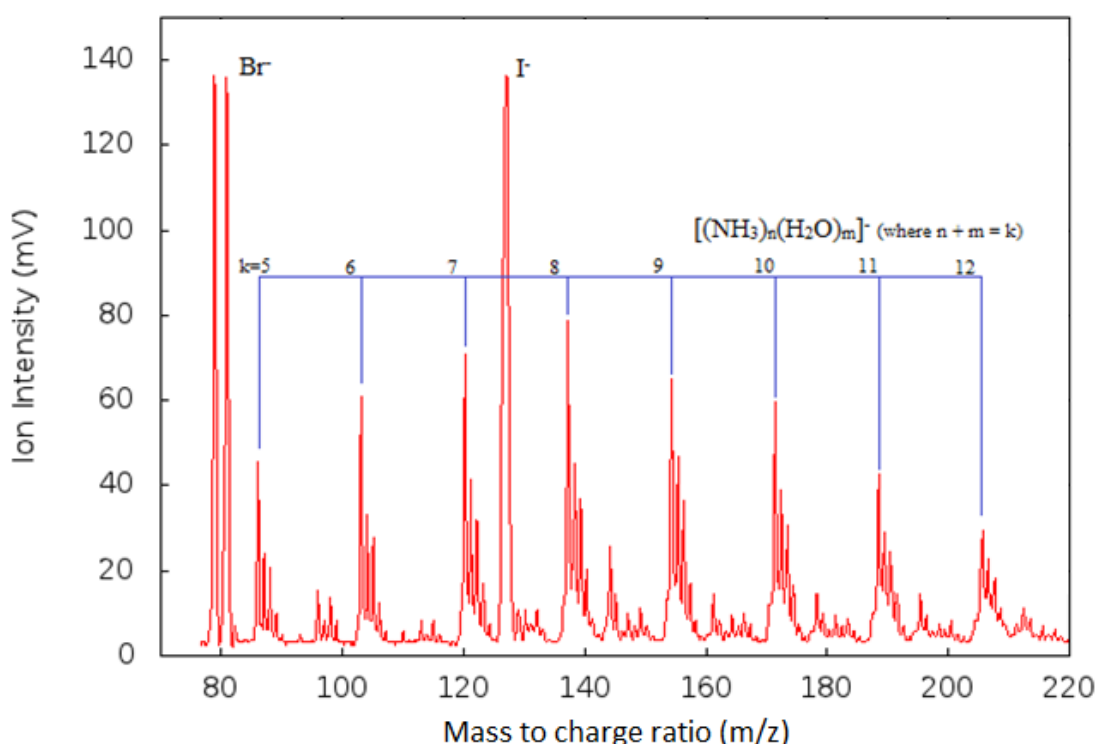


Figure 22 - The mass spectrum taken using a 12 : 88 gas mixture of, ammonia : argon. An unknown cluster possibly $\text{OH}^- \cdots (\text{H}_2\text{O})_n(\text{NH}_3)_m$ is shown here. Note: the intensity peaks of Cl^- extend off the scale shown here.

The fine peak structure observed here results from substitution of water for ammonia in the clusters. This could also cause a fine peak structure in the solvated electron-

ammonia clusters in Figure 21, however this was unobservable due to such a large scale and the gradual loss of resolution as the mass of clusters increases.

I believe there is great potential for research here starting with confirmation of the composition of these clusters moving into how such clustering effects the electronic structure of its components.

5.4.4 Mass Peak of 16

Figure 23 shows the first optimised production of a species of atomic mass 16 using the TOF-PES. While ideally this would be the amidogen anion it is instead oxide (O^-) as will be shown later in Photoelectron Spectra: Results 5.5.3. This spectrum was attained while using formamide with a gas mixture of 0.08 : 99.92, formamide : argon and shows close to 100 mV of a species with atomic mass 16 being detected at the ion detector. The familiar Cl^- and Br^- are present however I^- was not present in this system as the TOF-MS had to be calibrated to look specifically at lower atomic mass species, and measures were taken to reduce the amount of residual and trace gasses within the system as detailed in [Complications] and [Modifications].

Photoelectron spectra of the ions present in this mass spectrum were then taken to confirm the NH_2^- peak was indeed what was expected and not another ion of similar mass (see Photoelectron Spectra).

$Cl^- \cdots (Ar)$ can also be seen as well as O_2^- and OH^- . O_2^- is generated from oxygen in the gas mixing chamber which is present in part due to the low vapour pressure of formamide. The low vapour pressure of formamide means that for enough formamide to diffuse into the gas mixing chamber it must be left for some time, allowing the atmosphere to leak into the gas mixing chamber while it is under vacuum. While these leaks are usually negligible they are the reason the TOF-PES needs to be under constant vacuum to maintain operating conditions. Therefore trace amounts of

atmospheric gasses were present in this gas mixture, producing O_2^- and OH^- from trace amounts of water vapour. This could also be a potential source of O^- for the TOF-PES.

