Fundamental Metal-Ligand Interactions and Gas-Phase Reaction Mechanisms Involving Metal Atoms and Clusters

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Brief Introduction
What exactly are we interested in?

General Interest: Metal-Ligand Interactions Relevant to Catalysis and H₂ Storage

A Prototypical “Two-State” Reaction: FeO⁺ + H₂ → Fe⁺ + H₂O

Topics of Interest in Project

What are we interested in?

**Topic I: \( M_n^{+/−} + L \) Binding Energies and Cluster Fragmentation dynamics**

**PREVIOUS WORK:** \( M-RG + mh\nu \rightarrow M^{+/−} + RG \left( ^1S_0 \right) \) (See poster for other e.g.)

317.5 nm photodissociation of Ag- Ar.

IDEA: Use VMI to determine \( D_0 \) values of \( M_n^{+/−} + L \) clusters of interest (e.g. \( L = H_2 \) for storage)
VMI Experiments on $M_n^{+/\,-}$ Clusters

Proposed Wiley-McLaren Stage of the New Experimental Setup

- Wiley-McLaren Repeller, Extractor and Ground Plates
- Einzel Lens Assembly
- Velocity-Map Imaging Detector
- VMI Lens Assembly
- Retractable MCP detector to be placed here
- Probe Laser (UV, Vis and/or IR)
- Float VMI plates at various potentials to control kinetic energies

Introduce Charge Metal Atoms/Clusters Here
Expts on Fe\(^+\)-(H\(_2\))\(_n\) and FeO\(^+\)-(H\(_2\))\(_n\) Clusters

Mass Spectrum of Fe\(^+\)-(H\(_2\))\(_n\) and FeO\(^+\)-(H\(_2\))\(_n\) Clusters

If V\(_{HH} > D_0 \rightarrow \) then IR photodissociation occurs!

\(D_0 = 3777 \text{ cm}^{-1}\)


Experiments towards IR-photodissociating these species currently underway!

Could IR excitation get us over the barriers?
Topics of Interest in Project

What are we interested in?

**Topic II: Product branching ratios in IR-driven cluster surface reactions**

**PREVIOUS WORK:** \( \text{Rh}_n \text{N}_2 \text{O}^+ + m \hbar \nu (\text{IR}) \rightarrow \text{Rh}_n \text{O}^+ + \text{N}_2 \) or \( \text{Rh}_n^+ + \text{N}_2 \text{O} \)

- Barrier to cluster surface reaction involves bending of O atom towards Rh atom.
- Activation of all three modes of molecularly absorbed \( \text{N}_2 \text{O} \) leads to oxide formation.
- VMI of products of more simple examples (e.g. \( \text{V}^+\text{-CO}_2 \)) will give information of PSDs upon IR-induced reactivity.

(Use IR-OPO/OPA Laser for this!)

Preliminary IR Experiments on M⁺-L Clusters

Experimental Setup

This experiment was designed to:

(i) See if we can make the stuff! (e.g. Fe-H₂⁺, FeO-H₂⁺, V⁺-CO₂ etc.)

(ii) See if we can induce IR-driven photodissociation.

(iii) Determine the structures (electronic and geometric) of clusters and their complexes. (e.g. Infra-Red Multiple Photon Dissociation (IRMPD) expts on Ar-tagged Rh₆(N₂O)⁺ proved N₂O was associatively bound).
Preliminary IR Experiments on M$^+$-L Clusters

Difference Spectrum of V$^+$-(CO$_2$)$_n$, VO$^+$-(CO$_2$)$_n$ and VCO$^+$-(CO$_2$)$_n$ Clusters

Monitoring cluster signal intensity as a function of IR energy will give us IRMPD spectra. (See poster for more details and spectra!)

IR on @ 2375 cm$^{-1}$ - Enhancement and Depletion observed!

IR off – Normal distribution of V$^+$-(CO$_2$) clusters

IR on – IR off
IR wavenumber: 2375 cm$^{-1}$

≥ V$^+$-(CO$_2$)$_5$ depletion is observed.
≤ V$^+$-(CO$_2$)$_4$ enhancement is observed.
There must be something interesting about V$^+$-(CO$_2$)$_4$…

VMI Experiments on $M_n^{+}$-L/RG Clusters

Proposed Preliminary Experiment: Photodissociation dynamics of $V^+\cdot CO_2$

**Topic II: Product branching ratios in IR-driven cluster surface reactions**

**Previous Example: Mode-Selective Chemistry of $V^+\cdot CO_2$**

- Photodissociation at 15801 cm$^{-1}$
- Photodissociation at 15777 cm$^{-1}$

One quantum of OCO asymmetric stretch at 2390 cm$^{-1}$

VMI of $V^+$ and $VO^+$ will provide insight into the PSDs with and without IR-excitation!

$D_o = 6050 \pm 320$ cm$^{-1}$

(Armentrout *et al.*)

Topics of Interest in Project
What are we interested in?

