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

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Viktoras Dryza
November, 2008.

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 Nb_3C_y (y = 0–4), Nb_4C_y (y = 0–6) and Nb_5C_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_3C_2, Nb_4C_4, Nb_5C_2 and Nb_5C_3 display the largest IP reductions for their corresponding cluster series.

The structures assigned to the IPs of the Nb_3C_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_3C_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_4C_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_4C_4. For Nb_4C_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_4C_5 and Nb_4C_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_4C_5 and Nb_4C_6 have one and two carbon atoms in a 2×2×2 fcc nanocrystal substituted with molecular C_2 units, respectively.

The structures assigned to the IPs of the Nb_5C_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_5C_5 and Nb_5C_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_3C_y (y = 0–3), Ta_4C_y (y = 0–4) and Ta_5C_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_3ZrC_y (y = 0–4) clusters are examined by PIE experiments and DFT calculations. The IP trend for the Ta_3ZrC_y cluster series is reasonably similar to that of the Ta_4C_y cluster series, although the IP reductions upon carbon addition are greater for the former. The structures assigned to the IPs of the Ta_3ZrC_y (y = 1–4) clusters are based on the carbon atoms attaching in turn to the metal faces of the tetrahedral Ta_3Zr 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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Publications

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Ionization Potentials of Tantalum-Carbide Clusters: An Experimental and Density Functional Theory Study
Dryza, V.; Addicoat, M.A.; Gascooke, J.R.; Buntine, M.A.; Metha, G.F. *J. Phys. Chem. A* **2005**, *109*, 11180.

Threshold Photo-ionization and Density Functional Theory Studies of the Niobium-Carbide Clusters Nb_3C_n (n = 1–4) and Nb_4C_n (n = 1–6)
Dryza, V.; Addicoat, M.A.; Gascooke, J.R.; Buntine, M.A.; Metha, G.F. *J. Phys. Chem. A* **2008**, *112*, 5582.

Onset of Carbon-Carbon Bonding in the Nb_5C_y (y = 0–6) Clusters: A Threshold Photo-ionisation and Density Functional Theory Study
Dryza, V.; Gascooke, J.R.; Buntine, M.A.; Metha, G.F. *PCCP* **2008**, (in press).

The following publications are currently in preparation from the work presented in this thesis:

Onset of Carbon-Carbon Bonding in the Ta_5C_y (y = 0–6) Clusters: A Threshold Photo-ionization and Density Functional Theory Study
Dryza, V.; Gascooke, J.R.; Buntine, M.A.; Metha, G.F. (in preparation).

Threshold Photo-ionization and Density Functional Theory Studies of Bimetallic-Carbide Clusters: Ta_3ZrC_y (y = 0–4)
Dryza, V.; Gascooke, J.R.; Buntine, M.A.; Metha, G.F. (in preparation).

Abbreviations

AO	Atomic Orbital
C	Carbon
DFT	Density Functional Theory
EA	Electron Affinity
ECP	Effective Core Potential
eV	Electron Volt
FC	Frank-Condon
FCC	Face-centred Cubic
FEL	Free Electron Laser
FWHM	Full Width at Half Maximum
GTO	Gaussian Type Orbital
HOMO	Highest Occupied Molecular Orbital
IP	Ionisation Potential
IR	Infrared
LUMO	Lowest Unoccupied Molecular Orbital
MO	Molecular Orbital
MPD	Multi-photon Dissociation
MPI	Multi-photon Ionisation
MRCI	Multi-Reference Configuration Interaction
Nb	Niobium
NBO	Natural Bond Order
PES	Potential Energy Surface
PFI-ZEKE	Pulsed Field Ionisation Zero Electron Kinetic Energy
PIE	Photo-ionisation Efficiency
REMPI	Resonance Enhanced Multi-photon Ionisation
SPI	Single-photon Ionisation
Ta	Tantalum
TOF-MS	Time-of-flight Mass-spectrometer
ZPE	Zero-point Energies
Zr	Zirconium

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