THRESHOLD PHOTO-IONISATION AND DENSITY FUNCTIONAL THEORY STUDIES OF METAL-CARBIDE CLUSTERS

Viktoras Dryza

A thesis submitted in total fulfillment of the requirements for the degree of Doctor of Philosophy

November, 2008

Department of Chemistry
The University of Adelaide
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Dedicated to my Dad.
“Serenity now, serenity now!”
- Frank Costanza (Seinfeld, Season 9/Episode 3)
Abstract

Neutral gas-phase metal-carbide clusters are generated by laser ablation and are detected in the constructed time-of-flight mass-spectrometer by laser ionisation. Photo-ionisation efficiency (PIE) experiments are performed on the metal-carbide clusters to determine their ionisation potentials (IPs). Complimentary density functional theory (DFT) calculations are performed on the energetically favorable structural isomers of the metal-carbide clusters. Comparison between the calculated IPs of the isomers and the experimental IP allows the carrier of the observed ionisation onset for a metal-carbide cluster to be assigned.

The niobium-carbide clusters $\text{Nb}_3\text{C}_y$ ($y = 0–4$), $\text{Nb}_4\text{C}_y$ ($y = 0–6$) and $\text{Nb}_5\text{C}_y$ ($y = 0–6$) are examined by PIE experiments and DFT calculations. The IPs of the niobium-carbide clusters are found to be either left reasonably unchanged from the IPs of the bare metal clusters or moderately reduced. The clusters $\text{Nb}_3\text{C}_2$, $\text{Nb}_4\text{C}_4$, $\text{Nb}_5\text{C}_2$ and $\text{Nb}_5\text{C}_3$ display the largest IP reductions for their corresponding cluster series.

The structures assigned to the IPs of the $\text{Nb}_3\text{C}_y$ ($y = 1–3$) clusters are based on the carbon atoms attaching to the niobium faces and/or niobium-niobium edges of the triangular $\text{Nb}_3$ cluster. However, for $\text{Nb}_3\text{C}_4$ the ionisation onset is assigned to a low-lying isomer, which contains a molecular $\text{C}_2$ unit, rather than the lowest energy isomer, a niobium atom deficient $2\times2\times2$ face-centred cubic (fcc) nanocrystal structure.

The structures assigned to the IPs of the $\text{Nb}_4\text{C}_y$ ($y = 1–4$) clusters are based on the carbon atoms attaching in turn to the niobium faces of the tetrahedral $\text{Nb}_4$ cluster, developing a $2\times2\times2$ fcc nanocrystal structure for $\text{Nb}_4\text{C}_4$. For $\text{Nb}_4\text{C}_3$ two ionisation onsets are observed; one weak onset at low energy and another more intense onset at high energy. It is proposed that the two onsets are due to ionisation from both a metastable $^3A_1$ state and the ground $^1A_1$ state of the lowest energy isomer. The ionisation onsets of $\text{Nb}_4\text{C}_5$ and $\text{Nb}_4\text{C}_6$ are also proposed to originate from metastable triplet states of the lowest energy isomers, with the transitions from the ground singlet states calculated to be greater than the highest.
achievable photon energy in the laboratory. The structures of Nb$_4$C$_5$ and Nb$_4$C$_6$ have one and two carbon atoms in a $2\times2\times2$ fcc nanocrystal substituted with molecular C$_2$ units, respectively.

The structures assigned to the IPs of the Nb$_5$C$_y$ ($y = 1–6$) clusters are based on the underlying Nb$_5$ cluster being in either a “prolate” or “oblate” trigonal bipyramid geometry; the former has six niobium faces available for carbon addition, while the latter has two niobium butterfly motifs and two niobium faces available for carbon addition. Both the structures of Nb$_5$C$_5$ and Nb$_5$C$_6$ have the underlying Nb$_5$ cluster in the oblate trigonal bipyramid geometry and contain one and two molecular C$_2$ units, respectively.

The tantalum-carbide clusters Ta$_3$C$_y$ ($y = 0–3$), Ta$_4$C$_y$ ($y = 0–4$) and Ta$_5$C$_y$ ($y = 0–6$) are examined by PIE experiments and DFT calculations. The IPs of the tantalum-carbide clusters in each series show trends that are very similar to the corresponding iso-valent niobium-carbide cluster series, although the IP reductions upon carbon addition are smaller for the former. For the vast majority of tantalum-carbide clusters, the same structural isomer is assigned to the ionisation onset as that assigned for the corresponding niobium-carbide cluster.

Bimetallic tantalum-zirconium-carbide clusters are generated using a constructed double ablation cluster source. The Ta$_3$ZrC$_y$ ($y = 0–4$) clusters are examined by PIE experiments and DFT calculations. The IP trend for the Ta$_3$ZrC$_y$ cluster series is reasonably similar to that of the Ta$_4$C$_y$ cluster series, although the IP reductions upon carbon addition are greater for the former. The structures assigned to the IPs of the Ta$_3$ZrC$_y$ ($y = 1–4$) clusters are based on the carbon atoms attaching in turn to the metal faces of the tetrahedral Ta$_3$Zr cluster.

In summary, the work presented in this thesis demonstrates that the structures of metal-carbide clusters can be inferred by the determination of their IPs through PIE experiments in combination with DFT calculations on candidate structural isomers.
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The niobium-carbide clusters Nb$_3$C$_y$ ($y = 0–4$), Nb$_4$C$_y$ ($y = 0–6$) and Nb$_5$C$_y$ ($y = 0–6$) are examined by PIE experiments and DFT calculations. The IPs of the niobium-carbide clusters are found to be either left reasonably unchanged from the IPs of the bare metal clusters or moderately reduced. The clusters Nb$_3$C$_2$, Nb$_4$C$_4$, Nb$_5$C$_2$ and Nb$_5$C$_3$ display the largest IP reductions for their corresponding cluster series.

The structures assigned to the IPs of the Nb$_3$C$_y$ ($y = 1–3$) clusters are based on the carbon atoms attaching to the niobium faces and/or niobium-niobium edges of the triangular Nb$_3$ cluster. However, for Nb$_3$C$_4$ the ionisation onset is assigned to a low-lying isomer, which contains a molecular C$_2$ unit, rather than the lowest energy isomer, a niobium atom deficient 2×2×2 face-centred cubic (fcc) nanocrystal structure.

The structures assigned to the IPs of the Nb$_4$C$_y$ ($y = 1–4$) clusters are based on the carbon atoms attaching in turn to the niobium faces of the tetrahedral Nb$_4$ cluster, developing a 2×2×2 fcc nanocrystal structure for Nb$_4$C$_4$. For Nb$_4$C$_3$ two ionisation onsets are observed; one weak onset at low energy and another more intense onset at high energy. It is proposed that the two onsets are due to ionisation from both a metastable $^3A_1$ state and the ground $^1A_1$ state of the lowest energy isomer. The ionisation onsets of Nb$_4$C$_5$ and Nb$_4$C$_6$ are also proposed to originate from metastable triplet states of the lowest energy isomers, with the transitions from the ground singlet states calculated to be greater than the highest.
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The structures assigned to the IPs of the Nb₅Cy (y = 1–6) clusters are based on the underlying Nb₅ cluster being in either a “prolate” or “oblate” trigonal bipyramid geometry; the former has six niobium faces available for carbon addition, while the latter has two niobium butterfly motifs and two niobium faces available for carbon addition. Both the structures of Nb₅C₅ and Nb₅C₆ have the underlying Nb₅ cluster in the oblate trigonal bipyramid geometry and contain one and two molecular C₂ units, respectively.

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Bimetallic tantalum-zirconium-carbide clusters are generated using a constructed double ablation cluster source. The Ta₃ZrCy (y = 0–4) clusters are examined by PIE experiments and DFT calculations. The IP trend for the Ta₃ZrCy cluster series is reasonably similar to that of the Ta₅Cy cluster series, although the IP reductions upon carbon addition are greater for the former. The structures assigned to the IPs of the Ta₃ZrCy (y = 1–4) clusters are based on the carbon atoms attaching in turn to the metal faces of the tetrahedral Ta₃Zr cluster.

In summary, the work presented in this thesis demonstrates that the structures of metal-carbide clusters can be inferred by the determination of their IPs through PIE experiments in combination with DFT calculations on candidate structural isomers.
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Chapter 1: Introduction to Metal-Carbide Clusters

1.1 Generation and Distribution of Metal-Carbide Clusters

Metal-carbide clusters rose to prominence as a new class of molecular cluster when Castleman and co-workers discovered a lone “super abundant” peak in the nascent cation mass spectrum generated from the reaction of laser ablated titanium and a hydrocarbon gas.\(^1\) The peak was assigned to a species with stoichiometry Ti\(_8\)C\(_{12}\), following confirmation with isotopic substituted \(^{13}\)C hydrocarbon gas. Incidentally, it was the same laser ablation technique that was integral to the generation and discovery of the buckminsterfullerene cation (C\(_{60}^+\)).\(^2\)

Castleman and co-workers initially proposed a pentagonal dodecahedron structure of \(T_h\) symmetry, based on the hypothetical C\(_{20}\) fullerene, to explain the exceptional stability of this species. This structure has twelve fused five-membered rings, each containing two titanium and three carbon atoms. Alternatively, this structure can be thought of as a cube of titanium atoms with six C\(_2\) units bound along each face of the cube. Therefore, based on this proposed structure, the Ti\(_8\)C\(_{12}\) species was given the label Metallocarbohedrene, or “Metcar” for short.

Interest further heightened in metal-carbide clusters when Duncan and co-workers found new titanium-carbide cluster peaks in addition to the Metcar species in their nascent cation mass spectrum, which was generated in a similar fashion as Castleman and co-workers.\(^3\) These new peaks also displayed enhanced abundance like that of the Metcar species, with the most abundant peak assigned to a species of stoichiometry Ti\(_{14}\)C\(_{13}\). Duncan and co-workers proposed a 3×3×3 face-centred cubic (fcc) crystalline structure for this species. Less dominant peaks were also observed at geometric closing stoichiometries for other fcc crystalline structures; e.g. 3×3×4, 3×4×4 and 3×4×5. As such these new types of crystalline species were categorized as “nanocrystals”. Therefore, metal-carbide clusters are generally grouped into two bonding motifs: Metcars or nanocrystals.\(^4\)
Chapter 1: Introduction to Metal-Carbide Clusters

Very soon after the discovery of the titanium Metcar, both the Castleman and Duncan groups found that the enhanced stability of the Metcar species was not confined to titanium but occurred for several other early transition metals (e.g. Zr, Hf, V, Nb, Cr and Mo).\textsuperscript{3,5-8} Duncan and co-workers showed that both the Metcar and nanocrystal species could be produced together for certain transition metals.\textsuperscript{3} While the Metcar and nanocrystal species were abundant for these other early transition metals, peaks for metal-carbide clusters of different stoichiometries were also prominent, unlike for titanium. Furthermore, Duncan and co-workers also were able to generate the Metcar species for the less reactive later transition metals (\textit{i.e.} Fe, Co, Cu and Ni), however they did not display any enhanced abundance.\textsuperscript{7,9}

While the majority of work performed has been based on cationic clusters, neutral metal-carbide clusters have also been shown to be generated in abundance by laser ablation.\textsuperscript{6,10-14} Photo-ionisation of the neutral metal-carbides clusters in molecular beams have shown similar mass distributions as the cations, although with quite varying intensities. However, the true distribution of neutrals in the molecular beam is not a direct representation of the distribution obtained by photo-ionisation due to certain factors (\textit{e.g.} ionisation potentials, ionisation cross-sections and fragmentation).

Further details on the initial generation and development of investigations on the Metcar and nanocrystal species can be found in the following review.\textsuperscript{15}
1.2 The Structures of the Ti$_8$C$_{12}$ “Metcar” and Ti$_{14}$C$_{13}$ “Nanocrystal”

Although the initial computational investigations on the titanium Metcar were mainly based on the pentagonal dodecahedron structure, Dance was the first to propose a new isomer for Ti$_8$C$_{12}$ (Figure 1-1a), which was calculated to be much lower in energy and is now accepted to be the structure of the Metcar species.$^{16}$ Dance’s isomer was a variant on the pentagonal dodecahedron structure where in combination with the C$_2$ units being rotated, the metal atoms were distorted into two distinct positions; either those belonging to an inner tetrahedron or those belonging to a larger outer tetrahedron, capping the faces of the inner one. The C$_2$ units are bound to the metal atoms in an arrangement where they interact end-on with the metal atoms contained in the outer tetrahedron and side-on with the metal atoms contained in the inner tetrahedron. The ideal symmetry of this cluster is $T_d$, although recent high level calculations predict slight distortions from this symmetry to be lower in energy.$^{17,18}$

Very little debate existed about the proposed structure of Ti$_{14}$C$_{13}$; a 3×3×3 fcc nanocrystal (Figure 1-1b). Indeed bulk titanium-carbide has a fcc crystal structure. Calculations on this structure support its proposed stability and $O_h$ (or near) symmetry.$^{19-22}$

![Figure 1-1: a) Ti$_8$C$_{12}$ "Metcar" b) Ti$_{14}$C$_{13}$ "Nanocrystal".](image)

The structures for these two species are consistent with all the experimental results obtained; including photo-dissociation,$^{3,23}$ reactivity,$^{14,24,25}$ ion mobility$^{26}$ and spectroscopic investigations.$^{13,27}$ The proposed structures of the Ti$_8$C$_{12}$ Metcar and
Chapter 1: Introduction to Metal-Carbide Clusters

$\text{Ti}_{14}\text{C}_{13}$ nanocrystal are calculated to be the same for several other early transition metals.\textsuperscript{17,21,28,29} Rohmer, Benard and Poblet have produced an excellent review on the structure, reactivity and growth pathways of metal-carbide clusters in relation to experimental and computational investigations, with a special focus on the Metcar species.\textsuperscript{30} However, the most convincing evidence for the proposed structures for these two species came from experiments performed in the same period as this review and as such were not included.

Collaborative work by Meijer, von Helden, Duncan and co-workers have shown that infrared (IR) spectral information can be obtained for neutral metal-carbide clusters via the application of IR resonance enhanced multi-photon ionisation (REMPI) using a tunable IR free electron laser (FEL).\textsuperscript{31-33} The clusters are excited to energies at which they undergo delayed ionization, a process enhanced on vibrational resonances that relate to molecular structure. Vastly different spectra were observed for the $\text{Ti}_8\text{C}_{12}$ Metcar compared to the $\text{Ti}_{14}\text{C}_{13}$ nanocrystal. The former has a strong absorbance near 1400 cm\textsuperscript{-1}, which is attributed to carbon-carbon bonding, and the latter absorbs at 500 and 650 cm\textsuperscript{-1}, which is attributed to titanium-carbon bonding.
1.3 **Potential Applications of Metal-Carbide Clusters**

While metal-carbide clusters possess a dense manifold of electronic states due to the metals’ open $d$-orbitals, the arrangement of these states and hence properties can still change significantly with the addition of another atom, be it a metal or carbon atom; *i.e.* quantum effects are still prominent at this size range. Metal-carbide clusters have been proposed for many applications in nanotechnology such as quantum wires, nano-catalysts and hydrogen storage.

Work by Wang and Cheng identified an abundant peak in the nascent anion spectrum of titanium-carbide clusters at a stoichiometry of $\text{Ti}_{13}\text{C}_{22}$ and measured its photo-electron spectrum. This stoichiometry, observed in cationic zirconium-carbide clusters, was proposed by Castleman and co-workers to have a double cage structure composed of two fused Metcar units. However, utilising computational calculations Wang and Cheng found a structure of $\text{Ti}_{13}\text{C}_{22}$, which can be considered as a $3\times3\times3$ $\text{Ti}_{13}\text{C}_{14}$ nanocrystal where the eight corner carbon atoms have been substituted with eight C$_2$ units, to be lower in energy than the double cage structure and to also display better agreement with the experimental results. They proposed a novel layer-by-layer cubic growth pathway involving C$_2$ units (*i.e.* linking alternate $\text{Ti}_4\text{C}(\text{C}_2)_4$ and $\text{Ti}_5\text{C}_4$ layers) to account for experimentally observed abundant peaks, previously explained by multi-cage growth. The highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap of $\text{Ti}_{13}\text{C}_{22}$ was calculated to be surprisingly small. By calculating a five layered structure (*i.e.* $\text{Ti}_{22}\text{C}_{35}$) they showed that the HOMO-LUMO gap decreased with increasing cluster size. Utilising this property it was proposed that this growth pattern could generate novel one dimensional quantum wires, whose transport properties depended on their length.

Recent quantum chemical calculations by Muckerman and co-workers have proposed $\text{Ti}_8\text{C}_{12}$ to be an exciting new nano-catalyst for hydrodesulfurisation (*i.e.* the removal of sulfur from hydrocarbon fuels). Specifically they found, compared to the industrial catalysts, that for the hydrodesulfurisation of thiophene on $\text{Ti}_8\text{C}_{12}$ the hydrogen dissociation and carbon-sulfur bond cleavage are more facile and the removal of sulfur is energetically comparable. However, previous calculations for
thiophene adsorption on Mo₈C₁₂ showed that it does not lead to spontaneous carbon-sulfur bond cleavage, as a result of the steric repulsion between the C₂ units and thiophene overcoming the high reactivity of the molybdenum atoms. These two studies demonstrate that the properties of a metal-carbide cluster can significantly change according to its transition metal composition and also that C₂ units can influence their reactivity. Furthermore, this highlights the potential application of metal-carbide clusters as efficient nanocatalysts, by tailoring their composition for specific purposes.

Hydrogen storage has recently become the subject of intense investigation due to hydrogen being a suitable clean fuel. Reversible dihydrogen adsorption near standard conditions is essential for a material to be suitable for hydrogen storage (i.e. $E_{\text{binding}} = 0.2–0.6$ eV/H₂), as well as a high weight-percentage of hydrogen adsorption. Computational work by Zhao and co-workers has shown that the Ti₈C₁₂ Metcar and Ti₁₄C₁₃ nanocrystal are potential candidates for hydrogen storage, as they are quite reasonable at meeting both these conditions. The titanium atoms coordinate multiple dihydrogen ligands, with the total capacity of dihydrogen molecules being 17 for Ti₈C₁₂ and 34 for Ti₁₄C₁₃. More than 80% of the dihydrogen molecules are bound in the energy range between 0.17–0.89 eV/H₂.
1.4 Scope of this Thesis

The main body of this thesis is concerned with the determination of the structures for small metal-carbide clusters through a combined experimental and computational approach. Small metal-carbide clusters in this size range (three to five metal atoms) have not been extensively studied, with several species having unknown structures. This thesis can be considered to be divided into three major sections.

The first section of this thesis (Chapter 4) describes the construction of a time-of-flight mass-spectrometer (TOF-MS) which, in conjunction with the laser ablation cluster source, has the desired properties of generating a sufficient amount and a stable distribution of neutral gas-phase metal-carbide clusters, in addition to a satisfactory mass resolution to separate the clusters.

The second section of this thesis (Chapters 5 and 6) involves the determination of experimental ionisation potentials (IPs) by photo-ionisation efficiency (PIE) experiments for Group 5 transition metal-carbide clusters. Clusters which contain three to five niobium or tantalum atoms are examined; \( M_xC_y \), where \( M = \text{Nb/Ta} \) and \( x = 3-5 \). Coupled with this experimental investigation, the lowest energy isomers of the metal-carbide clusters are calculated using density functional theory (DFT). Where there is agreement between the experimental IP and calculated IP of the lowest energy, or a low-lying, isomer for a metal-carbide cluster, the carrier of the ionisation onset is assigned.

The third section of this thesis (Chapter 7) involves the development of a double laser ablation cluster source to generate bimetallic-carbide clusters of suitable composition for experimental investigation. PIE experiments are conducted to determine the IPs of tantalum-zirconium-carbide clusters which contain three tantalum atoms and one zirconium atom; \( \text{Ta}_3\text{ZrC}_y \). The lowest energy isomers of the bimetallic-carbide clusters are calculated using DFT. Again, where there is agreement between the experimental IP and calculated IP of the lowest energy, or a low-lying, isomer for a bimetallic-carbide cluster, the carrier of the ionisation onset is assigned.
Chapter 1: Introduction to Metal-Carbide Clusters

1.5 Why Determine the Ionisation Potentials of Metal-Carbide Clusters?

Metal-carbide clusters have so far only been generated in the gas-phase at low densities and as such may only be investigated with certain spectroscopic techniques. However, metal-carbide clusters resist study with traditional spectroscopic techniques such as REMPI or laser induced fluorescence. A dense manifold of electronic states are found for systems containing multiple transition metal atoms with partially filled d-orbitals. This creates a near continuous absorption of light for these clusters, which is unstructured so that practical information can not be extracted. Furthermore, vibrational information is also difficult to obtain due to the heavy metal atoms causing metal-carbide clusters to possess low energy vibrational modes, which are often not accessible with conventional laboratory laser systems. This creates a dense vibronic manifold which, coupled with the dense electronic manifold, efficiently deactivates excited electronic states by non-radiative pathways, thereby inhibiting fluorescence.

However, spectroscopic experiments which determine the IP or EA (Electron Affinity) are relatively simple to implement for metal-carbide clusters, as they can be performed without the need of excited electronic states. Indeed IPs and EAs have been the two most readily determined physical properties of bare transition metal clusters. However, only a limited number of studies have determined the IPs of transition metal clusters with main group atoms attached. The previous IP studies on metal-carbide clusters have only been applied to certain species rather than a systematic survey, which is applied in this thesis.

The IP of a molecule is one of its most important fundamental physical properties. Not only do IPs give insight into the electronic structure of molecules but are directly relevant to chemical behaviour, since they are a measure of a molecules ability to donate electrons in a chemical reaction. They are also beneficial in experiments which ultimately detect the molecule as a cation, such as in mass spectrometry.