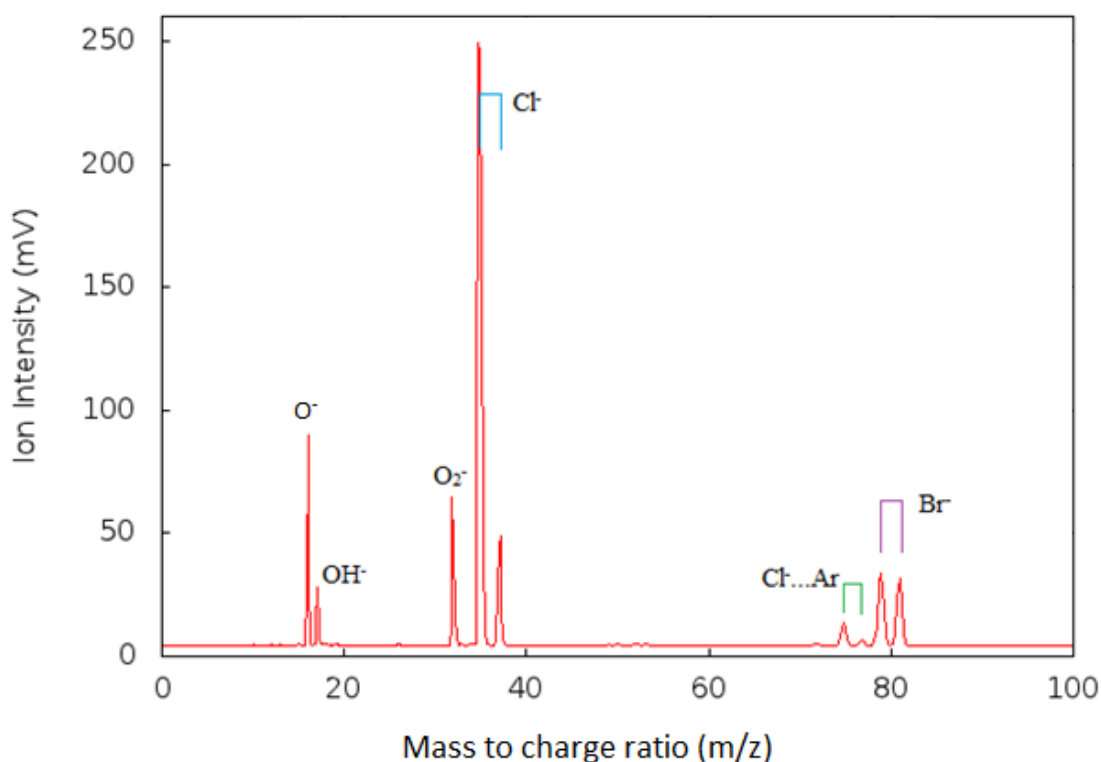


Figure 23 - The mass spectrum taken with 0.08 : 99.92 gas mixture, formamide : argon.

5.4.5 Attempts at NH_2^- clusters

Believing the peak at m/z 16 was NH_2^- attempts were made to try and produce $NH_2^- \cdots CO$. Figure 24 shows the most successful attempt using a 0.08 : 7 : 92.92 gas mixture of formamide : carbon monoxide : argon. As can be seen there is a considerably lower overall intensity of ions with the m/z peak of 16 down to 3 mV from 100 mV. A number of other species can be observed including the C^- , C_2^- , CN^- , $OH^- \cdots CO$ (which has been previously investigated by Continetti *et al.*⁹²) and the $Cl^- \cdots (CO)_n$ ($n=1,2$) clusters which have been previously investigated by Lapere *et al.*⁹³ A mass peak is observed at 44amu the expected mass of $NH_2^- \cdots CO$, however only in very trace amounts, measuring a fraction of a millivolt on the oscilloscope as seen in

Figure 25. This problem arises from the low yield of the mass 16 species in the gas mixture (as cluster production is always a fraction of the parent ion production.)