In this study, determination of the experimental IPs of metal-carbide clusters is also extremely beneficial in providing a physical property for comparison to computational
investigations. Since different structural isomers of a metal-carbide cluster species will generally have different IPs, determination of the experimental IP helps to guide the search for the lowest energy isomer by either including or excluding potential candidates. Knowledge of the structures of small metal-carbide clusters is important in understanding their potential applications and the growth patterns towards larger clusters. Furthermore, the availability of this experimental data may help to refine the computational theory, so as to accurately predict physical and chemical properties of transition metal containing clusters.
1.6 References

Chapter 2: Experimental Approach

2.1 Laser Ablation

2.1.1 Laser Ablation Theory

Early attempts to generate bare transition metal clusters in the gas-phase were not a straightforward process. In the condensed-phase they are influenced by stabilising ligands and solvent effects. Supersonic beams of alkali metal clusters have been prepared by heating the entire nozzle and source above the boiling point of the metal.\(^1\)\(^2\) However, this technique is difficult to apply to transition metal clusters due to their high boiling points. Also, spectroscopic investigation is hampered due to the high internal energies caused by the extreme temperatures.

Smalley and co-workers re-invigorated this field with the development of the laser ablation source in 1981.\(^3\) Laser ablation involves the laser vaporisation of a metal target, by a focussed laser pulse, coupled with a supersonic expansion to produce internally cold gas-phase metal clusters for spectroscopic examination. The laser pulse deposits sufficient energy into the metal surface to liberate hot gas-phase metal atoms, cations, anion and electrons, creating a plasma. The temperature of the plasma is estimated to be as high as 10 000 K.\(^4\) Not only did they demonstrate the ability to generate bare metal clusters, but also metal-ligand clusters by seeding the carrier gas.

In a laser ablation cluster source the metal is most commonly used in the form of a rod or disc, which is slowly rotated so that a fresh metal surface is always being ablated. Metal rods are held in an “ablation cap”, which tightly contains the rod, while also allowing it to rotate freely. Above to the rod’s surface to be ablated is a small aperture, with its size just large enough to allow the focussed ablation laser beam through. A straight gas channel, which runs across the entire ablation cap, also passes across the face of the ablated section of rod. A pulsed nozzle is connected at one end of the channel, which directs the carrier gas pulse over the ablated area of the rod. The carrier gas is usually an inert noble gas such as helium. The firing of the ablation laser is timed to occur on the leading edge of the rising gas pulse, which entrains the
plasma. The gas channel can then either immediately terminate into the vacuum or direct the gas pulse into a condensation tube.

A condensation tube is simply another channel. The use of a condensation tube is preferred, as when the gas pulse travels down the narrow channel, collisions between the ablated products instigate cluster growth, while collisions between the clusters and the inert carrier gas bring the clusters to thermal equilibrium. For clusters which have high binding energies, considerable internal energy is deposited during their formation by condensation reactions, so that numerous further collisions with the carrier gas are needed to relax the clusters. However, a sufficiently long condensation tube should achieve quenching of this “condensation energy”. The length and shape of the condensation tube can be adjusted to maximise generation of specific cluster sizes, with larger clusters generally produced using longer condensation tubes. The condensation tube then terminates, with the carrier gas containing the generated clusters exiting into vacuum by a supersonic expansion.

The use of a condensation tube is critical for the growth of clusters yet the limitation of its use is a decrease in the effective backing pressure of the carrier gas before the supersonic expansion into the vacuum. As a result the efficiency of the expansion to cool the clusters’ internal rotational and vibrational energies is reduced compared to a traditional expansion. It is believed that rotational cooling is received, as transition metal dimers have been found to be rotationally cold. However, it has been demonstrated by examination of the time-resolved thermionic emission of small niobium clusters that if the condensation tube is sufficiently long the vibrational temperature of the clusters in the expansion is given by the temperature of the condensation tube.

Another effect of the decreased effective backing pressure is the incomplete equilibrium of the relative velocities in the expansion. This effect is referred to as “velocity slip” and causes the lighter clusters in the expansion to obtain higher velocities than the heavier clusters. Velocity slip has been beneficial for pulsed field ionisation zero electron kinetic energy (PFI-ZEKE) photoelectron spectroscopy studies of metal and metal-ligand clusters, so as to ensure the origin of the electron signal.
In regards to generating metal-carbide clusters, these types of clusters have been generated by either seeding the carrier gas with a suitable hydrocarbon \(^4,8-10\) or the ablation of a metal-carbide target.\(^8-10\) The relative hydrocarbon concentration can have a significant effect on the metal-carbide cluster distribution,\(^11\) yet the nature of the hydrocarbon has been shown to have only a slight effect.\(^4\) This latter point, coupled with the observation that metal-carbide clusters with hydrogen atoms attached are absent, can be attributed to complicated processes occurring in the laser induced plasma. It is believed that through collisions with hot metal atoms and clusters the hydrocarbons gain sufficient energy to enable them to lose all their hydrogens and become either naked carbon atoms or small carbon clusters, which in turn react with thermalised metal atoms and clusters.\(^4\) The ability to produce large carbon clusters, in addition to metal-carbide clusters, is evidence for the process of hydrocarbon dissociation occurring in the ablation source.\(^12\) However, one must not discount the properties of the specific metal in the plasma. It has been proposed that highly reactive metals can assist a series of insertion and elimination steps in the hydrocarbons, which eventually results in efficient metal-carbide formation and virtually no residual hydrogen.\(^9\) Reactions of cold pre-formed neutral niobium clusters with various hydrocarbons have exhibited extensive dehydrogenation.\(^13-15\) This is consistent with the observation that the reactive early transition metals can generate metal-carbide clusters by the seeding technique, while the less reactive later transition metals require the ablation of a metal-carbide target.\(^9\)

### 2.1.2 Experimental Design and Operation

The metal-carbide clusters are generated in a home-built laser ablation source, shown in Figure 2-1. The ablation source consists of an ablation cap, condensation tube, pulsed nozzle and a screw mechanism motor.

The important features of the stainless steel ablation cap are a rod channel, gas channel and ablation aperture. The rod channel is designed to hold a 5 mm diameter rod, with enough clearance for the rod to be simultaneously translated and rotated by a screw mechanism motor (Oriel Motor Mike 18014). Perpendicular to the rod channel
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is the gas channel of 2 mm diameter, which passes straight through the ablation cap and also partially overlaps with the edge of the rod channel. Above this overlap area is the ablation aperture, which has a diameter of ~0.4 mm at the point of access to the rod and gas channels. At one end of the gas channel the output of a pulsed nozzle (General Valve, series 9, 500 µm orifice) is attached. At the other end a brass condensation tube connects to the ablation cap and serves to extend the gas channel. It is 2 mm in diameter and has a length of 15 mm.

Figure 2-1: Laser ablation source used to generate metal-carbide clusters. Dimensions given mm.

The rod is attached by rubber tubing to the screw mechanism motor, which is held just below the ablation cap. A lever protruding from the motor, which moves in the direction of the rod’s translation, reverses the translational and rotational direction of the rod by triggering a pair of limit switches. The length of rod typically ablated is 15 mm.

To make the ablation source suitable to be located in high vacuum, it is built off a conflat flange, which is attached to the source chamber of the TOF-MS (see Section 4.1). The flange has a central hole which has a hollow brass cylinder, attached by an
Chapter 2: Experimental Approach

o-ring seal, extending from it. The flange also contains electrical feed-throughs, which connects the screw mechanism motor and limit switches to the motor control box, located externally.

The end of the extension cylinder is designed to seat the body of the pulsed nozzle inside the hollow cavity of the cylinder, while enabling the back of the nozzle’s face plate to lie against the flat end surface of the cylinder. Situated immediately behind the nozzle faceplate is a groove containing an o-ring. An insert is then placed on top the flat end surface of the cylinder, with the former having a central hole fitted to the size of the nozzle faceplate. The thickness of this insert is equal to that of the faceplate, so as to create a flat surface which contains the output of the pulsed nozzle. The ablation cap is then attached to this flat surface, with its gas channel centred on the output of the pulsed nozzle. The insert also has attached to it the screw mechanism motor and the limit switch assembly.

Metal-carbide clusters are generated by ablation of the appropriate metal rod (niobium, tantalum and zirconium rods sourced from Goodfellow at 99.5% purity). A helium carrier gas (CIG, 99.98% purity) seeded with ~ 0.02% acetylene (BOC, 99.0% purity) is prepared in a gas manifold. The carrier gas is fed to the pulsed nozzle from the gas manifold with a backing pressure of ~ 80 psi. The gas pulse width is typically ~ 150 µs, controlled by a home-built nozzle driver. Laser ablation is performed with the 532 nm output of a Nd:YAG laser (Big Sky Laser, ULTRA-CFR) running at 10 Hz. The ablation laser is focussed through the ablation aperture with a 30 cm focal length lens, with the focal point at the surface of the metal rod. The ablation laser power used is 5–6 mJ per pulse, measured with a pyrometer (Ophir PE10BB head). The peak laser ablation power at the rod’s surface is estimated to be ~ 0.8 GWcm⁻².
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2.2 Photo-ionisation Efficiency (PIE)

2.2.1 Photo-ionisation Theory

One of the most important measurable physical properties of a molecule is its IP. The IP is defined as the minimum energy required to remove an electron from an atom or molecule. The ionisation process requires a substantial amount of energy and IPs are usually given in units of electron volts (eV). \[ 1 \text{ eV} = 8065.5 \text{ cm}^{-1} = 96.485 \text{ kJ mol}^{-1} = 23.061 \text{ kcal mol}^{-1}. \]

As the molecular orbitals (MOs) of a molecule increase in energy, there eventually becomes a point where an electron residing in these high energy MOs is at quite a distance from the ionic core and tends to “see” it as a concentrated point charge. As a result the excited electron and ionic core can take on the general aspects of the interaction between the proton and the electron in the hydrogen atom. Moons of this type are called Rydberg states. As the Rydberg states continue to increase in energy their spacing gets closer and closer together, until the changes are negligible. When an electron is given enough energy to take it beyond any of the molecule’s bound Rydberg states and escape the binding force of the molecular ionic core, the molecule is said to be ionised. Therefore, the Rydberg series converges to the IP.

Ionisation can still be considered as an electronic transition, as it is a transition between the potential energy surfaces (PES) of the initial neutral and final cation states; i.e. as the photon energy increases above the IP, transitions can occur to vibrational and electronic states of the cation. Photo-ionisation can take place at any photon energy above the IP, not just when it is resonant with a cationic state. The difference between the photon energy and the energy of the accessible cationic states (lower in energy than the photon energy) will be transferred into kinetic energy. Essentially all the kinetic energy will be taken away by the electron as it is substantial lighter than the molecule.

The probability of an electronic transition occurring is proportional to the square of the transition dipole moment. If we consider the electronic and vibrational
wavefunction to be separable (i.e. the Born-Oppenheimer principle) and that an electron in a transition moves between electronic states so rapidly that the nuclear positions are virtually unchanged (i.e. the Frank-Condon (FC) principle), the transition dipole moment for an electronic transition can be written as:\(^1^4\)

\[
M = \int \Psi_i^\prime \hat{\mu} \Psi_i d\tau_s \int \Psi_f^\prime \Psi_f d\tau_s \int \Psi_i^\prime \Psi_i d\tau_n
\]

where:

- \(M\) is the transition dipole moment.
- \(\Psi_i\) and \(\Psi_i^\prime\) are the electronic wavefunctions of the initial and final states, respectively.
- \(\Psi_f\) and \(\Psi_f^\prime\) are the spin wavefunctions of the initial and final states, respectively.
- \(\Psi_s\) and \(\Psi_s^\prime\) are the vibrational wavefunctions of the initial and final states, respectively.
- \(\hat{\mu}\) is the dipole moment operator.

There are three components to consider; two which depend on the electrons coordinates and one which depends on the nuclear coordinates. The first integral is the basis of electronic orbital selection rules and the second integral is the basis of electronic spin selection rules. The third integral represents the overlap of vibrational wavefunctions for the final and initial electronic states and its square is called the FC factor. If any of the integrals are zero, the transition is considered “forbidden”.

The orbital selection rules relating to changes in orbital angular momentum can be neglected for photo-ionisation as transitions to all states of the cation are allowed.\(^1^3\) This is because the ionised electron can depart possessing any amount of angular momentum required for its conservation. In this case the final state electronic wavefunction involves terms for the molecular ion and the ejected electron.\(^1^5\)
During the photo-ionisation transition the molecule’s electrons do not change their spin. However, as one electron is now lost the spin selection rule for ionisation is:

\[ \Delta S = \pm \frac{1}{2} \]

where: \( S \) is the total spin of the molecule.

The FC factor is necessary as the equilibrium geometries of the final and initial electronic states may be quite different. This means that the ionisation transition will only be able to access portions of the cationic PES which have geometries close to that of the initial neutral state. Therefore, the most probable transition will be to the vibronic level in the cationic state which involves as little change from the initial position and momentum of the nuclei in the neutral state. Yet this will not be the only transition that occurs as the molecule is not stationary in the initial state equilibrium geometry, due to zero-point vibrational motion.

\[ \text{Figure 2-2: Schematic displaying the difference between the adiabatic and vertical IPs.} \]
When describing the IP of a molecule, there are two terms that are used: the adiabatic IP and the vertical IP (Figure 2-2). The adiabatic IP corresponds to the transition from the ground state of the neutral to the ground state of the cation, where the term ground state indicates that the molecule is in its lowest electronic, vibration and rotational level. The vertical IP corresponds to the most probable transition from the ground state of the neutral to the cation. The vertical ionisation process is a consequence of the FC principle. Therefore, the vertical IP must always be greater than or equal to the adiabatic IP.

There are essentially three types of photo-ionisation techniques possible: single-photon ionisation (SPI), multi-photon ionisation (MPI) and resonance enhanced multi-photon ionisation (REMPI). SPI is simply the process of ionisation occurring by the absorption of a single photon of energy equal to, or greater than, the IP. For MPI and REMPI, however, the photon energies used are less than the IP.

For MPI, the first absorbed photon excites the molecule to a so-called “virtual” intermediate state. A further photon can be absorbed from this virtual state. If the combined energy of the two photons is equal to, or greater than, the IP, the molecule will be ionised. If not, a new virtual state is created and the process can repeat itself until ionisation occurs. The photons can be considered to be absorbed simultaneously due to the extremely short lifetime of the virtual state ($\sim 10^{-15}$ s). The photon fluence required for MPI can be achieved using pulsed lasers.

REMPI is a special case of MPI where the molecule is excited via a resonant intermediate electronic state. The excited electronic state has a well-defined lifetime from which absorption of a second photon with sufficient energy will ionise the molecule. REMPI is a substantially more probable process than MPI, involving the same number of photons, because there can be a substantially greater time difference between the separately absorbed photons.

For non-resonant MPI, the relationship between ion current and photon fluence can be described by equation:

$$ion\ current \propto (photon\ fluence)^N$$
where: \( N \) is the number of photons required to achieve ionisation
and is an integer.

Therefore, it can be seen that for SPI the ion current will be linearly dependant to
photon fluence, while MPI will show higher order dependence.

### 2.2.2 PIE Theory

Photo-ionisation efficiency (PIE) experiments are performed to determine the IP of a
molecule. This technique involves irradiating the species with photons from a laser,
whose energies are scanned in the vicinity of the IPs. The experiment is designed to
detect the species as cations once they are ionised, usually done in conjunction with a
TOF-MS. Therefore, as the photon energy is scanned there will be an increase in the
ion current of a species once the photons have an energy equal to, or greater than, its
IP.

As MPI can occur at any photon energy below the IP, PIE experiments are performed
under photon fluences where SPI is by far the dominant ionisation process. Therefore,
theoretically, ion current will only be observed for a species once the photon energy is
equal to or greater than the IP.

A PIE spectrum is obtained by plotting the ratio of a cluster’s ion current to photon
fluence against photon energy. The ion current collected must be normalised to the
fluence at each photon energy used, as a greater fluence will result in greater ion
current. Under SPI conditions the ion current is linearly proportional to photon
fluence, so normalisation can be simply performed by dividing the ion current by the
 photon fluence. From herein the ion current normalised to photon fluence will be
referred to as the “ion signal”.

The shapes of PIE spectra are primarily influenced by the difference between the
equilibrium geometries of the neutral and cation, with the relative vibrational
frequencies affecting them to a much lesser extent.\(^\text{16}\) For a particular cationic
vibrational mode to have a tendency for FC overlap upon ionisation, the motion of the vibration should be similar to the motion related to the geometry change between the neutral and cation equilibrium geometries. If there is a substantial geometry change in the direction of the normal co-ordinates for only one mode, then only this mode will show any significant FC activity for the ionisation transition. When this is the case, assuming independence of the vibrational modes, it is helpful to consider the polyatomic molecule’s ionisation process as occurring between two one-dimensional PES.

If there are negligible equilibrium geometry differences between the neutral and cation, the FC factor will be greatest for ionisation to the ground vibronic state of the cation. FC factors for transitions to higher cationic vibrational states rapidly drop after the ground vibronic state, as the wavefunctions of the former have both negative and positive contributions which yield smaller integrations. The PIE spectrum in this case will exhibit a very strong sharp rise in ion signal once the photon energy is equal to the transition to the ground vibronic state of the cation. The ion signal will continue at the same level until the next FC allowed transition is reached, resulting in a small increase in the ion signal. Quite quickly, transitions to higher vibrational states of the cation become negligible and the ion signal will remain constant with increasing photon energy.

If we now consider the case where there is an intermediate change in molecular equilibrium geometry upon ionisation, the transition to the ground vibronic state of the cation will no longer have the largest FC factor. The FC factors for transitions will increase as the cationic vibrational levels increase, until the transition with the maximum FC factor is reached. After this state the FC factors will decrease until the FC factors for further vibrational states are zero. The PIE spectrum in this case will display a step-like function for the ion signal with increasing photon energy. Hence, the most FC favoured transition will result in the largest increase in ion signal. If the difference in equilibrium geometry between the neutral and cation is significantly large, it is possible that the ground vibronic state of the cation cannot be accessed.

Excited vibrational levels may be populated in the neutral state. As transition from these levels may have FC allowed transitions to the ground vibronic state of the
cation, it is possible that ionisation can occur at photon energies lower than the adiabatic IP. Again there will be increases in the ion signal for each FC allowed transition, yet now the increase is not only proportional to the FC factor, but also to the relative population of the initial (neutral) vibrational state.

The interpretation of PIE spectra to unambiguously assign the adiabatic or vertical IP is far from straightforward. A method proposed by Watanabe derives the adiabatic IP from the first deviation from linearity, with increasing photon energy, of the logarithm of the ion signal.\textsuperscript{17} This procedure assumes that the thermal tails in the ionisation threshold region have true exponential behaviour. Another method, which is the most commonly used, is the linearisation procedure.\textsuperscript{16} In this procedure the adiabatic IP is determined by the intersection of two lines fitted by linear regression; one to the initial linear rise of the ion signal and one to the baseline ion signal.

The vertical IP can be assigned by use of the displaced harmonic oscillators model. This model assumes that the neutral and cation can be described by harmonic potentials with the same vibrational frequencies and that photo-ionisation is a step-like function.\textsuperscript{18} The vertical IP is therefore assigned to the point of maximum increase in ion signal; \textit{i.e.} the maximum of the first derivative of the ion signal against photon energy.

### 2.2.3 PIE of Transition Metal Containing Clusters

PIE experiments on clusters containing multiple open $d$-shell transition metal atoms are problematic, as the dense electronic manifolds cause the clusters to suffer from a propensity for MPI/REMPI. Indeed large optical cross sections have been measured for small niobium clusters, by photo-depletion of their rare gas van der Waals complexes, which were found to be continuous above 2 eV and generally increased with photon energy.\textsuperscript{19,20} Knickelbein and co-workers observed departure from linear ion current dependence for Ni$_4$, at photon energies above the IP, to occur at photon fluences greater than 750 $\mu$Jcm$^{-2}$.\textsuperscript{21} They recommended that PIE experiments of metal clusters be performed at photon fluences of 400 $\mu$Jcm$^{-2}$ or less, so that MPI is negligible.
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The shapes of PIE spectra for metal-carbide clusters will be complicated by transitions occurring from populated excited neutral state levels, fragmentation of larger clusters and the presence of isomers.

The internal energy of the clusters is reduced due to the cooling received in a supersonic expansion. However, as the metal-carbide clusters may possess high internal energies in the cluster source (due to incomplete quenching of their condensation energy), they will still possess a finite amount of internal energy after this cooling.\(^{22}\) A metal-carbide cluster may also possess quite low energy vibrational modes, which can be populated at low vibrational temperatures. This effect causes non-zero ionisation below the IP with the PIE spectra to display thermal tails, which can be much larger than \(kT\) when the equilibrium geometry of the neutral and cation are significantly different.\(^1\)

Absorption of one or multiple photons with a combined energy greater than the cluster’s IP and the energy of the lowest cationic dissociation channel can lead to fragmentation. This fragmentation can produce an ion signal for a smaller cluster species despite the photon energy being below its IP. Cationic fragmentation can be minimised by using low photon fluences to avoid MPI and employing photon energies not substantially greater than the IP. Due to the dense electronic manifolds of metal-carbide clusters it is also possible that if a photon is absorbed of an energy below the IP, yet above the lowest dissociation channel energy, that coupling to the dissociation continuum will occur regardless of the initial excited state.\(^{23}\) However, dissociation of a neutral cluster is not expected to give rise to ionic fragments.

The occurrence of fragmentation can be difficult to predict when quite a large number of cluster species are present, as their IPs and cationic dissociation energies are rarely known. Armentrout and co-workers have measured the bond dissociation energies (via the neutral metal atom channel) of bare metal niobium and tantalum cluster cations containing up to 11 and 4 atoms, respectively.\(^{24}\) The dissociation energies exceeded 4.6 and 6.6 eV for the niobium and tantalum clusters, respectively. Several metal-carbide clusters have also been shown to exhibit thermionic emission, indicating that their dissociation energies are competitive with their ionisation
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energies.\textsuperscript{28-31} Calculations on cationic niobium-carbide clusters indicate binding energies per atom greater than 3 eV.\textsuperscript{25} Consequently, the photon energies employed in this study, under SPI conditions, are not expected to result in significant fragmentation after ionisation.

Certain cluster species may have several energetically favourable isomers. As different structural isomers will generally have different IPs, any isomer present at significant concentration in the experiment will contribute to the ion signal, once its IP is reached. As the threshold ionisation technique favours the detection of the isomer with the lowest IP, if the lowest energy isomer possesses the lowest IP, it may be difficult to distinguish the ionisation onset of other isomers in the PIE spectrum. However, in cases where a low-lying isomer possesses a lower IP, there may be evidence of separate onsets. Previous studies on niobium clusters have shown this double ionisation onset behaviour for Nb\textsubscript{9} and the presence of two isomers indicated by the ability to selectively titrate the more reactive isomer with D\textsubscript{2} and record the PIE spectrum of the unreactive isomer, which displays only a single onset.\textsuperscript{26}

The Watanabe method has been found to be unsuitable for extracting the adiabatic IP from PIE spectra of metal clusters, as their thermal tails do not display exponential behaviour due to MPI and fragmentation.\textsuperscript{21} Ablation cluster sources also suffer from signal fluctuations and therefore do not exhibit extremely high signal-to-noise ratios. Due to the extreme number of unknown variables in the photo-ionisation dynamics of metal containing clusters, the linearisation procedure is most commonly used as it is easily implemented and provides an internally consistent approach to reducing the data. The extracted IPs from this procedure are technically considered as being vertical, as it is unknown if the ground vibronic state of the cation can be accessed. However, in most cases the onsets of ionisation will be good approximations to the adiabatic IPs, due to minimal differences in the equilibrium geometries between the neutral and cation, especially for large clusters.
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2.2.4 Experimental Procedure for PIE Experiments

All PIE experiments are performed with the frequency-doubled output of a tunable dye laser (LAS GMBH LDL 2051) which is pumped by the 355 nm output of a Nd:YAG (Spectra-Physics GCR-10) running at 10 Hz. PIE experiments are performed in conjunction with a TOF-MS (see Section 4.1). The separation of the frequency-doubled output from the residual fundamental output is achieved with a system of four pellin-broca prisms. This arrangement also allows the wavelength of the dye laser to be scanned, while maintaining a constant beam direction for the frequency-doubled output.

The minimum ultraviolet wavelength achievable by frequency-doubling the fundamental output of the dye laser using a BBO crystal is 214 nm (5.79 eV). Laser light of wavelengths lower than 214 nm is generated by Stimulated Raman Scattering. Here the frequency-doubled output from the dye laser is passed through a Raman cell (RS-1 Quantel) containing 100 psi of hydrogen gas. The vibrational stretch frequency of hydrogen is Raman active, with the energy difference between the ground state and first vibrational state being $4161 \text{ cm}^{-1}$.\(^{27}\) The emerging beam is dispersed into the Rayleigh, Stokes and Anti-stokes lines by a pellin-broca prism, with the first Anti-stokes line selected for the PIE experiments with an iris. The frequency-doubled output of the dye laser or the Stimulated Raman Scattering Anti-stokes line will from herein be referred to as the “ionisation laser”. PIE experiments are conducted at wavelength step sizes of 0.2 nm. This corresponds to step sizes of ~ 0.005–0.003 eV in the wavelength region investigated (210–285 nm).

The ionisation laser beam is expanded by a factor of $\times 5$ and collimated by a telescope consisting of two lenses with focal lengths of 50 mm and 250 mm to enable the photon fluence to be low enough for MPI to be negligible, while also providing a large beam area to maximise ion signal. The central portion of the beam is selected with an adjustable iris of ~ 5 mm in diameter. The separation distance between the telescope lenses is adjusted according to the wavelength region being investigated, due to the wavelength dependence of the focal points.
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Large power fluctuations for the ionisation laser with wavelength hampered initial PIE experiments. These fluctuations arose from the natural variation in output power of the specific laser dye used and that the stepper motor used to tune the phase-matching angle of the doubling crystal did not track as calibrated, rather than pulse-to-pulse ionisation laser instability. Power fluctuations which range between SPI and MPI conditions cause MPI and fragmentation to contribute to the clusters’ ion current, which cannot be corrected for by laser power normalisation.

Contribution to a cluster’s ion signal from MPI and fragmentation can be almost totally eliminated and kept quite constant by attenuating the ionisation laser power at each wavelength to within a constant pre-determined level. This is achieved by a computer program written to incorporate the stepper motor of the doubling crystal, a pyrometer (Ophir PE10BB head), boxcar integrator (Stanford Research Systems SR250) and a digital oscilloscope (LeCroy 9350 AM, 500 MHz).

The pyrometer power meter (Ophir Nova II) is equipped with an oscilloscope adapter, which transmits a flat-top pulse proportional to the laser pulse energy. This flat-top output pulse is not linked directly to the oscilloscope as its rise time is on the order of ~3 ms. This is significantly longer than the μs flight times of the ions collected in the TOF-MS, so both signals could not be simultaneously displayed on the oscilloscope while maintaining the sufficiently high sample rate required for recording mass spectra. Therefore, the output from the power meter is first put into the boxcar integrator, with a small section of the flat top pulse integrated, with this value sent to the oscilloscope. As a result the laser power correlated with a mass spectrum trace from a single laser pulse is actually the laser power used to collect the previous trace. This effect is negligible as the pulse-to-pulse fluctuation of the ionisation laser is small and large averaging of traces at each wavelength minimises the relative amount of laser power pulses incorrectly included and excluded.

The relative timing of the pulsed nozzle, ablation and ionisation lasers is controlled by a digital delay generator (Griffith University, TARDIS II), which ensures pulse stability to within 1 ns. The molecular beam is overlapped perpendicularly with the ionisation laser, with its power measured by the pyrometer as it exits the TOF-MS.
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The optimum laser power required to gain sufficient ion signal while minimising MPI and fragmentation is determined to be ~ 50 µJ. The corresponding photon fluence (~250 µJcm\(^{-2}\)) is much lower than that recommended in other metal cluster PIE studies.\(^{21}\) The corresponding voltage delivered from the boxcar integrator to the oscilloscope for this laser power is set as the pre-determined laser power level for the PIE experiments.

The program for attenuating the laser power requires this pre-determined laser power level voltage and a polynomial function for the doubling crystal stepper motor position to achieve maximum frequency-doubling efficiency against laser wavelength. At each wavelength the program first positions the stepper motor 200 steps before the position for maximum doubling, as calculated from the polynomial. Usually there is only a very small amount of ionisation laser power at this motor position. The laser power level at this motor position is averaged for 10 laser pulses. If this averaged value is within ±7% of the pre-determined laser power level the motor will remain at its present position, collecting an averaged mass spectrum and laser power for 1000 pulses.

However, if the laser power value obtained is below the pre-determined range the motor will take further steps towards the motor position calculated for maximum frequency-doubling. The number of steps taken is scaled relative to the fraction of the current laser power value to the pre-determined level, so that a smaller amount of steps are taken as the motor position approaches the pre-determined level. The laser power is then again collected for 10 laser pulses. This routine is continued until the laser power value obtained is in the acceptable range. If at any point the laser power is greater than the pre-determined level by 7%, the motor will step backwards by 200 steps and start the routine again. Also, if the pre-determined range is not attained within 30 attempts, the mass spectrum is recorded at the last laser power level attained.

The summed mass spectrum, laser power and wavelength are then downloaded to a computer and stored, with the dye laser then moved to the next wavelength position.
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Large shot-to-shot signal fluctuations are characteristic of metal containing cluster species generated by laser ablation sources. This is primarily due to inhomogeneities in the surface of the ablated rod.\textsuperscript{28} To compensate for this fluctuation the time taken to average the mass spectrum at each wavelength corresponds to one complete translation/rotation cycle of the rod, \textit{i.e.} 100s. Therefore, the fluctuation of cluster signal as a function of different areas of the ablated rod will be reasonably constant at each wavelength data point.

Long term drift of the cluster signal can also occur. Our experimental setup does not allow this effect to be compensated for, but its occurrence can be detected. This is done by recording the laser power and several cluster species intensities from the mass spectrum collected for the first wavelength point. Immediately after the PIE scan is finished, the laser is returned to the starting wavelength with a mass spectrum recorded again. If the recorded cluster species intensities, relative to laser power, are sufficiently similar to those recorded initially, the cluster source’s long term drift is considered negligible and the scan is acceptable for analysis. PIE scans are always performed from shorter to longer wavelength, so that as many species as possible are ionised and their intensities recorded for monitoring long term drift.

Once a scan is completed it can be opened by a program to display the mass spectrum collected at each wavelength. The flight times, between which the area is integrated, can be set to a specific cluster peak. The program then integrates that area of the mass spectrum at each wavelength and creates a file containing columns for the wavelength, integrated area and laser power. The integrated area can then be normalised, by dividing by the laser power, to give the cluster’s ion signal at each wavelength.

The wavelength of the ionisation laser is then converted into units of energy. This is first done by converting the wavelength into vacuum wavenumbers. The ionisation laser energy is then corrected to the actual energy. This is determined by use of an opto-galvanic cell, which measures the dye lasers fundamental output. Also ionisation in an electric field (used to accelerate the ions in the TOF-MS) lowers the IP of cluster species. The photon energy is corrected for this effect by $6.1 \times (\text{Electric Field})^{1/2}$ (in
cm$^{-1}$, where $E$ is in Vcm$^{-1}$), recommended for ionisation in a residual static electric field. The totally corrected ionisation laser photon energy in vacuum wavenumbers is then converted into electron volts.

PIE spectra are then created by plotting the cluster ion signal against photon energy (in eV). As described previously, linear lines are fitted to the baseline signal and the sharp initial linear rise in ion signal, with the IP assigned to be the intersection of these two lines. The extracted IP is expected to be a good approximation to the cluster’s adiabatic IP. It is difficult to assign a statistical error associated with the linearisation procedure as it is subjective as to which data points are included in the linear rise. However, the general precision to which the IPs can be extracted is estimated to be $\pm 0.05$ eV.
2.3 References

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Chapter 3: Computational Approach

3.1 Introduction to Density Functional Theory (DFT)

The electronic energy of a non-linear molecule, with \(N\) number of atoms, as a function of the atoms’ relative co-ordinates can be described by a \(3N-6\) dimensional PES. Stable equilibrium structural isomers correspond to minima on the PES, where the potential energy increases in each dimension. Of the minima, the lowest in energy is referred to as the global minimum, with all others referred to as local minima. Two minima are connected via a first order saddle point. A first order saddle point has the potential energy increasing in all but one dimension and corresponds to the transition state geometry linking the two structural isomers.

Locating the global minimum and low-lying local minima is required for interpreting the experimental IP results obtained for the metal-carbide clusters. Therefore, a method is required to calculate the energy of a cluster as a function of its atoms’ relative co-ordinates. Here density functional theory (DFT) is utilised to calculate the energy, as it has been found to provide reasonably accurate results on the energetics and structures of molecules for a comparatively small amount of computational time.\(^1\) DFT is ideal for investigating metal-carbide clusters, which possess partially filled \(d\)-orbitals leading to inherently complicated electronic structures and several energetically favourable low-lying structural isomers due to the availability of multidirectional bonding.

The premise behind DFT is that the energy of a molecule can be determined from its electron density, rather than its wavefunction. This proposal was proved by Hohenberg and Kohn in their first theorem: given a ground state electron density and the density functional it is possible, in principle, to calculate all properties of the molecule, including the wavefunction.\(^2\)

The second theorem of Hohenberg and Kohn is very similar to the variational principle: the energy obtained from the density functional of a trial electron density
Chapter 3: Computational Approach

will be an upper bound to the true energy obtained from the density functional of the true ground state electron density. A functional is a function of a function; i.e. the energy is a function of the electron density, which is a function of three Cartesian coordinates. However, the exact form of the density functional is unknown.

Continuing work by Kohn and Sham separated the density functional into certain components as follows:


where:  
\( F_{KS}[\rho] \) is the Kohn-Sham functional.  
\( T[\rho] \) is the kinetic energy of the electrons.  
\( V_{NN} \) is the potential energy of the nuclear-nuclear repulsion.  
\( V_{NE}[\rho] \) is the potential energy of the nuclear-electron attraction.  
\( J[\rho] \) is the electron-electron repulsion energy.  
\( E_X[\rho] \) and \( E_C[\rho] \) are the exchange energy and correlation energy of the electron-electron interactions, respectively.

All the terms apart from \( V_{NN} \) are functions of the electron density. The three terms \( T[\rho] \), \( V_{NE}[\rho] \) and \( J[\rho] \) correspond to the classical energy of the electron density. The remaining two terms \( E_X[\rho] \) and \( E_C[\rho] \) essentially account for the Pauli Principle and that electrons correlated their movements so as not to be in the same place at the same time, respectively. Of major importance and investigation is the form of these two latter functionals.

The simplest approximation for the forms of \( E_X[\rho] \) and \( E_C[\rho] \) is based only on the electron density and called a local density approximation. To obtain more accurate results than this local approximation, complex functionals based on both the electron density and the gradient of the electron density, to account for the non-homogeneity of the true electron density, are utilised. These types of functionals are referred to as gradient-corrected functionals. There are also hybrid DFT methods that combine a mixture of DFT and Hartree Fock exchange.
3.2 Basis Sets

A basis set is a set of basis functions used to describe the shape and behaviour of the atomic orbitals (AOs) in an atom. In DFT a determinant is used to establish the electron density, from which the energy is computed. A determinant is formed from one-electron Kohn-Sham orbitals, which are in turn formed from the basis functions.

There are several basis functions available to describe an AO, with the slater type orbitals being the most accurate. However, the use of slater type orbitals are quite computationally exhaustive, with gaussian type orbitals (GTOs) employed instead, due to their computational convenience. Several combinations of GTOs are needed to properly describe the shape and behaviour of an AO. A basis set therefore assigns the number and type of GTOs to describe the AOs of an atom. The use of a single GTO is an unreasonable basis function to properly describe an AO. The first procedure to increase the accuracy of the description is to use several linear combinations of primitive GTOs to generate a single basis function. Such a basis function is referred to as being contracted.

Further improvement can be achieved by representing each AO with two or more basis functions of differing size. This allows the AO to adjust its size depending on the bonding it is involved in. For example a double zeta basis set has two different sized basis functions for each AO. Furthermore, as core electrons do not have a significant role in bonding, a split valence basis set describes the core AOs less accurately than the valence AOs. Upon bonding, AOs can distort from their idealised shapes. This effect is described by polarised basis sets, which allow flexibility in the AOs by adding polarisation basis functions with higher angular momentum beyond what is normally ascribed to these orbitals. To describe electrons which are far away from the nucleus, diffuse basis functions can also be included.

For molecules containing transition metals, which have a large number of electrons present, it is computationally unfeasible to include all electrons in the calculations. The core electrons are not significantly involved in bonding interactions, but shield the valence electrons from the nuclear charge. Therefore, effective core potentials
(ECPs) can be used, which incorporate the core electrons into the potential term of the nucleus. ECPs can also include relativistic effects.
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3.3 Computational Method and Procedure for Metal-Carbide Clusters

Several DFT methods exist, which include different combinations of an exchange functional and a correlation functional. The B3P86 method is employed in this study, which incorporates Beck’s three parameter hybrid exchange functional (B3) with the Perdew gradient-corrected 1986 correlation functional (P86).\(^4\,^5\) This DFT method is chosen to examine the metal-carbide clusters in this thesis, as Yang and co-workers found that of several examined DFT methods, B3P86 gave the best overall match to the experimental electronic, geometric and vibrational properties of the benchmark metal-carbide cluster \(\text{Nb}_3\text{C}_2\).\(^6\)

The SDD basis set is chosen as it is commonly used for transition metals, superseding the previously popular LANL2DZ basis set, with the former featuring a larger basis set contraction compared to the latter.\(^7\,^8\) The SDD basis set describes the transition metals’ core electrons (28 for zirconium and niobium and 60 for tantalum) with a Stuttgart-Dresden relativistic ECP.\(^7\) The remaining valence orbitals of the transition metal atoms and valance orbitals of the carbon atoms are described with a Dunning–Huzinaga valence double-zeta basis set (D95V).\(^9\)

For selected niobium-carbide cluster isomers, subsequent calculations were repeated using the Dunning correlation consistent polarised valence triple zeta basis set augmented with diffuse functions (aug-cc-pVTZ)\(^10\,^11\) on the carbon atoms in an effort to improve the treatment of these atoms, which is herein referred to as the "extended" basis set. The basis set for the transition metals remains unchanged for the extended basis set (i.e. SDD).

Geometry optimisation and harmonic vibrational frequency calculations are performed with the Gaussian 03 platform.\(^12\) A range of geometric isomers are located for each neutral metal-carbide cluster species at the two lowest spin multiplicities (i.e. singlet & triplet or doublet & quartet for species with an even or odd number of electrons, respectively) and are initially optimised using the SDD basis set. The relative energies of the isomers calculated by this DFT method are generally expected
to be accurate within ~ 0.5 eV. As a large number of isomers are possible for species containing multiple open d-shell transition metals, the starting geometries chosen for optimisation are generally based on certain structural motifs which have been shown to be energetically favourable for niobium-carbide clusters. Therefore, there is confidence in that the global minimum has been located. For the niobium-carbide cluster isomers, upon identifying all reasonably low-lying isomers (typically within 0.7 eV of the global minimum), subsequent calculations are repeated with the extended basis set. Selected isomers for the tantalum-carbide and tantalum-zirconium carbide clusters, based on the niobium-carbide cluster results, are only examined with the SDD basis set. For both basis sets, all isomers are initially optimised without any geometry constraint. The minimised isomers are then examined to determine any symmetry properties and the calculations are again repeated within the highest identified symmetry point group. The symmetry-constrained energy is subsequently compared to the unconstrained energy to ensure that there is no difference. All isomers are characterised with vibrational frequency calculations to determine whether the optimised structure is a true minimum. Similar geometric minima are also identified on the cationic surface for each isomer. For the niobium-carbide clusters, all reported energetics, ionisation potentials and molecular symmetries (inc. term symbols) are obtained with the extended basis set.

The adiabatic ionisation energies are calculated as the difference in energy between the lowest electronic state of the neutral and the lowest electronic state of the cation for the same isomer (which can be accessed following the selection rule for ionisation $\Delta S = \pm \frac{1}{2}$). Although ionisation energies excluding and including zero-point energies (ZPE) are presented, only the latter numbers will be considered for discussion.

The absolute accuracy of the calculated IPs are expected to be within ~ 1 eV of the experimental values. As will be shown, the calculated IPs of all the metal-carbide cluster isomers with the current computational method overestimate the experimental values. However, this study is concerned with the IP following sequential addition of carbon atoms to a bare metal cluster. It is anticipated that although the absolute calculated IPs are not accurate to the experimental IPs, the relative trends of both should be consistent if the calculated IPs are for those isomers for which the
experimental IPs have been recorded. Therefore, a linear offset is applied to the calculated IP values of the metal-carbide cluster isomers in each series, so that the calculated IP of the bare metal cluster overlaps with its experimental value. This offset calculated IP will be herein referred to as the “IP†”.

It is unknown if this applied offset, derived from the bare metal clusters, is the most suitable offset for the metal-carbide clusters, due to the different nature of bonding between these systems. A point in favour of the similar offsets for the two types of clusters is that the HOMOs of selected niobium-carbide clusters have been found to be primarily metallic in character. Therefore, providing the IP offset is applied to the correct isomer of the bare metal cluster present in our experiment, the current scaling procedure is considered to be reasonable. Many of the bare metal clusters in this study have extensive experimental evidence supporting their calculated global minimum structures, unlike the metal-carbide clusters. As will be seen, the experimental IPs of Nb$_3$C$_2$, Nb$_4$C$_4$ and Nb$_5$C$_3$ show excellent agreement with the IP†’s calculated for the structural isomers based on the available experimental structural data. Furthermore, the overall good agreement between the calculated IP†’s and the experimental values in each cluster series, despite different offsets being applied, indicates that the IP overestimation from this computational method is related to the type and number of metal atoms present.

All presented geometries of the metal-carbide cluster isomers have bonds drawn between the metal atoms if their distance is less than, or equal to, the covalent radius of the two metal atom combined; i.e. Nb-Nb ≤ 2.74 Å, Ta-Ta ≤ 2.76 Å and Ta-Zr ≤ 2.86 Å, respectively. Metal-carbon bonds are drawn at bond lengths less than or equal to 2.35 Å. This distance is longer than the covalent radius of the metal atom and carbon atom combined (2.14–2.25 Å) to signify the importance of metal-carbon bonding and back-bonding effects for isomers with carbon moiety units. Carbon-carbon bonds are drawn as follows; 1.60 Å > single bond > 1.40 Å > double bond > 1.25 Å > triple bond. Atomic charges are also determined by Natural Bond Order (NBO) calculations (NBO version 3). Illustrative representations of MOs are generated with the cubegen utility in Gaussian 03, with the iso-surface set to 0.05 electronsÅ$^{-3}$. 
3.4 References

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Chapter 4: The Time-of-Flight Mass-Spectrometer

The proposed PIE experiments of metal-carbide clusters need to be conducted in conjunction with a TOF-MS, which enables the ionised clusters to be separated from each other according to mass. Theoretical principles of time-of-flight mass spectrometry can be found in several reviews.\textsuperscript{1,2}

Before PIE experiments could be conducted, the operational features of the TOF-MS such as sufficient and stable generation of the neutral metal-carbide clusters and satisfactory mass resolution of the ionised clusters need to be acceptable. Since the original TOF-MS (shown in Appendix I) was not able to meet these criteria, a new TOF-MS was designed and constructed, utilising the original TOF-MS materials as well as incorporating newly constructed materials.

4.1 The Constructed TOF-MS Apparatus

The constructed TOF-MS apparatus is shown in Figure 4-1. The TOF-MS consists of a source chamber (one six-way cross) and a flight/detection chamber (one six-way cross, two T-pieces and one extension nipple). The source chamber contains the laser ablation cluster source, while the flight/detection chamber contains the ion acceleration assembly, ion optics assembly, field-free drift region and ion detector.