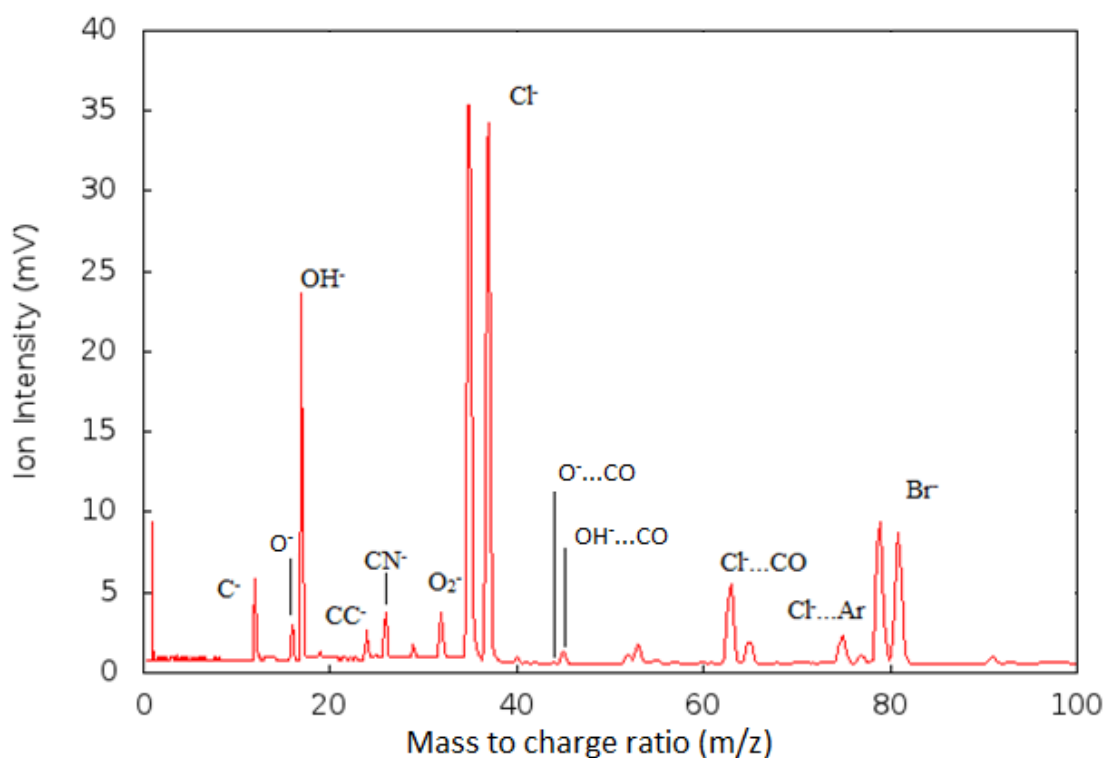


Figure 24 - The mass spectrum attained using the 0.08 : 7 : 92.92 gas mixture, formamide : carbon monoxide : argon. This was the most successful attempt to attain amidogen anion complexes.

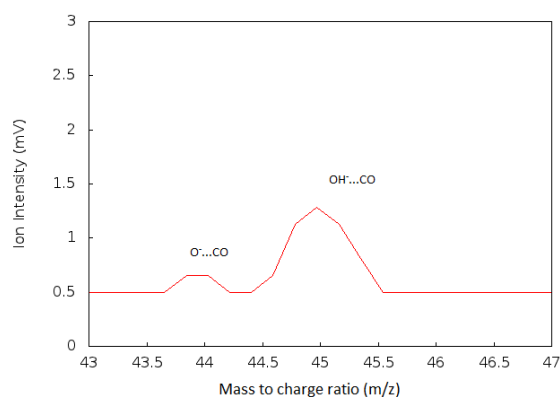


Figure 25 – An expanded view of peaks at $m/z = 44$ and 45 , which were originally believed to be $\text{NH}_2^- \cdots \text{CO}$ and $\text{OH}^- \cdots \text{CO}$.

5.5 Photoelectron Spectra

Unfortunately the amidogen anion was unable to be produced with the desired complexing ligands and so there are no new photoelectron spectra to report. However, photoelectron spectra were taken of the what was thought to be the amidogen and superoxide anion (with photoelectron spectra of chloride and bromide also recorded for calibration.) The resulting photoelectron spectra show vertical detachment energies of superoxide to be ~ 1.2 eV and the amidogen anion to be ~ 1.4 eV although with very wide peaks.

5.5.1 Calibration

Shown in **Error! Reference source not found.** and **Error! Reference source not found.** are the acquired photoelectron spectra of bromide and chloride respectively. The bromide photoelectron spectrum has been left with electron Time-of-Flight on the x-axis as bromide has been used for a reliable calibration. The two vertical detachment energies of bromide observed are known to occur at 3.817 eV and 3.380 eV. While the vertical detachment energies of chloride are also known as 3.724 eV and 3.614 eV the TOF-PES is unable to resolve to this level currently and hence the chloride photoelectron spectrum cannot be used for calibration. This leaves only the bromide spectrum for calibration and when calibrating for spectra of species with much lower masses and vertical detachment energies this leads to a large extrapolation. To increase the accuracy of the calibration curve an older calibration curve was used for the analysis of the photoelectron spectra. This calibration curve is the result of averaging up to 10 spectra for the iodide and bromide anions taken over various days and ensuring that spectra features are consistent.