Each chamber is pumped by a 6-inch diffusion pump (Varian VHS-6), used in conjunction with liquid nitrogen condensation traps. Both diffusion pumps are backed by rotary pumps (Welch 1397). The chambers are differentially pumped, as a sandwich flange containing a home-made skimmer (3 mm diameter) is inserted between the source and flight/detection chambers. Background pressures of \(\sim 1 \times 10^{-7}\) torr are achieved in both chambers, measured by separate ion gauges (Dunniway T100K) contained in each chamber.
Figure 4-1: The constructed TOF-MS used to conduct PIE experiments, shown in the (a) side-on and (b) isometric orientation.
Chapter 4: The Time-of-Flight Mass-Spectrometer

The source chamber contains the laser ablation cluster source, which is mounted off the end flange (see Section 2.1.2). The side flanges on the source chamber have window ports, which the ablation laser is focussed through to access the cluster source. The clusters generated in the cluster source exit from the condensation tube by a supersonic expansion, with the central region of this expansion selected by the skimmer, located 15 cm away, creating a molecular beam which then passes into the flight/detection chamber. The operational pressures in the source and flight/detection chambers are typically $4 \times 10^{-5}$ and $3 \times 10^{-6}$ torr, respectively.

One of the deficiencies of the original TOF-MS was that it was not differentially pumped. Having differentially pumped source and flight/detection chambers allows a greater amount of carrier gas can be introduced, while maintaining a low pressure in the flight/detection chamber so that the ion detector can be operated at optimum conditions. Increasing the quantity of carrier gas increases the number of collisions in the condensation tube, enabling a greater number of condensation reactions between the ablated products to take place and for the generated clusters from these reactions to be collisionally cooled. Having a differentially pumped TOF-MS was found to be critical in generating metal-carbide clusters containing both multiple metal and carbon atoms.

The six-way cross of the flight/detection chamber contains the ion acceleration assembly and ion optics assembly, with both suspended from a sandwich flange attached on top of the six-way cross. The ion acceleration assembly consists of a Wiley-McLaren three electrode acceleration stack, which accelerates the ionised clusters towards the ion detector. The electrodes are circular aluminium plates, each 7 cm in diameter and 2 mm in width. The three electrodes are labelled (from bottom to top) “the repeller”, “the extractor” and “the ground” electrodes. The repeller and extractor electrodes are held at high positive voltages; 2.60 and 2.12 kV, respectively. The ground electrode is held at ground potential. The electrodes are arranged to have spacings of 25 mm between the repeller and extractor, and 20 mm between the extractor and ground.
Chapter 4: The Time-of-Flight Mass-Spectrometer

Neutral clusters in the molecular beam which enter the middle region between the repeller and extractor electrodes are ionised by the ionisation laser, which enters and exits through window ports on the side flanges of the six-way cross. The repeller and extractor electrodes also serve to remove any nascent cluster ions in the molecular beam from entering this region. The laser ionised clusters are then accelerated towards the field-free drift region by the two electric fields; one between the repeller and extractor electrodes and the other between the extractor and ground electrodes. The extractor and ground electrodes each have a 15 mm hole in their centre, with nickel mesh attached over these holes to create a homogeneous electric field, while also allowing high ion transmission.

The ion extraction regime is perpendicular; i.e. the ionised clusters are accelerated in a direction which is perpendicular to the direction the clusters travel in the molecular beam. A perpendicular ion extraction regime is advantageous over a linear regime, which was the configuration of the original TOF-MS. Clusters of equal mass ionised at the same point and time, but with different initial velocities will have different final velocities after acceleration, leading to a spread in their arrival times at the ion detector and hence a decrease in mass resolution. The initial velocities of the clusters are vastly reduced by the use of a supersonic expansion in combination with a skimmer to generate a molecular beam, which has a very narrow velocity distribution and unidirectional movement. However, a perpendicular ion extraction regime enables the initial velocity distribution to be reduced even further, as in the molecular beam there is a minimal initial velocity component in the axis of acceleration. The disadvantage of perpendicular extraction is that it creates a “mass window” effect, where the heavier clusters initial velocities perpendicular to the ion extraction will displace them during their longer flight times, so as they may not reach the ion detector.

Before the ions travel from the ion acceleration assembly into the field-free drift region they pass through the ion optics assembly, which is attached to a plate (held at ground potential) 10 mm above the ground electrode. The ion optics assembly consists of an einzel lens (10 mm internal diameter) and vertical and horizontal deflectors, which are used to focus and steer the ion packet accelerated from the ion acceleration assembly into the field-free drift region and towards the ion detector. As
the lighter clusters are accelerated to higher velocities than the heavier clusters, the lighter ions will travel the field-free drift region and reach the ion detector in a shorter time than the heavier ions. As the flight time of a cluster ion is proportional to the square root of its mass, this effectively separates the clusters according to mass (for singly charged ions).

The total distance between laser ionisation and the ion detector is \(\sim 100\) cm. The front plate of the dual micro-channel plate ion detector (El Mul MCP-M585) is typically held at \(-800\) V, the second plate at \(-500\) V and the collection plate (anode) at ground. A nickel mesh at ground potential is placed in front of the ion detector to preventing stray electric fields entering the field-free drift region. The output current from the ion detector is then amplified \(125\times\) fold (\(5\times5\times5\)) by a pre-amplifier (Stanford Research SR250) before being displayed on a digital oscilloscope (LeCroy Model 9350AM, 500 MHz). The signal on the oscilloscope is then downloaded to a computer for further analysis.

As will be shown in chapters 5–7, the constructed TOF-MS apparatus was able to generate sufficient and stable neutral metal-carbide cluster signal, in addition to satisfactory mass resolution, for PIE experiments to be conducted.
4.2 References


Chapter 5: Niobium-Carbide Clusters

The following two chapters (5 and 6) are concerned with the determination of the structures of neutral metal-carbide clusters for the group 5 transition metals niobium and tantalum, respectively. Clusters in the size range containing three to five metal atoms \((i.e. \text{M}_x\text{C}_y)\), where \(M = \text{Nb}/\text{Ta}\) and \(x = 3–5\) are investigated through a combination of PIE experiments, which determine their IPs, and DFT calculations on their energetically favourable isomers. Where there is agreement between the experimental IP and calculated IP of the lowest energy, or a low-lying, isomer for a metal-carbide cluster, the carrier of the experimental ionisation onset is assigned.

5.1 Introduction to Niobium and Tantalum-Carbide Clusters

Neutral and cationic niobium-carbide and tantalum-carbide clusters have previously been experimentally observed in the size range of interest in this thesis.\(^1\)\(^-\)\(^7\) It has been found for larger niobium-carbide clusters \((x \geq 8)\) that favoured production of either the Metcar and proposed multi-caged species, or nanocrystal species can be influenced by the experimental conditions, indicating that not only thermodynamic but also kinetic factors are involved.\(^2\) Tantalum-carbide clusters on the other hand have been shown to exclusively generate nanocrystal species.\(^8\)

Photo-dissociation experiments on cationic niobium-carbide clusters have been performed by Duncan and co-workers.\(^3\) In the size range of interest in this thesis, they found \(\text{Nb}_4\text{C}_4^+\) and \(\text{Nb}_2\text{C}_3^+\) to be prominent species in the nascent distribution from the ablation source. The authors proposed the structure of \(\text{Nb}_4\text{C}_4\) to be a \(2\times2\times2\) fcc nanocrystal and the structure of \(\text{Nb}_2\text{C}_3\) to be a substituted \(2\times2\times2\) fcc nanocrystal, where one carbon atom is replaced with a niobium atom. For the photo-dissociation of larger niobium-carbide clusters the \(\text{Nb}_4\text{C}_4^+\) fragment was frequently generated, indicating an enhanced stability for this species.

Soon after these photo-dissociation experiments, Freiser and co-workers studied the reactivity of \(\text{Nb}_4\text{C}_4^+\) with \(\text{O}_2\), \(\text{H}_2\text{O}\) and \(\text{CH}_3\text{OH}\).\(^9\) The reactivity with \(\text{O}_2\) formed \(\text{Nb}_4\text{C}_2^+\) and presumably two \(\text{CO}\) molecules. For the reactions with \(\text{H}_2\text{O}\) and \(\text{CH}_3\text{OH}\),
the first molecule simply attached and addition of a second molecule eliminated H₂ to form nb₄C₄(OH)₂⁺ and nb₄C₄(OCH₃)₂⁺, respectively. A maximum of two additional molecules then further attached to these species. The authors also performed ab initio calculations on the proposed nanocrystal structure of Nb₄C₄ and found good agreement between the calculated electronic structure and the observed experimental reactivity. Calculations were also performed on Nb₄C₂, with the proposed structure having the two carbon atoms bound to separate niobium faces of the underlying tetrahedral niobium cluster. This brought forward the idea that the structures of metal-carbide clusters can exist as fragments of geometrically closed nanocrystals.

Further work by Freiser and co-workers focussed on the reactivity of Nb₅C₇⁺ with a range of molecules. In this study collisional-induced dissociation was also performed on Nb₅C₇⁺, with the major fragments identified being Nb₄C₄⁺ and Nb₅C₆⁺. The structure proposed and calculated for Nb₅C₆ was that of a (corner) niobium depleted 2×2×3 nanocrystal.

Threshold photo-ionisation of neutral niobium-carbide clusters have also been performed by Brock and Duncan. In the mass spectrum the species Nb₃C₂, Nb₄C₄ and Nb₅C₆ were slightly more prominent than other species in the size range investigated in this thesis. While the power dependence of the Metcar species was the focus of the study, the IP of Nb₄C₄ was proposed to be greater than 5.76 eV.

Work by Yang, Hackett and co-workers have investigated several bare transition metal cluster and transition metal-ligand cluster complexes by PFI-ZEKE photoelectron spectroscopy. Of interest to the present study, they investigated the species Nb₃C₂ and Nb₅C₂, with their IPs determined to be 5.04 and 4.60 eV, respectively. The IP of Nb₄C₄ was also determined by PIE in this investigation (4.43 eV), which was found to be much lower in energy than that proposed from the earlier power dependence study. The recorded PFI-ZEKE spectrum of Nb₃C₂ displayed a relatively long vibronic progression. This spectrum was compared with the simulated PFI-ZEKE spectrum of the lowest energy isomer calculated by DFT, which showed excellent agreement. This isomer has a trigonal bipyramid geometry, where the carbon atoms are bound to opposite faces of the triangular Nb₃ cluster.
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(Figure 5-1). The PFI-ZEKE spectrum of Nb$_3$C$_2$ did not display a vibrational progression, with only the 0-0 transition and a small number of sequence bands observed. No calculations on the structure of Nb$_3$C$_2$ were performed.

Neutral tantalum-carbide clusters in the size range of the present study have previously been investigated by our research group. Mass spectra obtained by MPI at 532 nm and 355 nm displayed tantalum-carbide clusters containing up to five tantalum atoms. Species with an equal number of tantalum and carbon atoms displayed slightly greater abundance. However, as the spectra were obtained under MPI conditions, fragmentation is expected to be quite prominent. DFT calculations were also performed on the Ta$_x$C$_y$ clusters, where $x$ and $y \leq 4$. For Ta$_4$C$_4$ the $2 \times 2 \times 2$ nanocrystal structure was found to be the lowest in energy, with the structures of smaller clusters mainly based on fragments of this nanocrystal.

IR-REMPI spectra have been collected for various niobium-carbide and tantalum-carbide clusters by Meijer, von Helden and co-workers using a tuneable IR-FEL. Single broad absorption resonances were observed for Nb$_4$C$_4$ and Nb$_5$C$_3$, centred at 675 and 660 cm$^{-1}$, respectively. The observed resonances are similar to one of two IR-active phonon modes of the metallic NbC (100) surface and are direct evidence for the proposed nanocrystalline structure of Nb$_4$C$_4$ (Figure 5-1). Furthermore, this discounts a structure which contains carbon-carbon bonding, as this would possess a strong absorbance near 1250 cm$^{-1}$, such as that observed for the Nb$_8$C$_{12}$ Metcar. For Nb$_5$C$_3$ the resonance is similar to Nb$_4$C$_4$, indicating that the proposed $2 \times 2 \times 2$ cubic structure for the former species is quite plausible (Figure 5-1). Similar absorption resonances and results were also obtained for Ta$_4$C$_4$ and Ta$_5$C$_3$.

Harris and Dance have carried out a very extensive and thorough study on the calculated structures for a large range of niobium-carbide clusters using DFT, including several species investigated in this thesis. Overall the authors came to some general conclusions on structural patterns present in niobium-carbide clusters. Of importance to this study are the following: 1. Geometrically closed nanocrystal structures are quite favourable and nanocrystal fragments are favourable for Nb$_x$C$_y$ clusters where $x > y$; 2. For Nb$_x$C$_y$ clusters where $y > x$, favourable structures are
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based on $x \approx y \ Nb_xC_y$ clusters, where the carbon atoms are substituted with $C_2$ units; 3. While $C_2$ units are favourable, long carbon chains are not; 4. $Nb_4C_2$ substructures (where a $C_2$ unit is bound across an open niobium butterfly motif) contained in larger $Nb_xC_y$ clusters are favourable.

*Figure 5-1*: Niobium-carbide clusters which have been previously spectroscopically characterised and the structures assigned from those studies (ref [5] and [7]).
5.2 Photo-ionisation Efficiency Experiments

A mass spectrum of niobium-carbide clusters ionised at 225 nm, under the SPI conditions used to conduct a PIE scan (see Section 2.2.4), is shown in Figure 5-2. The observed mass distribution comprises of clusters containing up to eleven Nb atoms. Note that the mass window effect (see Section 4.1) is not prominent for the generated clusters, as investigations with the ion deflectors do not show any significant deviations from this mass distribution. An abundant peak for the Metcar stoichiometry (i.e. Nb₈C₁₂) is not observed, although this is not surprising as it has been proposed to have an IP higher than the photon energy available at 215 nm by a power dependence study.⁴

![Figure 5-2: Mass spectrum of ionised neutral Nb₈C₁₂ clusters obtained by single-photon ionisation (225 nm).](image)

Parts a–e of Figure 5-3 show a portion of the mass spectra of niobium-carbide clusters following ionisation at five different wavelengths; 280, 265, 240, 225 and 210 nm, collected under otherwise identical conditions. In the spectrum recorded at 210 nm (Figure 5-3e), clusters containing Nb₃ appear with 0, 2–4 C atoms attached and clusters containing Nb₄ and Nb₅ appear with 0–6 C atoms attached.

By contrast to that recorded at 210 nm, the spectrum at 280 nm (Figure 5-3a) shows the intensity of all species decreasing dramatically to near baseline levels. At this
wavelength, none of the species are ionised with one photon and the residual signal is
due to MPI and possibly fragmentation. Although these peaks could be diminished
completely by lowering the laser power, this was not possible without severely
affecting the signal-to-noise ratio of the shorter-wavelength spectra. Following
ionisation at 265 nm (Figure 5-3b) Nb\textsubscript{4}C\textsubscript{4} dramatically increases in intensity, with
Nb\textsubscript{4}C\textsubscript{3} increasing slightly and Nb\textsubscript{2}C\textsubscript{2} and Nb\textsubscript{2}C\textsubscript{3} also appearing. At 240 nm (Figure
5-3c), the clusters Nb\textsubscript{3}C\textsubscript{2} and Nb\textsubscript{5}C\textsubscript{5} appear, with Nb\textsubscript{5}C\textsubscript{4} and Nb\textsubscript{5}C\textsubscript{5} and Nb\textsubscript{5}C\textsubscript{6} also
increasing in intensity by this wavelength. At 225 nm (Figure 5-3d), the clusters
Nb\textsubscript{3}C\textsubscript{3}, Nb\textsubscript{4}C\textsubscript{2}, Nb\textsubscript{4}C\textsubscript{6}, Nb\textsubscript{5} and Nb\textsubscript{5}C appear. Finally back to 210 nm, the remaining
clusters Nb\textsubscript{3}, Nb\textsubscript{3}C\textsubscript{4}, Nb\textsubscript{4}, and Nb\textsubscript{4}C are present, with Nb\textsubscript{4}C\textsubscript{3} showing a marked rise in
its previous intensity.

PIE spectra are recorded by monitoring the signal of each species as a function of
photon energy. PIE spectra for the Nb\textsubscript{3}C\textsubscript{y} (y = 0–4), Nb\textsubscript{4}C\textsubscript{y} (y = 0–6) and Nb\textsubscript{5}C\textsubscript{y} (y =
0–6) clusters are shown in parts a–e of Figure 5-4, a–g of Figure 5-5 and a–g of
Figure 5-6, respectively. Most clusters show a dramatic rise from the baseline (e.g.
Nb\textsubscript{3}C\textsubscript{2}, Nb\textsubscript{3}C\textsubscript{4}, Nb\textsubscript{4}C\textsubscript{4}, Nb\textsubscript{5}C\textsubscript{2}, Nb\textsubscript{5}C\textsubscript{3} and Nb\textsubscript{5}C\textsubscript{6}) indicating good FC overlap between
the ground electronic states of the neutral and cation. Many PIE spectra display a
leveling off of ion signal quite quickly after the linear rise (e.g. Nb\textsubscript{3}C\textsubscript{2}, Nb\textsubscript{3}C\textsubscript{4} and
Nb\textsubscript{5}C\textsubscript{6}) indicating that the highest energy FC-allowed transition is quickly attained.
However, the clusters Nb\textsubscript{3}C\textsubscript{3}, Nb\textsubscript{4}C, Nb\textsubscript{5}C\textsubscript{4} and Nb\textsubscript{5}C\textsubscript{5} show gradual onsets of
ionisation, suggesting a notable geometry change between the neutral and cation. The
PIE spectra of Nb\textsubscript{4}C\textsubscript{2}, Nb\textsubscript{4}C\textsubscript{4}, Nb\textsubscript{5}C\textsubscript{2} and Nb\textsubscript{5}C\textsubscript{3} occasionally contain slight structure,
possibly due to either FC allowed transitions being reached or onsets due to low
abundance isomers. Furthermore, some PIE spectra show ion signal activity just prior
to a dramatic rise (e.g. Nb\textsubscript{3}C\textsubscript{3} and Nb\textsubscript{5}C\textsubscript{4}). This effect is believed to originate from
ionisation occurring from thermally populated excited vibrational levels of the cluster.
For all spectra (except Nb\textsubscript{3}C, see below) two lines are fitted; one to the baseline and
one to the linear rise of signal, and their intersection defined as the IP. This procedure
is described in Section 2.2.4. This method provides a determination of the IP with an
estimated error of ±0.05 eV. As a check, the ionisation energies extracted for Nb\textsubscript{3},
Nb\textsubscript{3}C\textsubscript{2}, Nb\textsubscript{4}, Nb\textsubscript{4}C\textsubscript{4}, Nb\textsubscript{5} and Nb\textsubscript{5}C\textsubscript{2} are found to be in good agreement with those
previously determined.\textsuperscript{5,11,15,16}
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Figure 5-3: Mass spectra of Nb$_3$Cy, Nb$_4$Cy and Nb$_5$Cy clusters at four different ionisation wavelengths: (a) 285 nm, (b) 265 nm, (c) 240 nm, (d) 225 nm and (e) 210 nm.

Figure 5-4: Photo-ionisation efficiency spectra for the Nb$_3$Cy (y = 0–4) clusters. The determined IPs are also displayed.
Figure 5-5: Photo-ionisation efficiency spectra for the \( \text{Nb}_4\text{C}_y \) (\( y = 0–6 \)) clusters. The determined IPs are also displayed.

Figure 5-6: Photo-ionisation efficiency spectra for the \( \text{Nb}_5\text{C}_y \) (\( y = 0–6 \)) clusters. The determined IPs are also displayed.
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An IP has not been assigned to the cluster Nb$_3$C, as its PIE spectrum shows no observable onset up to the highest photon energy. Therefore, the IP of Nb$_3$C is assigned to be greater than the highest achievable photon energy in our laboratory (5.91 eV, 210 nm). The PIE spectrum of Nb$_4$C$_3$ displays two separate onsets at 5.72 and 4.52 eV. This will be discussed later in the section 5.4.2, but suffice to say at the moment it is the higher energy onset of greater intensity that is taken as the IP. The determined IPs for all the niobium-carbide clusters considered in this study are displayed in the PIE spectra and are also given later in the second column of Table 5-1, Table 5-2 and Table 5-3.

Firstly, it can be seen that the IPs of the bare niobium clusters Nb$_3$, Nb$_4$ and Nb$_5$ decrease with size, which has been found previously.$^{15}$ In the Nb$_3$C$_y$ series, relative to the IP of Nb$_3$, the greatest IP reduction is for the addition of two C atoms (−0.77 eV), with the reduction decreasing successively with the addition of three (−0.45 eV) and four (−0.14) C atoms, respectively. For the Nb$_4$C$_y$ series, addition of one and three C atoms to Nb$_4$ results in very slight changes in the IP, with increases of +0.16 and +0.12 eV, respectively. However, addition of two C atoms results in an intermediate IP reduction (−0.36 eV), while addition of four C atoms results in a significant IP reduction (−1.17 eV). Addition of five and six C atoms results in IP reductions of −0.86 eV and −0.26 eV, respectively. For the Nb$_5$C$_y$ series, addition of one C atom to Nb$_5$ only slightly reduces the IP (−0.13 eV). Addition of two and three C atoms though causes significant IP reductions of −0.86 and −0.88 eV, respectively. Addition of four, five and six C atoms to Nb$_5$ all cause similar intermediate IP reductions of −0.48, −0.44 and −0.39 eV, respectively.
5.3 **DFT Calculated Isomers**

All the calculated isomers considered for the *neutral* Nb$_x$C$_y$ clusters are shown in Figure 5-7 (Nb$_3$C$_y$, $y = 0$–4), Figure 5-8 (Nb$_4$C$_y$, $y = 0$–4), Figure 5-9 (Nb$_5$C$_3$), Figure 5-10 (Nb$_4$C$_6$), Figure 5-12 (Nb$_5$C$_y$, $y = 0$–3), Figure 5-13 (Nb$_5$C$_4$), Figure 5-14 (Nb$_5$C$_5$) and Figure 5-15 (Nb$_5$C$_6$). The relative energies ($\Delta E$ in eV) for each isomer of the neutral species are also given in the figures; the $\Delta E$ with the SDD (normal font) and extended (bold font) basis sets. For each isomer examined with the extended basis set, similar geometric minima are also identified on the *cationic* surface, although these are not included in the figures. Almost all discussion herein refers to the neutral systems but reference is made to the cationic systems when results can be compared with previous studies. All details *(i.e.* geometric and energy information) for both the neutral and cationic isomers examined with the extended basis set are contained in Appendix II and III.

### 5.3.1 The Nb$_3$C$_y$ ($y = 0$–4) Cluster Series

The neutral and cationic niobium trimer has been recently investigated at the DFT level with the B3LYP method by the separate groups of Fowler$^{17}$ and Balasubramanian.$^{18,19}$ Fowler and co-workers reported an obtuse isosceles triangle [$^2B_1$, $C_{2v}$] and an equilateral triangle [$^3A_1', D_{3h}$] as the lowest energy structures for Nb$_3$ and Nb$_3^+$, respectively. Balasubramanian and co-workers reported the same structure for the neutral, but obtain an obtuse triangle for the cation [$^3B_1$, $C_{2v}$]. These workers also performed multi-reference configuration-interaction (MRCI) calculations on Nb$_3$ and Nb$_3^+$, for which they obtained very similar geometries as their DFT calculations, although occasionally a different electronic state was found to be the ground state *(e.g.* the DFT calculation has the ground state of Nb$_3^+$ as a triplet but the MRCI calculation gives a quintet state, yet this state cannot be accessed via ionisation from the doublet state of the neutral). However, the multi-reference character of the ground state was calculated to be significant and highlights the fact that metal clusters, and presumably metal-carbide clusters, contain large amounts of electronic configuration mixing that may be difficult to properly treat with DFT.
Figure 5-7: Structures of calculated isomers for the neutral $\text{Nb}_3\text{C}_y$ ($y = 0–4$) clusters. Written beneath each isomer are the relative energies ($\Delta E$ in eV) calculated using the SDD (normal) and extended (bold) basis sets.
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For the present DFT study, the calculated lowest energy structure of Nb₃, \( \text{I} \ A \ [^2A'' \ , \ C_3] \), is a scalene triangle. Several isosceles triangular geometries were also tested, resulting in a higher energy minimum and two transition states; for which the imaginary frequencies of the latter lead to the structure of \( \text{I} \ A \). For the cationic state a highly-symmetric structure, \( \text{I} \ A^+ \ [^3A_1' \ , \ D_{3h}] \), is found to be the minimum, in agreement with Fowler. These results are consistent with Raman studies of Nb₃ deposited in an argon matrix, which suggest a near equilateral triangle\(^{20}\).

Two isomers have been found for Nb₃C that differ in the position of the C atom relative to the triangular Nb₃ cluster; one is planar with the C atom bound across a Nb-Nb edge, \( \text{II} \ A \ [^2A_1 \ , \ C_2v] \), and the other has the C atom bound to a Nb face, \( \text{II} \ B \ [^2A' \ , \ C_3] \). The former is found to lower in energy by 0.317 eV.

Only one isomer of Nb₃C₂ is investigated, \( \text{III} \ A \ [^2A' \ , \ C_3] \), which has the separated C atoms bound on opposite Nb faces of the triangular Nb₃ cluster, in agreement with the previous experimental/theory PFI-ZEKE work\(^5\). Because of the significance of this work, it is important to note that the calculated electronic state and geometry for the cation, \( \text{III} \ A^+ \ [^1A_1' \ , \ D_{3h}] \), is consistent with that study.

The lowest energy isomer of Nb₃C₃, \( \text{IV} \ A \ [^2A' \ , \ C_3] \), has one C atom bound to a face of the triangular Nb₃ cluster and the remaining two C atoms bound across separate Nb-Nb edges, in agreement with that found by Harris and Dance\(^{14}\). Isomer \( \text{IV} \ B \ [^2A \ , \ C_1] \) has a \( \Delta E \) of +0.229 eV and contains a C₂ unit bound to a Nb face of the triangular Nb₃ cluster, with the remaining C atom bound across a Nb-Nb edge. Incidentally, the second lowest energy isomer found by Harris and Dance (at 0.6 eV higher in energy) is found to be a transition state (not shown here) leading to \( \text{IV} \ A \).

The lowest energy isomer of Nb₃C₄ is \( \text{V} \ A \ [^2A'' \ , \ C_3] \), which has one C atom bound to a Nb face of the triangular Nb₃ cluster and the remaining three C atoms bound across separate Nb-Nb edges \( \text{i.e.} \) a Nb-deficient 2×2×2 nanocrystal), which was the only isomer investigated by Harris and Dance\(^{14}\). The next lowest energy isomer, \( \text{V} \ B \ [^2A \ , \ C_1] \), is only 0.183 eV higher in energy and contains a C₂ unit and a C atom bound to opposite Nb faces of the triangular Nb₃ cluster, with the remaining C atom bound
across a Nb-Nb edge. Inspection of the structures in Figure 5-7 shows that isomer \( V_A \) can re-arrange to become \( V_B \) by two of its edge-bound C atoms coming together to make a \( \text{C}_2 \) unit.

### 5.3.2 The \( \text{Nb}_4\text{C}_y \) (\( y = 0–6 \)) Cluster Series

As with the niobium trimer, the neutral and cationic niobium tetramer has been investigated by the groups of Fowler\(^{17}\) and Balasubramanian.\(^ {18,21}\) The latter group also investigated \( \text{Nb}_4 \) and \( \text{Nb}_4^+ \) at the more accurate MRCI level and found there to be significant contributions from several electronic configurations to the ground state. Both groups report an ideal tetrahedral geometry for the neutral \( ^1A_1, T_d \), using various computational methodologies. In this study the lowest energy isomer is also found to have ideal tetrahedral symmetry, \( \text{VI} \ A ^1A_1, T_d \). For the cation, Majumdar and Balasubramanian found the lowest energy DFT structure to be distorted from the ideal tetrahedral geometry \( ^2A', C_s \). Fowler and co-workers also found the lowest energy structure to be distorted \( ^2A_1, C_{2v} \). Similarly, here the lowest energy structure for the cation is a \( C_{2v} \) structure, \( \text{VI} \ A^+ ^2A_1, C_{2v} \), with one large, one intermediate and four small bond lengths. Optimisation of \( \text{Nb}_4^+ \) at the \( C_s \) symmetry reported by Majumdar and Balasubramanian, results in a geometry and energy negligibly different from the \( C_{2v} \) structure.

Two isomers are found for \( \text{Nb}_4\text{C} \) with the C atom binding either to a Nb face, \( \text{VII} \ A ^1A', C_s \), or a Nb-Nb edge, \( \text{VII} \ B ^1A_1, C_{2v} \), of the tetrahedral \( \text{Nb}_4 \) cluster. Isomer \( \text{VII} \ A \) is lower in energy by 0.561 eV.

The structure of the \( \text{Nb}_4\text{C}_2 \) cluster has been previously investigated by the separate groups of Freiser,\(^9\) Dance\(^ {14}\) and recently Parnis.\(^ {22}\) All groups state that the lowest energy isomer has the two C atoms binding to separate Nb faces of the tetrahedral \( \text{Nb}_4 \) cluster. Two isomers are considered for \( \text{Nb}_4\text{C}_2 \) here and, similarly, find this structure, \( \text{VIII} \ A ^1A_1, C_{2v} \), to be the lowest in energy. Isomer \( \text{VIII} \ B ^1A_1, C_{2v} \) has both C atoms bound across opposite sides of the open butterfly \( \text{Nb}_4 \) cluster and is higher in energy by 0.543 eV.
Figure 5-8: Structures of calculated isomers for the neutral Nb\textsubscript{4}C\textsubscript{y} (y = 0–4) clusters. Written beneath each isomer are the relative energies (\(\Delta E\) in eV) calculated using the SDD (normal) and extended (bold) basis sets.

The only isomer of the Nb\textsubscript{4}C\textsubscript{3} cluster calculated by Harris and Dance was that where all the C atoms bind to three separate Nb faces of the tetrahedral Nb\textsubscript{4} cluster.\textsuperscript{14} The present study also finds this nanocrystal fragment (i.e. a C-deficient 2×2×2
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nanocrystal), IX A \([-^1A_1, C_3v]\) to be the lowest energy isomer. With the SDD basis set, all other isomers are found to be substantially higher in energy (> 2 eV).

The results of many experimental and theoretical studies all support the proposal that the lowest energy isomer of Nb\(_4\)C\(_4\) has a structure where the four C atoms are bound to all the available Nb faces of the tetrahedral Nb\(_4\) cluster \(i.e.\) two interpenetrating tetrahedra of C\(_4\) and Nb\(_4\) resulting in the formation of a 2×2×2 cube. Freiser and co-workers were the first to calculate this isomer to support their experimental results.\(^9\)

The isomers of Nb\(_4\)C\(_4\) have been extensively studied by Harris and Dance, with eight isomers examined and the nanocrystal being significantly the lowest in energy.\(^{14}\) Consequently, only this isomer is explored and the calculations on the singlet surface yield a highly symmetric structure, X A \([-^1A_1, T_d]\). However, a triplet state \([^3B, C_2]\) that lies 0.067 eV lower in energy (Appendix II) is found, with its geometry distorted from ideal \(T_d\) symmetry.

The structure of the Nb\(_4\)C\(_5\) species has not been calculated before, although Harris and Dance have proposed for such a species that C\(_2\) units should be energetically favoured.\(^{14}\) Fifteen isomers are identified but only one is examined with the extended basis set, since all others are > 1.8 eV higher in energy with the SDD basis set. This isomer, XI A \([-^1A', C_s]\), indeed has a C atom from the 2×2×2 nanocrystal substituted with a C\(_2\) unit. The structure can also be considered as a C\(_2\) unit bound to the free Nb face of Nb\(_4\)C\(_3\) (IX A). From a simple valence bond perspective, structure XI A can be considered as an acetylide unit (C\(_2^2\)) undergoing \(\sigma\) interaction with one Nb atom and two side-on \(\pi\) interactions with the other two Nb atoms \(i.e.\) two 3-centre 2-electron bonds. A contrasting bonding picture can be considered for a C\(_2\) unit having an ethylene configuration (C\(_2^4\)) which would form two \(\sigma\) bonds with two Nb atoms and one side-on \(\pi\) interaction with the remaining Nb atom. If the Nb-C bonding in Nb\(_4\)C\(_4\) X A is considered as twelve Nb-C 2-centre 2-electron bonds, then substitution with a C\(_2\) unit in either configuration could lead to stable electronic structures. However, it is found that all starting geometries lead to an optimised structure consistent with the former description.
Figure 5-9: Structures of calculated isomers for the neutral Nb$_4$C$_5$ cluster. Written beneath each isomer are the relative energies ($\Delta E$ in eV) calculated using the SDD (normal) and extended (bold) basis sets.
Figure 5-10: Structures of calculated isomers for the neutral Nb₄C₆ cluster. Written beneath each isomer are the relative energies ($\Delta E$ in eV) calculated using the SDD (normal) and extended (bold) basis sets.
Despite the fact its stoichiometry is exactly half that of the Metcar species, no calculations on Nb₄C₆ have been previously reported. The EA of V₄C₆⁻ has recently been measured, which is iso-valent with Nb₄C₆⁻. Harris and Dance have proposed (but did not calculate) two isomers for Nb₄C₆, which they found to be key substructures incorporated into larger niobium-carbide clusters. These two isomers can be thought of as (unsymmetric) halves of the Metcar structure, each containing three C₂ units. The present calculations on Nb₄C₆ have resulted in fifteen isomeric structures, with the two isomers proposed by Harris and Dance (XII G and XII H) found to be substantially higher in energy with the SDD basis set (> 2 eV). Of the five lowest energy isomers examined with the extended basis set, the four lowest are based around a 2×2×2 nanocrystal with 2 × C atoms replaced by 2 × C₂ units oriented in various ways. The lowest energy isomer, XII A [¹A₁, C₂v], has both C₂ units bound in an acetylide configuration, with both units interacting side-on with the same two Nb atoms. By changing one of the C₂ units in XII A to have an ethylene configuration gives XII B [¹A¹, C₃], which is negligibly higher in energy (ΔE = +0.112 eV). Another isomer related to XII A is XII C [¹A, C₁]; where one C₂ unit is rotated ~90°, so that now there is one Nb atom which is σ bonded to one C₂ unit and interacts side-on with the other C₂ unit. XII C has a ΔE of +0.231 eV. The final isomer of Nb₄C₆ containing two C₂ units is XII D [¹A, C₂], where both C₂ units in XII A are rotated ~90° towards opposite sides of the cluster, which has a ΔE = +0.511 eV. The next low energy isomer, XII E [¹A¹, C₃], can be considered as a C₃ unit substituting one C atom in the 2×2×2 nanocrystal (i.e. a C₃ unit bound to the free Nb face of Nb₄C₃ IX A). It is +0.738 eV higher in energy than the global minimum.

5.3.3 The Nb₅C₆ (y = 0–6) Cluster Series

The structure of the neutral and cationic niobium pentamer have previously been investigated by Majumdar and Balasubramanian with the DFT and MRCI methods. For the DFT method a distorted trigonal bipyramid geometry was found for Nb₅ [²A₂, C₂v], whereas for Nb₅⁺ a distorted trigonal bipyramid of high spin multiplicity [³A₁, C₂v] was found. In this study the lowest energy structure of Nb₅ is also found to be a distorted prolate trigonal bipyramid (XIII A [²B₁, C₂v]).
electronic state is different than that of Majumdar and Balasubramanian with the DFT method, however it is the same as that obtained with the MRCI method. The lowest energy structure of \( \text{Nb}_5^+ \) \( A^+ \) \([A_1, C_{2v}]\) is found to agree with the previous work. Recent IR multi-photon dissociation (MPD) experiments with an IR-FEL on \( \text{Nb}_5^+\)-Ar and \( \text{Nb}_5^+\)-Ar are consistent with these calculated results.\(^{24}\)

Before the isomeric structures of the \( \text{Nb}_5 \text{C}_y \) clusters are discussed, it is useful to describe the geometries the underlying \( \text{Nb}_5 \) motif may have in these clusters (Figure 5-11). Analogous to the lowest energy \( \text{Nb}_5 \) structure, there is the prolate “trigonal bipyramid” geometry, where the two axial Nb atoms are at a longer distance to the centre of mass than the three equatorial Nb atoms. There may also be an “oblate trigonal bipyramid” geometry, where the two axial Nb atoms are at a shorter distance to the centre of mass than the three equatorial Nb atoms. This latter geometry is not favourable for the bare \( \text{Nb}_5 \) cluster as the three equatorial Nb atoms are not within a reasonable bonding distance of each other.\(^{21}\) However, this structure is beneficial for the \( \text{Nb}_5 \text{C}_y \) clusters as it creates three Nb butterfly motifs \( i.e. \) a \( \text{Nb}_4 \) sub-unit consisting of the two axial Nb atoms and two of the equatorial Nb atoms). However, as will be shown below, it is not energetically favourable for C atoms or units to bind across all three Nb butterfly motifs. Rather this oblate trigonal bipyramid geometry distorts significantly once two Nb butterfly motifs have C atoms or units bound across them, with the third becoming quite closed and instead creates two outer Nb faces for C atoms to bind to.

**Figure 5-11:** The two common underlying \( \text{Nb}_5 \) geometries contained in the \( \text{Nb}_5 \text{C}_y \) isomers; \( i.e. \) the trigonal bipyramid and oblate trigonal bipyramid geometries. The “\( A \)” and “\( E \)” labels refer to axial and equatorial atoms, respectively. The type and number of carbon addition bonding sites for each \( \text{Nb}_5 \) geometry are also given.
In general, the trigonal bipyramid Nb₅ cluster has six Nb faces for available for C addition. The situation where C atoms bind to these Nb faces is interesting as now at least two structural isomers are possible for the NbₓCᵧ (y = 2–4) clusters following this bonding approach. This is unlike the case for the Nb₄Cₓ clusters where after each C atom is bound to a Nb face of the tetrahedral Nb₄ cluster, the remaining faces are essentially equivalent for binding of the next C atom. Alternatively, the oblate trigonal bipyramid Nb₅ cluster has two Nb butterfly motifs and two outer Nb faces available for C addition.

Two isomers are found for Nb₅C; one with the C atom bound to a Nb face of the trigonal bipyramid Nb₅ cluster (XIV A [²A, C₁]), while the other has the C atom bound across a Nb butterfly motif of the oblate trigonal bipyramid Nb₅ cluster (XIV B [²A₁, C₂v]). Isomer XIV A is found to be the lowest in energy, although XIV B is negligibly higher in energy (∆E = +0.072 eV). Several structures attempted with Nb-Nb edge bound C atoms are either transition states or unstable, with optimisation leading to XIV A.

The structure of Nb₅C₂ has previously been investigated by Parnis and co-workers. They found the lowest energy isomer to have the two C atoms bound to separate Nb faces of the trigonal bipyramid Nb₅ cluster. In the present study, the lowest energy isomer XV A [²B₁, C₂v] has the C atoms bound across the two Nb butterfly motifs of the oblate trigonal bipyramid Nb₅ cluster. Isomer XV B [²A', C₄v] is that identified by Parnis and is only 0.118 eV higher in energy. XV B has C atoms bound to Nb faces next to each other that share a common axial Nb atom.

Harris and Dance have examined the structure of Nb₅C₃, with two isomers presented. One isomer had all three C atoms bound to three Nb faces of the trigonal bipyramid Nb₅ cluster, which all contain a common axial Nb atom. This structure can also be considered as a substituted 2×2×2 nanocrystal, where one C atom is substituted with a Nb atom. The other isomer, calculated to be ~ 2.5 eV higher in energy, had the C atoms binding across all three Nb butterfly motifs of the undistorted oblate trigonal bipyramid Nb₅ cluster, demonstrating that binding across all three Nb
butterfly motifs is unfavourable. In this study the substituted $2\times2\times2$ cubic isomer $\text{XVI A}$ [$^2A_1$, $C_{3v}$] is also found to be the lowest in energy. With the SDD basis set all other isomers are found to be substantially higher in energy ($> 2$ eV).

**Figure 5-12**: Structures of calculated isomers for the neutral $\text{Nb}_5\text{C}_y$ ($y = 0–3$) clusters. Written beneath each isomer are the relative energies ($\Delta E$ in eV) calculated using the SDD (normal) and extended (bold) basis sets.
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Several energetically competitive isomers are found for Nb$_5$C$_4$ with the SDD basis set, with the lowest four examined with the extended basis set. Two of the isomers are generated by binding all C atoms to separate Nb faces of the trigonal bipyramid Nb$_5$ cluster. The lowest energy isomer XVII A [$^2A', C_s$] has C atoms bound to all three of the available Nb faces which share a common axial Nb atom, with the last C atom bound to one of the three remaining available Nb faces which contain the second axial Nb atom. XVII D [$^2A, C_2$] is the fourth lowest energy isomer ($\Delta E = +0.650$ eV) and has the C atoms bound to two of the three available Nb faces on each side on the Nb$_5$ cluster, which contain opposite axial Nb atoms. The respective pairs of two C atoms

Figure 5-13: Structures of calculated isomers for the neutral Nb$_5$C$_4$ cluster. Written beneath each isomer are the relative energies ($\Delta E$ in eV) calculated using the SDD (normal) and extended (bold) basis sets.
are arranged so that one C atom of each set is bound to Nb faces next to one another. Isomers XVII B and XVII C have the Nb$_5$ cluster in the oblate trigonal bipyramid geometry. In XVII C [$^2A_1, C_{2v}$] C atoms are bound across each of the two Nb butterfly motifs with the remaining two C atoms bound to the two available outer Nb faces. Isomer XVII B [$^2A''$, $C_i$] can be generated from XVII C by one of the Nb butterfly motifs becoming closed while the other Nb butterfly motif opens, by a distortion of the common equatorial Nb atom. This results in the C atom bound across the open Nb butterfly motif now being bound to one of the inner Nb faces of the butterfly motif. XVII B can also be thought of as a Nb atom being bound above a C corner of the 2×2×2 nanocrystal. Isomers XVII B and XVII C are the second and third lowest energy isomers of Nb$_5$C$_4$ with a ΔE of +0.132 eV and +0.493 eV, respectively.

Four isomers of Nb$_5$C$_5$ are examined with the extended basis set. The lowest energy isomer XVIII A [$^2A', C_{i1}$] has an acetylide C$_2$ unit and C atom bound across the two Nb butterfly motifs of the oblate trigonal bipyramid Nb$_5$ cluster, with the remaining two C atoms bound to the two outer Nb faces. Isomer XVIII B [$^2A', C_{i2}$] has the five C atoms bound to all but one of the available Nb faces of the trigonal bipyramid Nb$_5$ cluster and is 0.333 eV higher in energy. Next is isomer XVIII C [$^2A, C_{11}$] (ΔE = +0.392 eV), which has the Nb$_5$ cluster in the oblate trigonal bipyramid geometry with a C atom bound across the one of the Nb butterfly motifs, which is quite closed, and two C atoms bound to the two outer Nb faces. For the remaining two C atoms, one is bound to an inner Nb face of the remaining open Nb butterfly motif, while the other C atom is bound across a Nb-Nb edge on the same Nb butterfly motif. This isomer can also be considered as a 2×2×3 nanocrystal fragment with a corner NbC unit removed. The final isomer is XVIII D [$^2A, C_{1}$] (ΔE = +0.599 eV), which has a C$_2$ unit bound across two Nb faces of the trigonal bipyramid Nb$_5$ cluster, with C atoms bound to three of the four remaining Nb faces.
Figure 5-14: Structures of calculated isomers for the neutral Nb$_5$C$_6$ cluster. Written beneath each isomer are the relative energies ($\Delta E$ in eV) calculated using the SDD (normal) and extended (bold) basis sets.