The calibration curve is generated by comparing the flight times of each species of known energy, in this case bromide, and the expected kinetic energy of each electron.

Relating time of flight of electrons to electron kinetic energy is reasonably simple and occurs as follows:

$$E_{KE} = \frac{1}{2}mv^2 \quad \text{Eq. 42}$$

$$v = \frac{d}{t} \quad \text{Eq. 43}$$

Combines to give:

$$E_{KE} = \frac{1}{2}md^2\left(\frac{1}{t^2}\right) \quad \text{Eq. 44}$$

Where E_{KE} is the kinetic energy of each electron and can be solved if the laser energy and binding energy of the anion is known (Eq. 36), m is the mass of an electron and v is the velocity of each electron. As we measure time-of-flight we introduce Eq. 43 where d is the length of the time-of-flight tube and t is the time taken to transverse the time-of-flight tube at velocity v . Equations Eq. 42 and Eq. 43 combine to give Eq. 44, using Eq. 44 a plot of E_{KE} versus $\frac{1}{t^2}$ can be made yielding a straight line with gradient $\frac{1}{2}md^2$. This graph can then be used to predict electron kinetic energies of other species based on time-of-flight of their electrons.

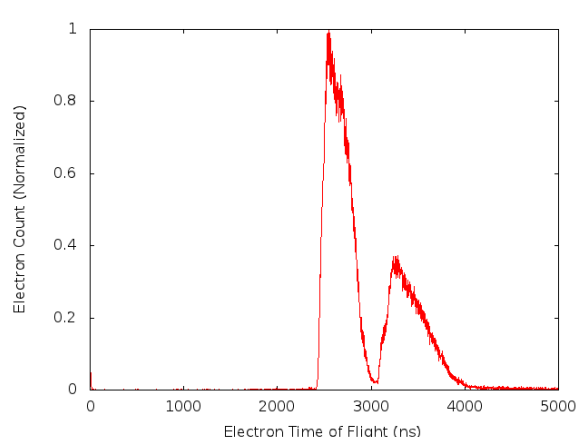


Figure 27 - The photoelectron spectrum of Br^- used for calibration of other spectra.

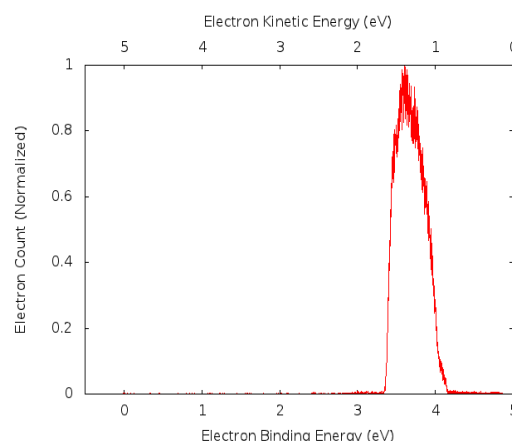


Figure 27 - The photoelectron spectrum of Cl^- .

5.5.2 Resolution

As previously mentioned two peaks are expected for the photoelectron spectrum of chloride where only one is observed. This is due to the resolution limits of the TOF-PES; the best resolution the current setup has achieved was ~0.3 eV from Lapere *et al.*⁷⁹ The best resolution achieved here is ~0.5 eV for the bromide spectrum and the worst at ~1.2 eV for the supposed amidogen anion spectrum. In order to resolve the individual peaks of chloride the resolution would have to be 0.1 eV or lower.

The considerable drop in the resolution of the photoelectron spectra taken is due to Doppler broadening caused by the velocity of each anion. Consider the Maxwell-Boltzmann distribution describing Doppler broadening for a thermal system shown in Eq. 45 is can be seen that the width of Doppler broadening will increase dramatically as the velocity increases. (as P increases Doppler broadening increases)

$$P dv = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{mv^2}{2kT}} dv \quad \text{Eq. 45}$$

While this rule does not exactly apply, as the ions have the same concerted motion and have low temperature, the trend applies as the velocity of each anion increases so too does the Doppler broadening. Add the fact that the same species anion does not necessarily have the same velocity as other anion of the same species due to problems that make special focussing necessary (5.6.3). Consequently heavier anions such as bromide will have a lower velocity and better resolution. Super Oxide and Oxide have much lower masses, hence much higher velocities experience a much higher degree of Doppler broadening. This takes the form of widened peaks and loss of resolution on the photoelectron spectra.