The structure of Nb$_5$C$_6$ has been examined previously by the groups of Freiser and Dance.$^{10,14}$ Freiser and co-workers proposed a 2×2×3 nanocrystal fragment as the structure of Nb$_5$C$_6$ with a C atom removed from a corner position. Harris and Dance considered two isomers; one where C atoms are bound to all six Nb faces of the trigonal bipyramid Nb$_5$ cluster and another where three C$_2$ units are each bound across two Nb faces of the same type of Nb$_5$ cluster. They found the former isomer to be ~1 eV lower in energy. In the current study the lowest energy isomer XIX A [$^2A_1$, $C_{2v}$] has the Nb$_5$ cluster in the oblate trigonal bipyramid geometry. Two acetylide C$_2$ units are bound across the two Nb butterfly motifs with the remaining two C atoms bound
to the two outer Nb faces. In isomer XIX B \( [^2B_1, C_{2v}] \) the Nb\(_5\) cluster is in the trigonal bipyramid geometry with an actylide C\(_2\) unit bound across two of the Nb faces, with C atoms bound to the remaining Nb faces. XIX B is considerably higher in energy (\( \Delta E \) of +1.112 eV) than XIX A.

**Figure 5-15:** Structures of calculated isomers for the neutral Nb\(_5\)C\(_6\) cluster. Written beneath each isomer are the relative energies (\( \Delta E \) in eV) calculated using the SDD (normal) and extended (bold) basis sets.

With the SDD basis set the two isomers of Nb\(_5\)C\(_6\) proposed by the respective groups of Freiser and Dance are found to be much higher in energy (> 1.4 eV) than the global minimum, with the former slightly the lower in energy. Interestingly, the isomer proposed by Harris and Dance (i.e. XIX G) can generate XIX B by two of the C atoms coming together to form a C\(_2\) unit. However, this distortion is only quite favourable to create one C\(_2\) unit, as shown here (i.e. XIX B and XIX E), as the Nb\(_5\) cluster can only distort to maintain one flat butterfly Nb motif for one C\(_2\) unit to bond across. When a second C\(_2\) unit is created both C\(_2\) units must sit across two faces of the
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trigonal bipyramid Nb$_5$ cluster as two flat Nb butterfly motifs cannot be maintained, which is unfavourable due to the diminished Nb-C-C $\sigma$ bonding angle.
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5.4 Comparison between Calculated and Experimental IPs

Ionisation transitions are considered for the lowest energy isomer, as well as the low-lying isomers, for each cluster species. The adiabatic ionisation energies are calculated as the difference in energy between the ground electronic state of the neutral and lowest energy electronic state of the cation, for the same isomer, which can be accessed following the $\Delta S = \pm \frac{1}{2}$ selection rule for ionisation. These ionisation energies are listed for the Nb$_3$C$_y$ ($y = 0–4$), Nb$_4$C$_y$ ($y = 0–6$) and Nb$_5$C$_y$ ($y = 0–6$) clusters in Table 5-1, Table 5-2 and Table 5-3, respectively. Note that although ionisation energies both excluding and including ZPE are listed in the tables, only the latter numbers are considered for discussion. In addition, experimental IPs and the calculated IPs for each of the isomers in the Nb$_3$C$_y$ ($y = 0–4$), Nb$_4$C$_y$ ($y = 0–6$) and Nb$_5$C$_y$ ($y = 0–6$) cluster series are also shown in Figure 5-16, Figure 5-17 and Figure 5-18, respectively.

5.4.1 The Nb$_3$C$_y$ ($y = 0–4$) Cluster Series

It is seen that the absolute calculated IPs for all the Nb$_3$C$_y$ cluster isomers are higher than the experimental values (Table 5-1). For example, for Nb$_3$ and Nb$_3$C$_2$ (two species which have had their structures and IPs previously determined), the calculations yield values that are overestimated by 0.368 eV and 0.560 eV, respectively.

Since this study is concerned with the IP following sequential addition of C atoms, the change in IP relative to the bare Nb$_x$ cluster is only considered and a linear offset is applied to the calculated IP values. For the Nb$_3$C$_y$ isomers, an offset of $-0.368$ eV is applied so that the calculated and experimental IPs of Nb$_3$ coincides. This offset value, denoted as IP$^\dagger$, is the value shown in the final column of Table 5-1. Figure 5-16 shows the calculated IP$^\dagger$'s of the isomers ($\triangle$) and experimental IP ($\blacktriangle$) for each Nb$_3$C$_y$ cluster species.
Table 5-1: List of experimental ionisation potentials (reported in eV) observed for Nb$_3$C$_y$ (y = 0–4) clusters. Also listed are calculated transitions and ionisation potentials: excluding ZPE, including ZPE, and offset IP (i.e. IP$^\dagger$).

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Expt. IP</th>
<th>Isomer</th>
<th>Calc. Transition</th>
<th>Calc. IP (exc. ZPE)</th>
<th>Calc. IP (inc. ZPE)</th>
<th>Calc. IP$^\dagger$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$_3$</td>
<td>5.79</td>
<td>I A</td>
<td>$^3A'_1 \leftarrow ^2A''$</td>
<td>6.146</td>
<td>6.158</td>
<td>5.790</td>
</tr>
<tr>
<td>Nb$_3$C</td>
<td>&gt; 5.91</td>
<td>II A</td>
<td>$^1A_1 \leftarrow ^2A_1$</td>
<td>7.072</td>
<td>7.070</td>
<td>6.702</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II B</td>
<td>$^1A'_1 \leftarrow ^2A'$</td>
<td>6.116</td>
<td>6.133</td>
<td>5.765</td>
</tr>
<tr>
<td>Nb$_3$C$_2$</td>
<td>5.02</td>
<td>III A</td>
<td>$^1A'_1 \leftarrow ^2A'$</td>
<td>5.560</td>
<td>5.580</td>
<td>5.212</td>
</tr>
<tr>
<td>Nb$_3$C$_3$</td>
<td>5.34</td>
<td>IV A</td>
<td>$^1A' \leftarrow ^2A'$</td>
<td>6.071</td>
<td>6.092</td>
<td>5.724</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IV B</td>
<td>$^3A \leftarrow ^2A$</td>
<td>6.950</td>
<td>6.953</td>
<td>6.585</td>
</tr>
<tr>
<td>Nb$_3$C$_4$</td>
<td>5.65</td>
<td>V A</td>
<td>$^1A' \leftarrow ^2A''$</td>
<td>6.727</td>
<td>6.725</td>
<td>6.357</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V B</td>
<td>$^1A \leftarrow ^2A$</td>
<td>6.094</td>
<td>6.113</td>
<td>5.745</td>
</tr>
</tbody>
</table>

Figure 5-16: Graph showing experimental IP values for the Nb$_3$C$_y$ clusters as a function of y. Also shown on the same scale are the offset values, IP$^\dagger$, calculated using DFT. The letters (A, B, etc.) denote the isomers for that particular cluster (see text for details). The upward pointing arrow for the Nb$_3$C datum represents the experimental IP being a lower bound.
As mentioned earlier, it is believed that the onset for ionisation of Nb$_3$C has not been reached and so it is marked as a lower bound at 5.91 eV. In agreement with this observation is the fact that the IP$^\dagger$ of Nb$_3$C II A is very high (6.702 eV). Another possibility is that isomer II B, calculated to be only 0.317 eV higher in energy than II A, is present in our experiment. However, II B has an IP$^\dagger$ at 5.765 eV which, if present in significant density in our experiment, should exhibit an ionisation onset. Since this is not the case it is contended that only isomer II A is generated and that photon energies around 6.7 eV (185 nm) are required to ionise it.

The calculated IP$^\dagger$ of Nb$_3$C$_2$ III A is in agreement with the experimental trend, which shows a large lowering of the IP, relative to Nb$_3$. The IP$^\dagger$ for III A is only 0.192 eV higher in energy than the experimental value, which provides an estimate of an acceptable deviation between the calculated IP$^\dagger$ and experimental IP.

The calculated IP$^\dagger$ increases from Nb$_3$C$_2$ for the lowest energy isomer of Nb$_3$C$_3$, IV A, although it is 0.384 eV higher in energy than the experimental IP. The next lowest energy isomer for Nb$_3$C$_3$ (IV B) is only 0.229 eV higher in energy, however, the IP$^\dagger$ of IV B is 1.245 eV higher than the experimental value. Therefore, isomer IV A is assumed to be present in our experiment and assigned to the experimental IP.

For Nb$_3$C$_4$ V A, the predicted IP$^\dagger$ is much higher than the experimental value by 0.707 eV (putting it beyond our experimental photon energy range), which is considered to be too great a difference. The next lowest energy isomer, V B, is only 0.183 eV higher in energy than V A and has a much more acceptable deviation between its calculated IP$^\dagger$ and the experimental IP (+0.095 eV). Furthermore, the cationic geometry of V A is quite different to the neutral state (as shown in Appendix III, two of the C atoms move significantly), whereas the cationic geometry of V B is similar to the neutral. In terms of FC overlap, isomer V B is expected to give rise to a rapid onset which is what is observed in the PIE curve. Since the energy difference between the isomers V A and V B is smaller than the expected accuracy of the DFT calculations (~0.5 eV), it is possible that (i) V B is in high abundance in the experiment or (ii) it may be the true global minimum. If both V A and V B are present in our experimental conditions then the onset for V A may appear at higher energy, however, no evidence of this was observed in the current photon range. Either way, it is proposed that isomer V B is
responsible for the observed IP at 5.65 eV. The assignment of the ionisation onset to this isomer is significant in that it contains a molecular C\textsubscript{2} unit, which suggests that C-C bonding is energetically stable for the Nb\textsubscript{3}C\textsubscript{4} cluster.

### 5.4.2 The Nb\textsubscript{4}C\textsubscript{y} (y = 0–6) Cluster Series

As observed for the Nb\textsubscript{3}C\textsubscript{y} cluster series, the absolute calculated IPs for all the Nb\textsubscript{4}C\textsubscript{y} cluster isomers are higher than the experimental values. Identical to the procedure for the Nb\textsubscript{3}C\textsubscript{y} series, a linear offset of −0.359 eV is applied to the Nb\textsubscript{4}C\textsubscript{y} isomers (i.e. the calculated and experimental IPs of Nb\textsubscript{4} overlap) and the resultant IP\textsuperscript{†} is the value shown in final column of Table 5-2. Figure 5-17 shows the calculated IP\textsuperscript{†}s of the isomers (\(\triangle\)) for each Nb\textsubscript{4}C\textsubscript{y} cluster species, as well as the experimental IP (\(\triangleup\)).

The calculated IP\textsuperscript{†} of Nb\textsubscript{4}C VII A is essentially identical to the experimental value, with a deviation of −0.006 eV. The IP\textsuperscript{†} of VII B is also within an acceptable range of the experimental value (+0.255 eV). However, as the IP\textsuperscript{†} of VII A is in much better agreement and is the lowest energy isomer by 0.561 eV, the observed ionisation onset is assigned to VII A.

For Nb\textsubscript{4}C\textsubscript{2} the deviation between the calculated IP\textsuperscript{†}s for VIII A and VIII B and the experimental value are +0.252 eV and +0.451 eV, respectively. As isomer VIII A is in better agreement with the experimental IP and calculated to be 0.543 eV lower in energy than VIII B, the ionisation onset is assigned to the former.

For Nb\textsubscript{4}C\textsubscript{3} the IP\textsuperscript{†} of the lowest energy isomer IX A is in excellent agreement with the dominant (second) ionisation onset at 5.72 eV, with a deviation of only −0.069 eV. Therefore, this experimental IP is assigned to this isomer. The origin of the first, low intensity, ionisation onset at 4.52 eV is not obvious. Fragmentation of larger clusters is ruled out on the basis of the high calculated binding energies of Nb\textsubscript{3}C\textsubscript{y} clusters\textsuperscript{14} and the low photon fluences employed in this study. All other isomers are calculated to be much higher in energy (> 2 eV), discounting that the initial onset is due to a low-lying isomer. However, a triplet state, \(^3A_1\), is calculated for IX A that is 0.990 eV higher in energy. This state may be metastable and could access the same cationic \(^2A_1\)
electronic state with an IP† of 4.686 eV, a deviation of only +0.166 eV from the weak ionisation onset. Therefore, it is proposed that the two experimental onsets observed for Nb$_4$C$_3$ are due to ionisation from both a metastable $^3A_1$ state and the lowest energy $^1A_1$ state of Nb$_4$C$_3$ IX A.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Expt. IP</th>
<th>Isomer</th>
<th>Transition</th>
<th>Calc. IP (exc. ZPE)</th>
<th>Calc. IP (inc. ZPE)</th>
<th>Calc. IP†</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb$_4$</td>
<td>5.60</td>
<td>VI A</td>
<td>$^2A_1$ ← $^1A_1$</td>
<td>5.964</td>
<td>5.959</td>
<td>5.600</td>
</tr>
<tr>
<td>Nb$_4$C</td>
<td>5.76</td>
<td>VII A</td>
<td>$^2A'$ ← $^1A'$</td>
<td>6.116</td>
<td>6.113</td>
<td>5.754</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VII B</td>
<td>$^2A''$ ← $^1A_1$</td>
<td>6.379</td>
<td>6.374</td>
<td>6.015</td>
</tr>
<tr>
<td>Nb$_4$C$_2$</td>
<td>5.24</td>
<td>VIII A</td>
<td>$^2B_1$ ← $^1A_1$</td>
<td>5.856</td>
<td>5.851</td>
<td>5.492</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VIII B</td>
<td>$^2B_2$ ← $^1A_1$</td>
<td>6.054</td>
<td>6.050</td>
<td>5.691</td>
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<tr>
<td>Nb$_4$C$_3$</td>
<td>5.72</td>
<td>IX A</td>
<td>$^2A_1$ ← $^1A_1$</td>
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<td>6.010</td>
<td>5.651</td>
</tr>
<tr>
<td></td>
<td>4.52</td>
<td></td>
<td>$^2A_1$ ← $^3A_1$</td>
<td>5.020</td>
<td>5.045</td>
<td>4.686</td>
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<td>4.873</td>
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<td>$^2B_1$ ← $^3B$</td>
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<td>XI A</td>
<td>$^2A'$ ← $^1A'$</td>
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<td>6.809</td>
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<td></td>
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<td>$^2A'$ ← $^3A$</td>
<td>5.892</td>
<td>5.921</td>
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<td>$^2A$ ← $^1A'$</td>
<td>6.926</td>
<td>6.916</td>
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<td>$^2A$ ← $^1A$</td>
<td>6.549</td>
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<td>$^2A'$ ← $^1A'$</td>
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</table>

Table 5-2: List of experimental ionisation potentials (reported in eV) observed for Nb$_y$C$_y$ ($y = 0–6$) clusters. Also listed are calculated transitions and ionisation potentials: excluding ZPE, including ZPE, and offset IP (i.e. IP†).
The only isomer presented for Nb$_4$C$_4$ is X A, for which the singlet $^1A_1$ and triplet $^3B$ electronic states are calculated to be separated by only 0.067 eV; the latter being lower in energy. Since the lowest energy cationic state is a doublet, the ionisation transition from either the singlet or triplet state could access this cationic state, with both deviations between the calculated IP$^+$s and experimental IP being reasonable (+0.084 eV and +0.177 eV, respectively). On this basis alone, it is impossible to definitively assign the onset to either spin multiplicity state. However, the calculated vibrational IR spectrum of the singlet $^1A_1$ state is found to be in better agreement with the experimental IR-REMPI spectrum of Nb$_4$C$_4$ and so is the state from which the ionisation transition is assigned. This is discussed in more detail in Section 5.5.1.

Only one isomer of Nb$_4$C$_5$ (XI A) is examined at the extended basis set, as all other isomers calculated with the SDD basis set are significantly higher in energy (> 1.8 eV). The calculated IP$^+$ of XI A is much higher than the experimental IP, with a deviation of +1.315 eV. Furthermore, the IP$^+$ indicates that, similar to NbC, the
experimental IP of XI A will be higher than our ionisation limit (i.e. > 5.91 eV), so even if the isomer were present under our experimental conditions an ionisation onset would not be observed. One possible explanation for this onset is similar to that of the initial (weak) ionisation onset of Nb₄C₃ IX A; that ionisation occurs from the (metastable) $^3A'$ electronic state of XI A, rather than the $^1A'$ electronic state. Since this state is 1.054 eV higher in energy than the singlet state, the calculated IP$^\dagger$ for this ionisation transition is 0.281 eV higher than the experimental IP, a much more acceptable deviation (see Figure 5-17). One point in favour of such an assignment is the appearance of the PIE curve, which is weak and flat, similar to that seen for Nb₄C₃. A firmer assignment could be made if a second, stronger onset was observed, but as discussed above, it is expected to be beyond the photon range of our experiment. Although only a tentative assignment, this is again significant because isomer IX A contains a molecular C₂ unit.

The calculated IP$^\dagger$s of five Nb₄C₆ isomers are examined, with four isomers (XII A, XII B, XII C and XII D) containing 2 × C₂ units which only differ in their geometry by the orientation and/or bonding of these two units. The IP$^\dagger$ for XII A has a deviation of +1.110 eV, relative to the experimental IP, and isomers XII B, XII C and XII D also have large deviations of +1.217, +0.852 and +0.892 eV, respectively. These deviations are considered to be too large to assign to the observed ionisation onset. Furthermore, the IP$^\dagger$s for all four isomers are greater than our highest achievable photon energy. The remaining isomer, XII E with a C₃ unit, has quite good agreement between the calculated IP$^\dagger$ and experimental IP (+0.149 eV). However, this isomer is calculated to lie significantly higher in energy than XII A (+0.738 eV) and so could not be reasonably expected to be present in the experiment. Another possibility for assigning the observed ionisation onset is a metastable excited state, like that proposed for Nb₄C₅. The XI A isomer has a $^3A$ electronic state lying 0.914 eV higher than the $^1A_1$ state. Excitation from this state to the cationic doublet state, gives an IP$^\dagger$ only 0.222 eV higher than experimental value. The appearance of a weak and flat PIE curve, like that observed for Nb₄C₃ and Nb₄C₅, is again consistent with the onset originating from a low abundance state such as a metastable electronic state. Clearly it is difficult to separate these two possibilities (see Figure 5-17), which...
lead to the conclusions that Nb$_4$C$_6$ either contains $2 \times C_2$ units or a C$_3$ unit. Due to similarity with the Nb$_4$C$_5$ system the former tentative assignment is preferred.

Related to the isomers of Nb$_4$C$_6$ are several computational studies on the neutral Ti$_4$C$_8$ cluster by Wang and co-workers, Sun and co-workers, and Poblet and co-workers. The isomers proposed by Wang and Sun were based on a $2 \times 2 \times 2$ nanocrystal with all the C atoms substituted with C$_2$ units, although they differ in their bonding arrangement; the former structure had all the C$_2$ units bound in an ethylene configuration (C$_2^4$) and the latter had all the C$_2$ units bound in an acetylide configuration (C$_2^2$). The later Poblet study compared these two isomers and found the acetylide isomer to be ~ 1.4 eV lower in energy; however, they found another isomer, containing two C$_4$ units, to be ~ 0.8 eV lower again. No evidence of Nb$_4$C$_8$ appears in our mass spectra, either because it is not made in great abundance in our source and/or its IP is greater than 5.91 eV.

5.4.3 The Nb$_5$C$_y$ ($y = 0–6$) Cluster Series

Identical to the procedure for the Nb$_3$C$_y$ and Nb$_4$C$_y$ cluster series, a linear offset is applied to the Nb$_5$C$_y$ isomers so that the calculated and experimental IPs of Nb$_5$ overlap, with the resultant IP$^\dagger$ shown in the final column of Table 5-3. The linear offset of 0.263 eV is slightly less than those applied for both the Nb$_3$C$_y$ and Nb$_4$C$_y$ series (−0.368 and −0.359 eV, respectively). Figure 5-18 shows the calculated IP$^\dagger$ s of the isomers (△) for each Nb$_5$C$_y$ cluster species, as well as the experimental IP (▲).

For Nb$_5$C the two energetically close isomers XIV A and XIV B both have calculated IP$^\dagger$ s in good agreement with the experimental value (deviations of +0.233 and +0.138 eV, respectively). As the IP$^\dagger$ s cannot distinguish between these two isomers, the ionisation onset is assigned to the lowest energy isomer (XIV A). This is not a definitive assignment though as XIV B is only very slightly higher in energy (ΔE = +0.072 eV).
Table 5-3: List of experimental ionisation potentials (reported in eV) observed for Nb$_5$C$_y$ ($y = 0–6$) clusters. Also listed are calculated transitions and ionisation potentials: excluding ZPE, including ZPE, and offset IP (i.e. IP$^\dagger$).

The experimental IP of Nb$_5$C$_2$ is quite low. The two Nb$_5$C$_2$ isomers XV A and XV B are calculated to be quite close in energy ($\Delta E = +0.118$) but exhibit quite different calculated IP$^\dagger$s. The lowest energy isomer XV A has an IP$^\dagger$ only 0.132 eV higher than the experimental value. Conversely, isomer XV B has a much higher IP$^\dagger$, with a deviation of +0.971 eV relative to the experimental IP. Therefore, the experimental IP is assigned to XV A. No definitive second ionisation onset is observed in the Nb$_5$C$_2$ PIE spectrum.
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Figure 5-18: Graph showing experimental IP values for the Nb$_5$C$_y$ clusters as a function of y. Also shown on the same scale are the offset values, IP$^\dagger$, calculated using DFT. The letters (A, B, etc.) denote the isomers for that particular cluster (see text for details).

For Nb$_5$C$_3$ only one isomer is examined at the extended basis set (XVI A), as all isomers with the SDD basis set are much higher in energy (> 2 eV). The calculated IP$^\dagger$ of XVI A is in good agreement with the experimental IP, with a deviation of +0.223 eV. Also the calculated IR vibrational spectrum of XVI A is in good agreement with the experimental Nb$_5$C$_3$ IR-REMPI spectrum (see Section 5.5.1).