The TOF-PES has an ion decelerator installed to try and improve this problem. By slowing down an ion before trying to observe its photoelectron spectra it is possible to

decrease the degree of Doppler broadening and increase the resolution. Additionally there is a mass gate available for use within the TOF-PES. The Mass gate reduces interference of other ionic species by only allowing species of a certain mass to charge ratio into the laser interaction chamber. Neither the mass gate nor the ion decelerator were used in the spectra taken for this research and are methods that could be used to improve the resolution in future trials.

5.5.3 Results

Figure 28 shows the photoelectron spectrum of O_2^- and the resolution seems unreasonable at first until a more accurate spectrum of O_2^- is consulted, overlay in Figure 28.⁵² Spin-orbit coupling causes considerable splitting of the O_2^- spectrum and hence the wide peak observed is a consequence of widening of the fine structure of the spectrum rather than being a single peak widened by poor resolution. The centre of the O_2^- spectrum is observed to sit higher than the expected 0.9 eV at ~1.2 eV however this can be attributed to calibration and poor resolution and considering the overlay in Figure 28 shows a close resemblance to what would be expected.

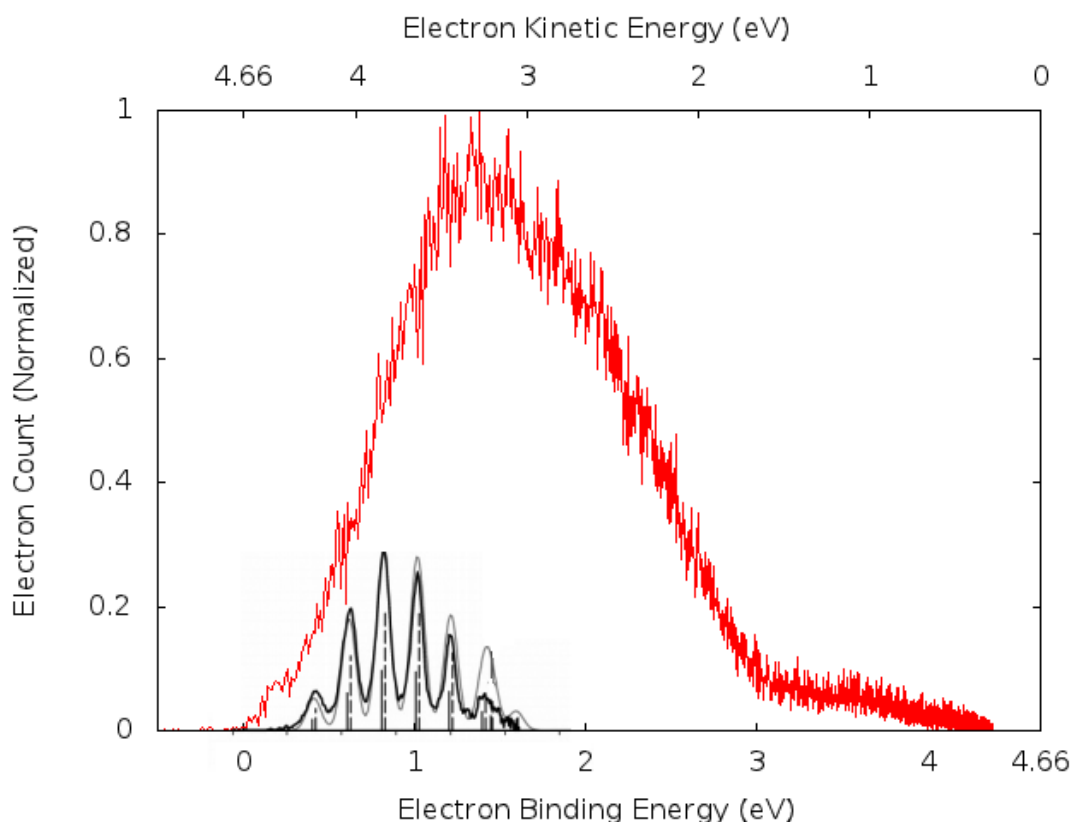


Figure 28 - The photoelectron spectrum of O_2^- overlaid with the spectrum of O_2^- acquired by Sanov *et al.*⁵²