The IP$^\dagger$s of four isomers for Nb$_5$C$_4$ are considered. The lowest energy isomer XVII A has a deviation of +0.516 between its calculated IP$^\dagger$ and the experimental value, which is on the borderline between what is considered to be an acceptable deviation. Of the remaining three isomers, XVII C has the smallest deviation between the calculated IP$^\dagger$ and experimental value (~0.103 eV). However, as the calculated IP$^\dagger$s of the isomers assigned to Nb$_5$C, Nb$_5$C$_2$ and Nb$_5$C$_3$ all overestimate the experimental IPs, the IP$^\dagger$ of XVII C is not consistent with this trend (see Figure 5-18). Furthermore, the experimental IP of Nb$_5$C$_4$ is very similar to those of Nb$_5$C$_5$ and Nb$_5$C$_6$, which is not held for Nb$_5$C$_4$ XVII C in comparison to the IP$^\dagger$s of the isomers assigned to the
onsets of Nb$_5$C$_5$ and Nb$_5$C$_6$ (see below). The remaining two isomers XVII B and XVII D both have calculated IP$^\dagger$'s in good agreement with the experimental IP, with deviations of +0.331 and +0.162 eV, respectively. However, as XVII B is much lower in energy than XVII D ($\Delta E = +0.132$ and +0.650 eV, respectively), the former is assigned to the experimental IP. This is not a definitive assignment as despite the IP$^\dagger$ of XVII B being in good agreement with the experimental value and having a low $\Delta E$, isomers XVII A and XVII D cannot be totally discounted.

The four Nb$_5$C$_5$ isomers XVIII A, XVIII B, XVIII C and XVIII D have deviations between the calculated IP$^\dagger$ and the experimental IP of +0.115 eV, +0.130 eV, +0.560 and +0.314, respectively. Isomer XVIII C is discounted due to its large deviation. The calculated IP$^\dagger$'s of XVIII A and XVIII B are in excellent agreement with the experimental value, while XVIII D is in reasonable agreement. However, isomer XVIII A is assigned to the experimental IP as it is the lowest energy isomer by 0.333 eV, relative to XVIII B. This assignment is an interesting result, as XVIII A contains a molecular C$_2$ unit.

For Nb$_5$C$_6$ the deviation between the calculated IP$^\dagger$'s and experimental value for the isomers XIX A and XIX B are +0.169 and +0.547 eV, respectively. As the IP$^\dagger$ of XIX A is in much better agreement with the experimental value and is calculated to be significantly the lowest energy isomer by 1.112 eV, it is assigned to the observed ionisation onset. Isomer XIX A contains two molecular C$_2$ units.
5.5 Discussion on Niobium-Carbide Clusters

5.5.1 Comparison to Previous Spectroscopic Data

The IPs of the niobium-carbide clusters Nb$_3$C$_2$, Nb$_4$C$_4$, and Nb$_5$C$_2$ have been determined in previous studies and our measurements are in excellent agreement.$^5$,$^11$ Furthermore, in these previous studies the species Nb$_3$C$_2$ and Nb$_5$C$_2$ had their PFI-ZEKE spectra recorded. The Nb$_5$C$_2$ spectrum was assigned to the trigonal bipyramid structural isomer.

The PFI-ZEKE spectrum of Nb$_5$C$_2$ showed a small number of bands separated by 9 cm$^{-1}$, with the first band assigned to the 0-0 transition. The other bands are believed to be sequence structure as the band intensities varied with the cluster source temperature. However, no calculations were performed on the isomeric structures of Nb$_5$C$_2$. As the calculated IP$^+$ of the lowest energy isomer in this thesis (Nb$_5$C$_2$ XV A) is in excellent agreement with the IP from the PFI-ZEKE and present PIE studies, it is proposed that this isomer is that for which the PFI-ZEKE spectrum was recorded. Examination of the calculated geometries (Appendix III) indeed shows no significant structural change upon ionisation, in agreement with the lack of vibrational progression observed. As this previous study was conducted utilising a liquid nitrogen cooled cluster source, there is a greater probability that the PFI-ZEKE spectrum results from the lowest energy isomer. This suggests that the extended basis set calculations for Nb$_5$C$_2$ are accurate in predicting the ordering of the XV A and XV B isomers, whereas the SDD basis set has XV B lower in energy.

The IR-REMPI spectra for Nb$_4$C$_4$ and Nb$_5$C$_3$ have been recorded previously.$^7$ Both experimental spectra display a single broad vibrational absorption band, centred at 675 and 660 cm$^{-1}$ for Nb$_4$C$_4$ and Nb$_5$C$_3$, respectively. The spectra were analysed by correlation with one of the two electron energy loss spectroscopy bands of the fcc (100) niobium-carbide surface,$^{28}$ which supported the notion of the 2×2×2 nanocrystal structure for Nb$_4$C$_4$ and a substituted 2×2×2 cubic structure for Nb$_5$C$_3$. The broad nature of the absorption is believed to be due to several reasons; overlapping vibrational modes, the multi-photon nature of the experiment and the finite internal
energy content of the clusters. Although spectra obtained in single photon IR absorption experiments are not identical to those obtained in IR-REMPI experiments (e.g. intensities of modes can be different due to differing vibrational anharmonicity and internal vibrational redistribution rates), they have been shown to be similar. Figure 5-19 (Nb₄C₄) and Figure 5-20 (Nb₅C₃) show the experimental spectra and our DFT-calculated IR spectra for the two species (between 370 and 760 cm⁻¹ with no scaling).

NOTE:
This figure is included on page 86 of the print copy of the thesis held in the University of Adelaide Library.

**Figure 5-19:** Calculated IR spectra (FWHM = 4 cm⁻¹) for Nb₄C₄ in the ¹A₁ (trace a) and ³B (trace b) electronic states. The upper trace shows the IR-REMPI spectrum of Nb₄C₄, reproduced with permission from Ref 7.

The only isomer considered here for Nb₄C₄ is X A (the 2×2×2 nanocrystal), for which singlet ¹A₁ and triplet ³B electronic states are calculated to be separated by only 0.067 eV; the latter being lower in energy. It may be possible to determine if one multiplicity state is preferred experimentally by re-examining the features of the IR-REMPI spectrum in combination the computational data. It is readily seen that two vastly different spectra are predicted for the two different states (Figure 5-19). Due to
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its high symmetry, the $^1A_1$ state only exhibits two features, both above 650 cm$^{-1}$, which are the IR-active triply-degenerate modes ($t_2$ in $T_d$) corresponding to in-phase and out-of-phase Nb-C vibrations. The motion of the atoms in one component of these two modes is shown in Figure 5-21. Although only one absorption band was observed in the experimental IR-REMPI spectrum, its breadth almost completely encompasses both of the calculated absorption bands. In contrast, the $^3B$ state exhibits many more intense features (both $a$ and $b$ modes in $C_2$ symmetry), particularly below 600 cm$^{-1}$, where there are no features in the experimental spectrum. Therefore, given the postulate that the conditions of generating metal-carbide clusters is similar between the two experiments (i.e. Ref. 7 and this study), it is contended that the Nb$_4$C$_4$ cluster exists in the singlet state and is the state from which the ionisation transition is assigned.

![Figure 5-20](image.jpg)

**Figure 5-20:** Calculated IR spectrum (FWHM = 4 cm$^{-1}$) for Nb$_5$C$_3$ (lower trace). The upper trace shows the IR-REMPI spectrum of Nb$_5$C$_3$, reproduced with permission from Ref 7.

The calculated IR spectrum of Nb$_5$C$_3$ XVI A is shown in Figure 5-20. This substituted 2×2×2 cubic isomer is found to be significantly the lowest in energy. The two most intense modes ($e$ and $a_1$ in $C_{3v}$) are observed at 691 and 709 cm$^{-1}$ (shown in Figure 5-21). These Nb-C absorption bands are in good agreement with the maximum of the IR-REMPI spectrum.

NOTE:
This figure is included on page 87 of the print copy of the thesis held in the University of Adelaide Library.
Figure 5-21: Shown are the two IR-active vibrational modes (one component only) calculated for the singlet state of Nb₄C₄. Also shown are the two most IR-active vibrational modes calculated for Nb₅C₃. Each mode is represented by the equilibrium position and two extrema.
5.5.2 Onset of Carbon-Carbon Bonding

In the growth patterns of niobium-carbide clusters it is important to know at what point during sequential carbon addition do the bonding arrangements change, \textit{i.e.} when does C-C bonding become favourable in addition to Nb-C bonding.

In the Nb$_3$C$_y$ cluster series C-C bonding was found to be energetically stable for Nb$_3$C$_y$ clusters when $y \geq 4$, as a very low-lying isomer ($\Delta E = +0.183$) containing a C$_2$ unit was assigned to the experimental IP. In the Nb$_4$C$_y$ cluster series, C-C bonding was found to occur when $y \geq 5$, with the lowest energy isomers for Nb$_4$C$_5$ and Nb$_4$C$_6$ containing one and two C$_2$ units, respectively. Therefore, for both the Nb$_3$C$_y$ and Nb$_4$C$_y$ series the onset of C-C bonding occurs when the number of C atoms is greater than the number of Nb atoms (\textit{i.e.} $y > x$).

The C-C bonding onset point is different in the Nb$_5$C$_y$ cluster series, where it is observed to occur when $y \geq 5$ (\textit{i.e.} $y \geq x$); the lowest energy isomers for Nb$_5$C$_5$ and Nb$_5$C$_6$ contain one and two C$_2$ units, respectively. This onset is quite surprising as there are still free Nb faces available on the prolate trigonal bipyramid Nb$_5$ cluster for C atoms to bind to. This is unlike the situation in the Nb$_4$C$_y$ series, where geometrically there are no more free Nb faces available on the tetrahedral Nb$_4$ cluster after Nb$_4$C$_4$. The reasoning for this different onset in the Nb$_5$C$_y$ series is unclear, although it appears to be related to the degree of oxidation that the Nb$_5$ cluster is willing to undergo, as a C atom (formally C$_4^-$) will oxidise the cluster more than an acetylide C$_2$ unit (formally C$_2^2-$). Indeed, analysis of the total charge on the Nb atoms in the two lowest energy isomers of Nb$_5$C$_5$ (Figure 5-22), which have an energy difference of 0.333 eV, show that the isomer containing a C$_2$ unit has a lower charge (+3.65) than the isomer containing no C-C bonding (+3.85). This extent of total charge on the Nb atoms due to oxidation seem to be favourable for the Nb$_5$ cluster, as the lowest energy isomer of Nb$_5$C$_6$ (which has two C$_2$ units) has a similar charge (+3.87) to the former two Nb$_5$C$_5$ isomers (see Appendix III). Additionally, the Nb butterfly motifs available in the oblate trigonal bipyramid Nb$_5$ cluster can totally satisfy the bonding requirements of an acetylide C$_2$ unit (two $\sigma$ and two $\pi$ bonds).
interactions), whereas the Nb faces on the tetrahedral Nb₄ cluster cannot (one σ and two π interactions).

Figure 5-22: The two lowest energy isomers of Nb₅C₅ and their NBO atomic charges: a) XVIII A and b) XVIII B.

5.5.3 Low-Lying Isomers and Metastable Electronic States

An interesting result of this study is the assignment of the observed ionisation onsets for Nb₃C₄, Nb₅C₄, and possibly Nb₄C₆, to a structural isomer that is not the global minimum. As stated before, this does not imply that low-lying isomers are not present for other species in our experiment but rather that the threshold ionisation technique favours the detection of isomers with the lower IP, with the caveat that they are present in sufficient concentration. If the initial onset of ionisation is strong (as would be for the lowest energy isomer), it is unlikely that further onsets due to other isomers will be discernable. Because of the uncertainty in the accuracy of the DFT calculations to predict the relative energies of isomers, it is entirely possible that any of the minima within 0.5 eV may be the global minimum. This is exemplified by the fact that even changing basis sets can lead to significant changes in relative energies; e.g. use of the extended basis set for the V A and V B isomers of Nb₃C₄ decreases the calculated energy difference from 0.679 to 0.183 eV, and for the XII A and XII E isomers of Nb₄C₆ increases the energy difference from 0.546 to 0.738 eV.

Under the conditions of a standard ablation source coupled to a condensation tube, where a large number of collisions with the carrier gas occur, clusters attain thermal equilibrium in the rotational and vibrational degrees of freedom.¹²,²⁹ Electronic cooling is somewhat different and long-lived electronically excited states are well known in several metal-containing systems.³⁰ However, this issue is deferred until
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later as it is the notion of isomer temperature that it is to be addressed first. This concept is well established from early microwave molecular beam studies of organic molecules where relative abundances of various isomers (or more correctly rotational conformers, which result from rotation of single bonds) with well-known energy differences can be controlled by varying the conditions (pressure, carrier gas, etc) of the supersonic expansion.31 One example is the rotation of the formyl group in propanal which produces two stable conformers with differing dihedral angles whose abundances can be controlled by changing the carrier gas and heating the source.31-33

The concept of isomers is less established for metal clusters due to the difficulty in experimentally determining their geometric structures. About 15 years ago, several groups published work that showed the presence of at least two isomers for the clusters Nb$_9$–Nb$_{12}$, which exhibited different chemical reactivity (with D$_2$ and N$_2$) and different IPs.15,34,35 For Nb$_9$, a bi-exponential fit to the reaction rate data revealed that the reactive isomer, $R$, is more abundant in the molecular beam than the unreactive isomer, $U$, by 25:1. The Nb$_9$ PIE curve showed an onset at 4.92 eV but following titration with D$_2$, (and hence removal of the $R$ form) the PIE curve revealed the onset of the $U$ form 0.28 eV higher in energy.15 More recently, IR-MPD experiments on the Nb$_9$-Ar cluster similarly showed the presence of two isomers, with different IR spectra, and a relative abundance of 1:0.3.36 These workers also calculated DFT structures and energies for three isomers ($A$, $B$ and $C$) which had relative energies of 0.0, 0.15 and 0.82 eV, respectively, but only $A$ and $B$ correlated with the IR spectra. These two isomers, $A$ and $B$, were then correlated with the previous IP and reactivity data and it was concluded that $B$ and $A$ were the $R$ and $U$ isomers, respectively. Although both sets of data confirm that the $B$ (or $R$) isomer is the more abundant in the various cluster sources, this isomer is calculated to be 0.15 eV higher than the global minimum energy structure.

As noted in a recent PIE study on carbon clusters generated by laser ablation, at highly elevated internal temperatures the relative concentration of isomers for a cluster species is not only dependant on their relative energies, but also their entropies.37 For example the cyclic structural isomer of C$_6$ is calculated to be ~0.66 eV lower in energy than the linear isomer, yet at ~1100 K they have similar free energies. Due to the high energy laser ablation process and large condensation energy
of metal-carbide clusters, the temperatures at which the clusters are formed and the
internal energies retained, due to incomplete quenching by the carrier gas, may be
several hundreds of degrees above room temperature. At these temperatures a low-
lying isomer may have a similar concentration to the lowest energy isomer, if the
former has a larger entropy component. Once these isomers exit the condensation tube
and supersonically expand into vacuum they will receive internal cooling, preserving
their relative concentrations from the hot cluster source. Although the actual
temperature of the clusters when they exit the cluster source is unknown, it is
anticipated that the clusters undergo collisional cooling in our long condensation tube
(15 mm). The IP values for several species (Nb$_3$, Nb$_4$, Nb$_3$C$_2$ and Nb$_5$C$_2$) are slightly
less (< 0.05 eV) than those measured in previous studies that utilise a liquid nitrogen-
cooled source, which is consistent for clusters with a vibrational temperature of ~300
K.$^{5,11,15}$ As the clusters will receive a certain extent of cooling in the supersonic
expansion, the temperature of the clusters in the condensation tube is estimated to be
somewhat greater than 300 K, so that entropy may play a part in the relative
concentration of isomers in our experiment.

Based upon the preceding discussion, it therefore seems reasonable that in the present
experiments one can consider two potentially observable isomers whose relative
abundance may vary from 1:1 (i.e. degenerate in energy) to 1:10, assuming that a
concentration of ~10% would be required for sufficient ion signal to be detected and
that they have similar efficiencies for ionisation. Therefore, it is possible that the
ionisation onsets of Nb$_3$C$_4$ and Nb$_5$C$_4$ are due to a low-lying isomer (Nb$_3$C$_4$ V B $\Delta E =
+0.183$ eV and Nb$_5$C$_4$ XVII B $\Delta E = +0.132$ eV). For Nb$_4$C$_6$, the calculated energy
difference is 4–5 fold higher (XII E, $\Delta E = +0.738$ eV) and the argument is less
convincing, hence the assignment to a metastable state is preferred, which is discussed
now.

For Nb$_4$C$_3$ (the first, weak onset), Nb$_4$C$_5$, and also Nb$_4$C$_6$, the onset of ionisation is
assigned to a transition that emanates from a long-lived, or metastable, electronic
state. For all three systems, the ground state is of singlet multiplicity and the proposed
metastable state is a triplet, both of which can access the lowest energy doublet state
of the cation. In this sense, the assignment is plausible in that one could argue that any
cluster species formed in the triplet state does not “collisionally cool” into the lower-energy singlet manifold, due to the forbidden spin-crossing. Such a metastable state would have to survive approximately $10^4-10^5$ collisions in the condensation tube before being supersonically cooled and isolated. Additionally, it would be required to have a lifetime of at least several microseconds, so that it does not radiate to the singlet ground state before being interrogated by the ionisation laser. Note that the situation is vastly different for the Nb$_3$C$_y$ and Nb$_5$C$_y$ clusters where the potentially metastable (excited) quartet states cannot access the lowest energy singlet state of the cations. Thus, even if significant population is maintained in the quartet states, the observed transition will be to a triplet (or quintet) state, which are calculated to be approximately the same energy as the doublet-singlet transition (see Appendix II) and hence will not be obvious in the PIE spectra.

Long-lived excited electronic states have certainly been observed in small metal-containing systems isolated in supersonic expansions. The CoC radical has a $^2\Sigma^+$ ground state, as observed by laser induced fluorescence, but electronic transitions from an excited $^2\Delta_{5/2}$ state only 221 cm$^{-1}$ higher in energy are also observed due to significant (metastable) abundance in the molecular beam.$^{30}$ Although it is well known that the density of states increases dramatically for dimers, trimers and larger clusters, and therefore a higher probability of deactivating excited spin states,$^{38}$ Morse and co-workers have recorded jet-cooled spectra directly from metastable excited states of Ni$_2$ (an $\Omega = 4$ state calculated to be $\sim 800$ cm$^{-1}$ higher than the $\Omega = 0$ ground state)$^{39}$ and Pt$_2$ (an unknown excited state, possibly $\Omega = 5$, that is calculated to be 614 cm$^{-1}$ higher than $\Omega = 0$ ground state).$^{40}$ For larger species, Scoles and co-workers recorded excitation spectra from metastable states of the Na$_3$ and K$_3$ alkali clusters formed in helium nanodroplets.$^{41}$ However, for larger transition metal clusters only recent IR-MPD experiments on the Nb$_5^+$-Ar and Nb$_6$-Ar clusters show spectral features possibly arising from both singlet and triplet states, calculated to be only 0.16 and 0.01 eV different in energy, respectively.$^{24}$ In both cases, the observation of spectroscopic signatures from two spin multiplicities is indicative of significant population residing in the higher energy state, thus making them metastable on the time scale of the experiment. To sum up this discussion, in the case of Nb$_4$C$_3$, the assignment of the initial, weak ionisation onset to a metastable triplet state, and not a
higher energy isomer, is considered to be very strong. For Nb\textsubscript{4}C\textsubscript{3} and Nb\textsubscript{4}C\textsubscript{5}, the assignment to a metastable state is the most plausible explanation, particularly given that both PIE curves are weak and flat, very similar to the first onset of Nb\textsubscript{4}C\textsubscript{3}, indicating low abundance.

### 5.5.4 IP trends, Molecular Orbitals and HOMO-LUMO gaps

The energy of an adiabatic ionisation transition is determined by the relative difference in energy between the ground states of the neutral and cation of a molecule. Koopmans theorem states that for a closed shell molecule the ionisation energy of an electron in a particular MO is approximately equal to the negative energy of the MO energy calculated by a self consistent field method.\textsuperscript{42} While Koopmans theorem does have limitations since electron correlation and electronic structure reorganisation upon ionisation is not considered, often these two effects cancel each other out.\textsuperscript{42} While DFT uses Kohn-Sham orbitals, which lack the physical implications of Hartree Fock orbitals, Koopmans theory has been shown to approximately hold for large molecular systems if the classical Coulomb electrostatic charging energy is incorporated.\textsuperscript{43}

As shown in Table 5-4, for the niobium-carbide cluster isomers assigned to experimental IPs for each species, the relative negative MO energies from which the electron is removed in the ionisation transition (predominantly always the HOMO) correlate extremely well with the experimental IP trend. Note that species where the ionisation onsets are assigned to metastable states (\textit{i.e.} Nb\textsubscript{4}C\textsubscript{3} and Nb\textsubscript{4}C\textsubscript{5}) are not considered. The negative MO energies range between 1.0 to 1.7 eV lower than the corresponding calculated IP, depending on the Nb\textsubscript{x}C\textsubscript{y} series. Agreement between the two trends shows that the energy of the HOMO is one of the primary factors in determining the IP of the niobium-carbide clusters.

Examination of the appearance of the HOMOs may give insight into its character and as to why certain clusters have low IPs, while others high IPs. Furthermore, the HOMO-LUMO gaps of the clusters are also presented (Table 5-4). The absolute value of the HOMO-LUMO gap can give an indication of the stability of a cluster and identify possible electronically “closed shell” species.
### Chapter 5: Niobium-Carbide Clusters

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<th>Cluster</th>
<th>Expt. IP</th>
<th>Calc. IP (inc. ZPE)</th>
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<th>Cation</th>
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**Table 5-4:** List of experimental IPs, calculated IPs (inc. ZPE), molecular orbital energies from which the ionisation transition occurs and the HOMO-LUMO gaps (neutral and cation) for the isomers assigned to the experimental ionisation onsets. Note that if a low-lying isomer has been assigned to an ionisation onset, the lowest energy isomer is also presented. All reported values in eV.
Chapter 5: Niobium-Carbide Clusters

$\text{Nb}_3\text{C}_y$ Clusters

For all $\text{Nb}_3\text{C}_y$ clusters, apart from $\text{Nb}_3$, the MO from which the ionisation transition occurs is the HOMO; i.e. the $\text{Nb}_3$ transition is from the neutral doublet state to cationic triplet, rather than the cationic singlet state. References made to changes in the geometry and charges can be inspected in Appendix III.