The photoelectron spectrum for the ion of m/z 16 is shown in Figure 29 with an overlay from the more recently published NH_2^- spectrum from Sanov *et al.*⁵² revealing the presence of the $^2\text{A}_1$ band for the first time. Our spectrum is higher than expected the expected 0.78 eV by ~ 0.8 eV for both peaks and led us to initially suspect that spectrum was instead attributed to OH^- , made possible if the timing of the laser was incorrect such that the m/z 17 ion was photodetached rather than m/z of 16. This is not the case, however, as no excited state band has ever been observed for OH^- using photoelectron spectroscopy. Instead what is actually being observed is the oxide anion O^- , with an ionisation energy of 1.461112 eV⁹⁴ with the next higher energy level that resolvable is at 15867.862 cm^{-1} ,⁹⁵ or 1.967 eV above the first vertical detachment energy placing it at ~ 3.4 eV on the photoelectron spectrum. This is almost exactly what is seen in the

photoelectron spectrum acquired here, therefore this species is indeed O^- and not NH_2^- as originally expected. The stick spectrum shown in Figure 29 is constructed from the known electron affinity and first excited state of the oxygen atom.^{94,95}

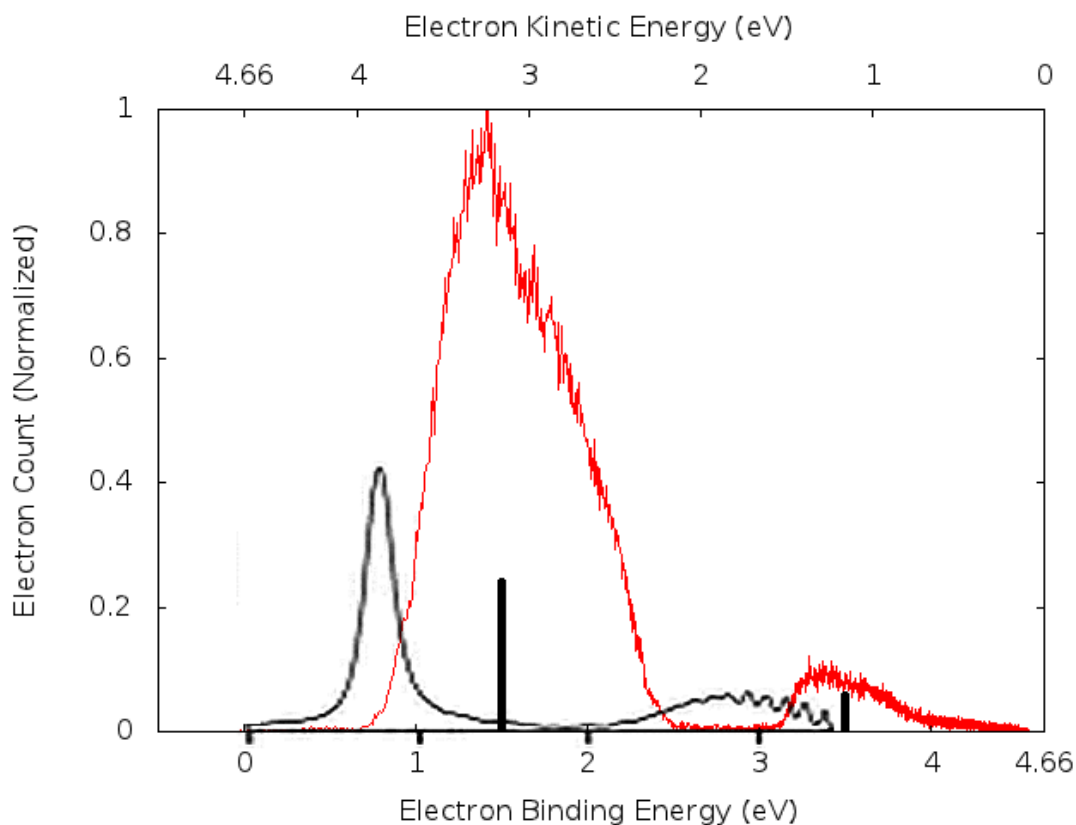


Figure 29 - The photoelectron spectrum of O^- overlaid with the photoelectron spectrum of NH_2^- from Sanov *et al.*⁵² The vertical lines show the expected locations of photoelectron peaks for photodetachment from O^- .

6. Future work

Considering the amidogen anion was not observed throughout this research there is still considerable work to be done and problems to overcome. Solutions to problems such as low electron kinetic energy from the filaments and low electron density in the gas expansion have been suggested and manufactured in this work but have yet to be installed and tested (see 5.2.5 for more detail). Additionally higher voltage electron sources could be considered such as the purchase of an electron gun or the construction

an electron source similar to that used by Prof. Allan McKinley in his PhD thesis capable of producing 1000 eV electrons.⁹⁶

Even though formamide was shown not to produce the amidogen anion testing other amidogen precursor substances such as n-butylamine and n-propylamine could not only yield the amidogen anion necessary for this research and could also yield other anions of interest too. Exotic species have produced in this research that have never been investigated before such as the clusters shown in Figure 22 and $I^- \cdots (NH_3)_n$ ($n=2, 3$) that are potential avenues for further research. Exotic species such as O^- , O_2^- , OH^- , C^- , CC^- and CN^- that have not been observed in this TOF-PES before have also been shown to be producible and are further avenues for gas phase solvation research.