For $\text{Nb}_3\text{I A}$ (HOMO–1) and $\text{Nb}_3\text{C II A}$ (HOMO) the MOs appear to be primarily Nb-Nb bonding in character (Figure 5-23). However, the HOMO of $\text{Nb}_3\text{C II A}$ is substantially lower in energy than the HOMO–1 of $\text{Nb}_3\text{ I A}$. This is an interesting result as the MOs are almost identical in appearance. The $\text{Nb}_3\text{C II A}$ HOMO is most likely lower in energy as the Nb atoms possess a positive charge, because of the interaction with the electronegative C atom.

The HOMO of $\text{Nb}_3\text{C}_2\text{ III A}$ is shown in Figure 5-24. It has an antibonding interaction across a Nb-Nb edge, explaining its low IP as removal of the electron from this MO stabilises the cation. Indeed, the Nb-Nb bond lengths decrease overall upon ionisation. Furthermore, the increase in the HOMO-LUMO gap is substantial upon ionisation (+1.93 eV), due to the quite different character of the degenerate HOMO/HOMO–1 and LUMO/LUMO+1 in the cation. The former are strongly Nb-Nb and Nb-C bonding, while the later are overall Nb-Nb antibonding in character (Figure 5-24). The origin of the Jahn-Teller distortion to $C_s$ symmetry in $\text{Nb}_3\text{C}_2\text{ III A}$ is because the addition of an electron in $\text{Nb}_3\text{C}_2^+$ III A$^+$ singly populates a degenerate orbital, which
has been noted before. The HOMO-LUMO gap in Nb$_3$C$_2^+$ III A$^+$ is the largest observed for all neutral and cationic niobium-carbide clusters investigated in this study (3.27 eV) and in consideration of the character for the HOMO and LUMO can be thought of as having a closed shell electronic structure.

The HOMOs of Nb$_3$C$_3$ IV A and Nb$_3$C$_4$ V B appear to be Nb-Nb bonding and overall Nb-Nb non-bonding/antibonding in character, respectively (Figure 5-25), although they are similar in energy. The HOMO of the lowest energy isomer of Nb$_3$C$_4$ (V A) is much lower in energy than that of the low-lying isomer (V B); i.e. VA has a higher IP than VB. This is due to the former being Nb-C bonding in character, which has been found to be the primary source of stability for niobium-carbide clusters.$^{14}$

![Figure 5-24: Calculated energy level diagrams for the neutral and cationic Nb$_3$C$_2$ cluster (occupied levels are blue, unoccupied are red). Also shown are illustrative representations for the HOMO of Nb$_3$C$_2$ and the HOMO/HOMO–1 and LUMO/LUMO+1 of Nb$_3$C$_2^+$. Isomer labels and MO symmetries are also given.](image-url)
Figure 5-25: Illustrative representations for the HOMOs of Nb$_3$C$_3$ and the two lowest energy isomers of Nb$_3$C$_4$. Isomer labels and MO symmetries are also given.

*Nb$_4$C$_y$ Clusters*

For all the discussed Nb$_4$C$_y$ clusters, the HOMO is the MO from which the ionisation transition occurs. References made to changes in the geometry and charges can be inspected in Appendix III.

Figure 5-26: Illustrative representations for the HOMOs of Nb$_4$, Nb$_4$C and Nb$_4$C$_2$. Isomer labels and MO symmetries are also given.

The HOMO of Nb$_4$ VI A is triply degenerate, totally occupied, and appears Nb-Nb bonding in character (Figure 5-26, only one component shown). Upon ionisation the geometry undergoes Jahn-Teller distortion to lower symmetry ($C_2$). The HOMOs of Nb$_4$C VII A and Nb$_4$C$_2$ VIII A have similar energies to that of Nb$_4$ VI A, with the HOMOs of the former two clusters being primarily Nb-Nb bonding in character also (Figure 5-26).
The HOMO of Nb$_4$C$_3$ IX A is also primarily Nb-Nb bonding in character (Figure 5-27). There is only one major bonding region, which is located above the free Nb face. This is consistent with the Nb-Nb edges and charges of the Nb atoms contained in this free Nb face both increasing considerably upon ionisation. The HOMO-LUMO gap is large for the neutral (2.36 eV), due to the different character of the neutral’s HOMO compared to the LUMO, with the latter being Nb non-bonding and localised on the unique Nb atom, which is opposite to the free Nb face (Figure 5-27).

![Figure 5-27](image_url)  
*Figure 5-27: Calculated energy level diagrams for the neutral and cationic Nb$_4$C$_3$ cluster (occupied levels are blue, unoccupied are red). Also shown are illustrative representations for the HOMO and LUMO of Nb$_4$C$_3$. Isomer labels and MO symmetries are also given.*

The energy of the HOMO for Nb$_4$C$_4$ X A is substantially higher than those of the previously discussed Nb$_4$C$_y$ isomers. This large difference appears to originate from the HOMO of Nb$_4$C$_4$ X A no longer appearing strongly Nb-Nb bonding in character.
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The degenerate HOMO/HOMO−1 has \( d_{x^2-y^2} \) AOs located on all four Nb atoms and arranged to have Nb-Nb bonding interactions (Figure 5-28, only one component shown). However, due to the long Nb-Nb bond lengths, the MOs are more likely closer to being Nb non-bonding in character, consistent with its low IP. The triply degenerate LUMO/LUMO+1/LUMO+2 appear to be weakly Nb antibonding/Nb non-bonding in character, with all Nb atoms having outwards pointing \( d_{z^2} \) AOs. (Figure 5-28, one component). As a result of its closed geometric structure, the electronic structure of \( \text{Nb}_4\text{C}_4 \) is unique, in that there is a large energy difference between the degenerate HOMO/HOMO−1 and the remaining occupied MOs. This is due to the latter being primarily Nb-C bonding in character.

**Figure 5-28:** Calculated energy level diagrams for the neutral and cationic singlet \( \text{Nb}_4\text{C}_4 \) cluster (occupied levels are blue, unoccupied are red). Also shown are illustrative representations for the HOMO and LUMO of the \( \text{Nb}_4\text{C}_4 \). Isomer labels and MO symmetries are also given.
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\textit{Nb}_3\textit{C}_\textit{y} \textit{Clusters}

For all \textit{Nb}_3\textit{C}_\textit{y} clusters, apart from \textit{Nb}_3\textit{C}_4, the MO from which the ionisation transition occurs is the HOMO. References made to changes in the geometry and charges can be inspected in Appendix III.

The HOMO of \textit{Nb}_3 \textit{XIII A} appears to be \textit{Nb} non-bonding in character, localised on the two axial \textit{Nb} atoms (Figure 5-29). Indeed these two \textit{Nb} atoms are the only atoms which significantly increase in charge upon ionisation. The HOMO of \textit{Nb}_3\textit{C} \textit{XIV A} is similar in energy and is also principally located on the two axial \textit{Nb} atoms (Figure 5-29).

\textit{Figure 5-29: Illustrative representations for the HOMOs of \textit{Nb}_3, \textit{Nb}_3\textit{C} and \textit{Nb}_3\textit{C}_2. Isomer labels and MO symmetries are also given.}

The calculated HOMOs of \textit{Nb}_3\textit{C}_2 \textit{XV A} and \textit{Nb}_3\textit{C}_3 \textit{XVI A} are similar in energy, with the two species having the two lowest IPs for the \textit{Nb}_3\textit{C}_\textit{y} series. Both HOMOs appear to be \textit{Nb} non-bonding in character. For \textit{Nb}_3\textit{C}_2 \textit{XV A} the HOMO is located on all three equatorial \textit{Nb} atoms (Figure 5-29), while for \textit{Nb}_3\textit{C}_3 \textit{XVI A} the HOMO is localised on the axial \textit{Nb} atom bound to all three \textit{C} atoms (Figure 5-30). It is unclear as to why both these clusters’ HOMOs are higher in energy relative to \textit{Nb}_3 \textit{XIII A} and \textit{Nb}_3\textit{C} \textit{XIV A}; both the latter also have HOMOs which also appear \textit{Nb} non-bonding in character. A possible reason for the higher energy of the HOMO for \textit{Nb}_3\textit{C}_3 \textit{XVI A} is that when occupied it has a destabilising repulsive effect from interaction with the three negatively charged \textit{C} atoms. Indeed, the \textit{Nb}-\textit{C} bond lengths between these atoms decrease significantly upon ionisation. Ionisation of \textit{Nb}_3\textit{C}_3 \textit{XVI A} causes the cation to possess a large HOMO-LUMO gap (2.97 eV).
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Figure 5-30: Calculated energy level diagrams for the neutral and cationic Nb$_5$C$_3$ cluster (occupied levels are blue, unoccupied are red). Also shown are illustrative representations for the HOMO and HOMO–1/HOMO–2 of Nb$_5$C$_3$. Isomer labels and MO symmetries are also given.

For Nb$_5$C$_4$ XVII B (HOMO–1), Nb$_5$C$_5$ XVIII A (HOMO) and Nb$_5$C$_6$ XIX A (HOMO) the MOs appear to be primarily weakly Nb-Nb bonding/Nb nonbonding in character (Figure 5-31 and Figure 5-32) and are similar in energy. For example, the HOMO of Nb$_5$C$_6$ XIX A is predominantly located on two equatorial Nb atoms, with the bond length between these two Nb atoms only very slightly decreasing upon ionisation.
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**Figure 5-31:** Illustrative representations for the HOMO and HOMO−1 of a low-lying isomer and the HOMO of the lowest energy isomer of Nb$_5$C$_4$. Isomer labels and MO symmetries are also given.

**Figure 5-32:** Illustrative representations for the HOMOs of Nb$_5$C$_5$ and Nb$_5$C$_6$. Isomer labels and MO symmetries are also given.

In summary, the HOMOs for the niobium-carbide clusters are found to be primarily Nb in character. The low IPs of Nb$_3$C$_2$ and Nb$_4$C$_4$ are shown to be due to their HOMOs being Nb-Nb antibonding and Nb non-bonding in character, respectively. Interpretation of the low IPs for Nb$_5$C$_2$ and Nb$_5$C$_3$ are less straight forward. The cationic electronic structure of Nb$_3$C$_2$ is found to possess the largest HOMO-LUMO gap of all the examined clusters and can be considered as having a closed shell electronic structure.

### 5.5.5 Thermodynamic Cycle

Niobium-carbide clusters are constructed from electropositive Nb and electronegative C atoms and consequently a certain component of ionic bonding will be present. Upon ionisation, the increase in charge will primarily be located on the Nb atoms and will
cause the electrostatic potential between the positive Nb and negative C atoms of the system to increase. However, certain geometries will enhance the electrostatic interaction upon ionisation. The thermodynamic cycle shown below infers that if the IP of a Nb$_x$C$_y$ cluster is lower than that of the corresponding bare Nb$_x$ cluster, then the Nb-C bonding is stronger in the cation than in the neutral:

\[
\text{IP Nb}_x - \text{IP Nb}_x\text{C}_y = D_0 \text{Nb}_x\text{C}_y^+ - D_0 \text{Nb}_x\text{C}_y
\]

The Nb$_x$C$_y$ clusters with the greatest reductions in IP relative to their corresponding bare Nb$_x$ cluster are Nb$_3$C$_2$, Nb$_4$C$_4$, Nb$_5$C$_2$ and Nb$_5$C$_3$. Based on their experimental IP values, these species have Nb-C dissociation energies which range between being 0.77 to 1.17 eV stronger in the cationic state relative to the neutral state. There is an overall decrease in the calculated Nb-C bond lengths for all the isomers assigned to the experimental IPs for these species (see Appendix III). The DFT calculations indicate that none of these isomers involves ionisation from a HOMO that is primarily Nb-C antibonding in character. The stronger Nb-C bonding upon ionisation is believed to be mainly electrostatic in nature, where the increase in positive charge on the underlying Nb$_x$ cluster is distributed in such a way to increase the Nb-C attraction.

For Nb$_3$C$_2$ **III A** and Nb$_4$C$_4$ **X A**, the cationic structures have symmetries of $D_{3h}$ and $D_{2d}$, respectively, which do not allow the clusters to possess a dipole moment. This facilitates a uniform contraction of all the Nb-C bond lengths. Indeed the fcc structure of Nb$_4$C$_4$ **X A** is the same as found in other solids which are electrostatically bound, e.g. NaCl. In Nb$_3$C$_2$ **XV A** the stronger Nb-C bonding in the cation appears to occur as the C atoms are reasonably evenly bound to every type of equivalent (by symmetry) Nb atom. As the increase in charge upon ionisation is quite equally delocalised over all the Nb atoms, the Nb-C electrostatic interaction will increase. For Nb$_5$C$_3$ **XVI A** this type of uniform Nb-C contraction scheme is not apparent. The increase in charge upon ionisation is greatest on the two axial Nb atoms, despite the HOMO being localised on the axial Nb atom bound to all the C atoms. The increase in the Nb-C electrostatic attraction between this axial Nb atom, which the HOMO is located on, appears quite strong as the Nb-C bond lengths decreases significantly.
5.6 Summary and Future Directions

In summary, this chapter has shown that the isomeric structures of niobium-carbide clusters can be inferred by the determination of their IPs by PIE experiments in combination with DFT calculations on candidate isomers. The clusters Nb$_3$C$_2$, Nb$_4$C$_4$, Nb$_5$C$_2$ and Nb$_5$C$_3$ display the largest IP reductions upon C addition for their corresponding cluster series.

By no means is this a definitive method for the determination of the structures, as energetically competitive isomers may have similar calculated IPs (e.g. Nb$_5$C and Nb$_5$C$_5$) and although there is confidence that the global minimum has been located, energetically favourable isomers may have not been identified computationally. Yet, determination of the experimental IPs was found to be critical in allowing structural assignments to be made for certain clusters where two isomers had relative energy differences quite smaller than the expected accuracy of the DFT calculations, but had sufficiently different calculated IPs (i.e. Nb$_3$C, Nb$_3$C$_3$, Nb$_3$C$_4$ and Nb$_5$C$_2$).

Although sufficient information was extracted from the PIE spectra for the majority of the niobium-carbide clusters examined in this study, exploration of the PIE to higher energies (than that available for this work) could confirm the isomers assigned to certain clusters. For Nb$_3$C, the lack of an observed ionisation onset was inferred as evidence that the calculated lowest energy isomer, which has a high IP, was the only isomer present. For Nb$_4$C$_5$ and Nb$_4$C$_6$ the observed weak ionisation onsets were tentatively assigned to metastable spin states of the calculated lowest energy isomers. Observation of further ionisation onsets at higher energies due to ionisation from the ground electronic state of these isomers would provide a more definitive answer for these clusters.

Interesting results were found for the isomers assigned to the ionisation onsets of Nb$_3$C$_4$, Nb$_4$C$_5$, Nb$_4$C$_6$, Nb$_5$C$_5$ and Nb$_5$C$_6$, where the structures contained C-C bonding in the form of C$_2$ units. Previous IR-REMPI studies on various M$_8$C$_{12}$ species have provided evidence of C$_2$ units; e.g. Nb$_8$C$_{12}$ has an absorption resonance at 1250 cm$^{-1}$. This technique could be applied to the clusters mention above to provide
evidence of the proposed C₂ units. Alternatively, the IR-MPD technique could be applied, which has been successful for rare gas complexes of neutral bare metal clusters. IR-MPD provides higher resolution than IR-REMPI and is applicable to clusters which do not undergo thermionic emission. Furthermore, IR-MPD could help elucidate the structure of certain clusters where distinguishing between two energetically close isomers was not possible on the basis of their calculated IPs alone and the assignment was made to the lowest energy isomer (i.e. Nb₄C, Nb₅C and Nb₅C₃).

Recently IR-MPD has been applied to investigate the two lowest energy isomers present for the neutral Nb₉ cluster (as described previously in Section 5.5.3). This experiment relies on both isomers being present in sufficient concentration and possessing reasonably different IPs so that two spectra can be collected; one of the lowest IP isomer and the other of both isomers combined. The Nb₃C₄ species would be an ideal candidate to investigate with this technique, as the observed ionisation onset was assigned to a low-lying isomer, with the lowest energy isomer calculated to have an IP greater than the highest available photon energy.

Metal-carbide clusters have been proposed for applications in nanotechnology such as molecular wires, nanocatalysis and hydrogen storage. From this study the niobium-carbide clusters Nb₃C₂, Nb₄C₃, Nb₅C₄, Nb₅C₃ and Nb₅C₆ are proposed to be interesting candidates for further investigation. The primary beneficial property of these clusters is that they are not calculated to have any low-lying isomers. This would permit experimental observations to be due to only one contributing isomer, allowing the results to be easier to interpret and model computationally. In addition, proposals are made for these species where altering the occupation of their electronic structures may induce favourable changes in the clusters properties; i.e. constructing an appropriate bimetallic-carbide cluster.

For Nb₃C₂, the cation was found to be considered as containing a closed shell electronic structure because of the large energy gap between its degenerate HOMO/HOMO−1 and LUMO/LUMO+1; the MOs being Nb-Nb/Nb-C bonding and Nb-Nb antibonding in character, respectively. Therefore, a closed shell electronic
structure may be achieved for a neutral \( \text{Nb}_2\text{MC}_2 \) cluster, where \( M \) is a transition metal containing one less electron than Nb. Alternatively, a stable neutral species may be generated by the addition of an atom with an extremely high electronegativity (e.g., a halogen) to \( \text{Nb}_3\text{C}_2 \), where the interaction with the atom is primarily ionic.

The structure of \( \text{Nb}_4\text{C}_3 \) is attractive as it contains a free Nb face, which could potentially be utilised as a surface for reactions to occur upon. From calculations on the structures of larger niobium-carbide clusters it was observed that non-dissociative addition of \( \text{C}_2 \) and \( \text{C}_3 \) units to this free Nb face were energetically favourable. Additionally, the HOMO of \( \text{Nb}_4\text{C}_3 \), which is totally filled, is Nb-Nb bonding in character and is located above the free Nb face. The properties of this free Nb face could be manipulated by altering the number of electrons in this MO.

Another interesting property of the \( \text{Nb}_4\text{C}_3 \) cluster is that the LUMO is Nb nonbonding in character, localised on the remaining Nb atom not involved in the free Nb face. By generating a bimetallic \( \text{M}_4\text{C}_3 \) cluster of suitable composition, electron density could be localised on this metal atom, switching the HOMO from the free metal face in \( \text{Nb}_4\text{C}_3 \) to the opposite side of the cluster. This situation is also similar in \( \text{Nb}_5\text{C}_3 \), where the singly occupied HOMO is also Nb nonbonding in character and localised on the unique Nb atom bound to all three C atoms. The degenerate HOMO\text{-1}/HOMO\text{-2} is Nb-Nb bonding between the remaining four Nb atoms. Like that described for \( \text{Nb}_4\text{C}_3 \), generation of an appropriate bimetallic \( \text{M}_5\text{C}_3 \) clusters could alternate between having the HOMO or LUMO localised on this one metal atom.

As a result of its closed geometric structure, the electronic structure of the \( 2\times2\times2 \) nanocrystal (\( \text{Nb}_4\text{C}_4 \)) is unique, in that there is a large energy difference between the degenerate HOMO/HOMO\text{-1} and the remaining occupied MOs. This is due to the latter being primarily Nb-C bonding in character. The HOMO/HOMO\text{-1} are essentially Nb nonbonding in character (with \( d_{\text{x}^2-\text{y}^2} \) AOs located on all four Nb atoms). The triply degenerate LUMO/LUMO+1/LUMO+2 appears to be weakly Nb antibonding/Nb nonbonding in character, with all Nb atoms having outwards pointing \( d_{\text{z}^2} \) AOs. This is interesting as the LUMOs are arranged to accept electron density, whereas the HOMOs are the correct symmetry for back-bonding (albeit \( \delta \) rather than
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$\pi$ symmetry). By removing electrons from the HOMO/ HOMO$-1$ by means of generating a bimetallic $\text{M}_4\text{C}_4$ clusters, the reactivity at these metal sites could be controlled. Indeed the reactivity of the $\text{Nb}_4\text{C}_4$ cation has provided intriguing results.$^9$

Lastly, the structure of the $\text{Nb}_5\text{C}_6$ cluster contains a combination of bonding motifs from both the extensively studied Metcar ($\text{M}_8\text{C}_{12}$) and nanocrystal (e.g. $\text{M}_4\text{C}_4$ and $\text{M}_{14}\text{C}_{13}$) species.$^{53}$ $\text{Nb}_5\text{C}_6$ contains two $\text{C}_2$ units which are bound in environments essentially the same to which they are found in the Metcar isomer. In other words, there are two types of Nb atoms; those only involved in $\sigma$ bonding with the $\text{C}_2$ units or those only involved in $\pi$ bonding with the $\text{C}_2$ units. The remaining two $\text{C}$ atoms are bound in environments essentially the same to which they are found in the $\text{Nb}_4\text{C}_4$ nanocrystal; i.e. C atoms bound to Nb faces. It would be interesting to examine how the interplay of these two bonding motifs effect the chemical properties of $\text{Nb}_5\text{C}_6$. Muckerman and co-workers have shown through DFT calculations that the $\text{C}_2$ units in $\text{Ti}_8\text{C}_{12}$ can be considered as reservoirs of negative charge, allowing the Ti atoms to act as Lewis acids when interacting with nucleophilic systems or to be oxidised by strongly electron withdrawing groups.$^{47,54}$

The next chapter will describe the examination of tantalum-carbide clusters, which are iso-valent to those niobium-carbide clusters examined here, through essentially identical PIE experiments and DFT calculations. The final chapter will then describe the generation and examination of novel bimetallic-carbide clusters, resulting in the first steps in our laboratory towards tailoring the properties of metal-carbide clusters in consideration of the proposals made in this chapter.
5.7 References

(38) Morse, M. D. Chem. Rev. 1986, 86, 1049.