Further investigation could also be conducted regarding the source of the noise generated within the TOF-PES. This could even involve modifying the machine to look at dissociative excitation directly or varying methods used to produce a plasma in the gas expansion.

Work to improve the resolution of the TOF-PES is always ongoing and had a considerable effect on the results of this work. In future optimisation of the laser wavelength should be considered for the best photoelectron spectra and this will be considerably easier now a tuneable laser is available. As work to improve the apparatus continues other photoelectron techniques such as Zero Kinetic Energy Spectroscopy (ZEKE) and Slow Electron Velocity map Imaging (SEVI).

While calculations have been carried out on the amidogen-(argon, carbon monoxide, water) there is room for improvement. Existing problems with some of these results have been highlighted and further investigation of these problems would be prudent. Additionally potential energy surfaces could be generated and spectra predicted based on these surfaces, some work to this effect has already been conducted by Schwartz *et*

*al.*⁷⁴ and Ennis *et al.*⁵⁰ The level of theory could be increased (pVQZ basis sets) or work could be done with other theoretical methods such as Density Functional Theory for comparison with CCSD(T) and MP2 methods used here. Calculations on larger amidogen clusters are also a potential area for work.

7. Conclusion

Numerous attempts have been made to produce the amidogen anion within the TOF-PES. Although unsuccessful, modifications to the TOF-PES have been proposed and constructed including increasing the voltage provided to the filaments, focusing filament electrons to a point in the gas expansion and moving the gas mixing station. All of these modifications were proposed with the aim of producing the amidogen anion and should make future attempts to produce exotic species within the TOF-PES much easier. Photoelectron spectra of O^- and O_2^- have been recorded as well as mass spectra of a number of exotic species suggesting avenues for further research.

Theoretical calculations have been carried out on the amidogen species and its clustering to single argon, carbon monoxide and water ligands. The optimised structures of each of these clusters have been reported and where possible the D_0 and predicted adiabatic detachment energy.

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9. Appendix

9.1 Source code for geometry generator

```
'''
Created on Oct 26, 2011

@author: stephen
'''

import numpy

import math

from math import pi

n = input("Enter desired number of points: ")    #number of points desired must be
even

r = input("Enter desired radius: ")

a = input("Enter number of arcs: ")

List=[]

i = 0

j = 1

#generates n-1 points along a arcs in a quarter sphere

if n <= 0:

    print "Positive numbers only"

elif n % 2 != 0:

    print "Even numbers only"

else:

    while j <= a:

        while i < n-1:
```

```

        List.append(numpy.array([r, i*pi/(n-1), j*pi/(2*a)]))

        i += 1

    i = 0

    j += 1

#turns a quarter sphere into a half sphere

k=1

while k < a:

    for element in List[(k-1)*n:k*n-1]:

        List.append(element + numpy.array([0, 0, pi/2]))

    k += 1

#turns a half sphere into a whole sphere

for element in List[: (n-1)*a + (a-1)*(n-1)]:

    List.append(element + numpy.array([0, pi, 0]))

#adds missed points

List.append(numpy.array([r, 0., 0.]))

List.append(numpy.array([r, 0, pi]))

i=0

#converts to xyz-coordinates

List2=[]

while i < (n-1)*(2*a-1)*2+2:

    List2.append(numpy.array([r*math.cos(List[i][1])*math.sin(List[i][2]), r*math.sin(List[i][1])*math.sin(List[i][2]), r*math.cos(List[i][2]))]))

    i += 1

```

Created on Nov 8, 2011

@author: stephen

'''

from Success import *

import numpy as np

import math

from math import pi

molecule = input("Enter desired molecule: ")

m = input("Mirror? (Yes=-1, No=1): ")

p = input("Enter desired sphere point: ")

if molecule=="H2O":

Geometry=([

("O", [0.0, 0.0, 0.0]),

("H", [0.0, 1.0, 0.0]),

("H", [1.0, 0.0, 0.0]))]

if molecule=="CO":

Geometry=([

("C", [0.0, 0.0, 0.0]),

("O", [1.138946, 0.0, 0.0]))]

if molecule=="NO2":

Geometry=([

("N", [0.0, 0.0, 0.0]),

("O", [-0.25, 1.25, 0.0]),

```

("O", [1.25, -0.25, 0.0]))

if molecule=="N2O":

    Geometry=(

        ("N", [-1.163888, 0.0, 0.0]),

        ("N", [-0.008564, 0.0, 0.0]),

        ("O", [1.172452, 0.0, 0.0]))

if molecule=="NO":

    Geometry=(

        ("N", [0.0, 0.0, 0.0]),

        ("O", [1.137128, 0.0, 0.0]))

if molecule=="NH2-":

    Geometry=(

        ("N", [0.0, 0.0, 0.0]),

        ("H", [0.0, 1.0, 0.0]),

        ("H", [1.0, 0.0, 0.0]))

if molecule=="NH3":

    Geometry=(

        ("N", [0.0, 0.0, 0.0]),

        ("H", [1.0, 0.0, 0.0]),

        ("H", [0.0, 1.0, 0.0]),

        ("H", [0.0, 0.0, 1.0]))

c1 = 0

i = 0

```

```

#finds the center of the molecule

while i < len(Geometry):

    c1 = c1 + np.array(Geometry[i][1])

    i += 1

c = c1/(len(Geometry))

#gives the molecule a new set of coordinates based on its center (i.e. the center is
now the origin)

i = 0

newGeometry = []

while i < len(Geometry):

    newGeometry.append(np.array(Geometry[i][1])-np.array(c))

    i += 1

#calculates the distance of each atom from the center of the molecule (radius)

distance = []

i = 0

while i < len(Geometry):

    distance.append(math.sqrt(math.pow(newGeometry[i][0],2) +
math.pow(newGeometry[i][1],2) + math.pow(newGeometry[i][2],2)))

    i += 1

#the angle between the x-axis and the vector of each atom on the xy-plane

theta = []

i = 0

while i < len(Geometry):

    if newGeometry[i][0] < 0:

        theta.append(math.atan(newGeometry[i][1]/newGeometry[i][0]) + pi)

    i += 1

```

```

        print 1

    else:

        theta.append(math.atan(newGeometry[i][1]/newGeometry[i][0]))

        i += 1

#numpy.cross(newGeometry[0],[0, 0, 1]

#the angle between the z-axis and the vector of each atom

i = 0

phi = []

while i < len(Geometry):

    phi.append(math.acos(newGeometry[i][2]/distance[i]))

    i += 1

#gives the molecule its new set of coordinates in spherical polar coordinates

newGeometryS = []

i = 0

while i < len(Geometry):

    newGeometryS.append([distance[i], theta[i], phi[i]])

    i += 1

PHI = List[p][2]

THETA = List [p][1]

#rotating the molecule according to the point on the sphere given

rotatedGeometry = []

i = 0

```

```

while i < len(Geometry):

    rotatedGeometry.append([distance[i],theta[i]+THETA, phi[i] + PHI])

    i += 1


rotatedGeometryxyz = []

i = 0
while i < len(Geometry):

    rotatedGeometryxyz.append(np.array([

rotatedGeometry[i][0]*math.cos(rotatedGeometry[i][1])*math.sin(rotatedGeometry[i][2]
),

rotatedGeometry[i][0]*math.sin(rotatedGeometry[i][1])*math.sin(rotatedGeometry[i][2]
),

                                rotatedGeometry[i][0]*math.cos(rotatedGeometry[i][2])

                                ]))

    i += 1


translatedGeometry = []

i = 0
while i < len(Geometry):

    translatedGeometry.append(List2[p] + rotatedGeometryxyz[i])

    i += 1


print c

print newGeometry

print phi

print newGeometryS

print rotatedGeometry

print rotatedGeometryxyz

```

```

i = 0

while i < len(Geometry):

    print translatedGeometry[i][0], translatedGeometry[i][1],
    translatedGeometry[i][2]

    i += 1

```

9.2 Images and geometry data for all complexes

The following structures and values were calculated using MP2 and CCSD(T) level theory employing Dunning's correlation consistent basis sets aug-cc-pVXZ (X = D, T) for hydrogen, carbon, oxygen and argon.⁶⁰⁻⁶² The level of theory and basis sets have been indicated where appropriate (aug-cc-pVTZ basis sets unless indicated otherwise).

Bond lengths are denoted $r(\text{A-B})$ and are given in Ångströms. Where two of the same bond length is given the longer bond is always closer to the other molecule.

Angles are denoted by $\theta(\text{A-B-C})$ and are given in degrees.

Zero point energy (zpe) given in kJ mol^{-1}

E_e and $E_{e/\text{BSSE}}$ are the electronic energies and those corrected for Basis Set Superposition Error (BSSE), given in hartrees.

D_o and D_e are calculated using BSSE corrected energies where possible (otherwise just the electronic energy) and are given in kJ mol^{-1} .