Topic III: Product quantum state distributions in reactions of metal atoms/ions/clusters

ONE PG FOCUS: $^{4,6}\text{FeO}^+ + \text{H}_2 \rightarrow ^{4,6}\text{Fe}^+ + \text{H}_2\text{O} (\nu_1, \nu_2, \nu_3)$

- How is the energy of the reaction partitioned into the various products ($E_J, E_v$ and/or $E_T$)?

- VMI of the reaction products, in combination with CT and QCT calculations (Bristol) will give information on these PSDs.

Crossed Molecular Beam Studies of $\text{M}_n^{+/-} + \text{H}_2$

Proposed Experimental Set-Up for $\text{M}_n^{+/-} + \text{H}_2$ (or any other reactants) Reactions

Introduce Metal Atoms/Clusters Here

Introduce Reactant Molecular Beam Here

May need to install an RF Octopole Ion Trap here to narrow $E_T$ distribution (similar to Wester et al.)

Reaction products are accelerated perpendicularly towards VMI MCP/Camera assembly

Float VMI plates at various potentials to control collision energies
Conclusions and Future Work
What we’ve done and where we are going

What have we achieved thus far?
• Finished design plans for the charged cluster and crossed molecular beam experiments. (Wiley-McLaren Assembly Built… now awaiting the Einzel Lens Assembly!)

• Observed IR-driven processes and performed IRMPD Experiments on the following systems: \( V^+-(CO_2)_n \), \( VO^+-(CO_2)_n \) and \( VCO^+-(CO_2)_n \) (also have IRMPD for Au counterparts!)

Plans for the future:
• Perform photodissociation VMI experiments on \( M^+-H_2 \) and \( M^+-CO_2 \) complexes.

• Use the IR-OPO/OPA Laser coupled with our VMI experiment to investigate product branching ratios (eventually performing multi-mass imaging of \( V^+ \) and \( VO^+ \) with PImMS Camera)

- \( V^+(CO_2) + hv \rightarrow V^+ + CO_2 \)
- \( V^+(CO_2) + hv \rightarrow VO^+ + CO \)

• Perform IRMPD Experiments on the following systems: \( M^+-(H_2)_n \), \( MO^+-(H_2)_n \), Cluster-CO complexes, \( M_n(N_2O)CO^+ \) clusters (and Ar-tagged counterparts)

Nomerotski et al., J. Instrum., 2010, 5
Programme Grant Team

SRM group PG-related:
Prof Stuart Mackenzie
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Graham A. Cooper (D.Phil Student)
Alastair Sharp (Part II – M+-CO₂)
Michael Kent (Part II – M+-H₂)

Other Collaborators:
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Prof Mike Ashfold (Bristol)
Prof Jeremy Harvey (Bristol)
Dr Stephanie Essafi (Bristol)
Extra Slides
IRMPD Experiments on $V^+-(\text{CO}_2)_n$ Clusters

A Little Bit of Background…

Normal Mass Spec (IR Laser OFF)

IR Laser ON

Difference Spectrum

To Investigate IR-Photodissociation Dynamics

To Determine Structures

asymmetric stretch (Free CO$_2$: 2349 cm$^{-1}$)

To Determine Structures
IRMPD Experiments on $V^+\text{-(CO}_2\text{)}_n$ Clusters

Mass Spectrum of $V^+\text{-(CO}_2\text{)}_n$, $\text{VO}^+\text{-(CO}_2\text{)}_n$ and $\text{VCO}^+\text{-(CO}_2\text{)}_n$ Clusters

15% CO$_2$/Ar Mix
(Backacking Pressure = 6 bar)
Topics of Interest in Project
What are we interested in?

**Topic I: Product quantum state distributions in reactions of metal atoms/ions/clusters**

**PREVIOUS EXAMPLE:** F⁻ + CH₃I → I⁻ + CH₃F

*Indicates a long-lived collision complex before substitution.*

*Direct Substitution Mechanism.*

*Found to indicate a 'roundabout' mechanism involving CH₃ rotation.*


- Develop a crossed molecular beam apparatus with VMI detection to determine the product state distributions of these reactions (& compare with CT and QCT calculations on full-dimensional *ab initio* PESs in collaboration with BRISTOL).
IRMPD Experiments on $V^+-(\text{CO}_2)_n$ Clusters

IRMPD Spectra of $V^+-(\text{CO}_2)_n$ Clusters

Two features observed at ca. 2351 cm$^{-1}$ and 2376 cm$^{-1}$:

- Feature at 2351 cm$^{-1}$ due to second-sphere CO$_2$ molecules. ($v_2$ of free CO$_2$ = 2349 cm$^{-1}$)
- Feature at 2376 cm$^{-1}$ due to directly co-ordinated CO$_2$ molecules, hence the blue-shift.
- Coordination number of $V^+$ in the gas-phase is 4. Hence, $n(\text{second-sphere CO}_2) = n(\text{total CO}_2) - 4$

Interesting feature arise at ca. 2398 cm$^{-1}$ from $V^+-(\text{CO}_2)_7$ onwards…

This is due to $V^{2+}$-$\text{C}_2\text{O}_4^-$ ion pair formation via an intracluster reaction of two CO$_2$ molecules!

From these IRMPD Expts:

(i) Depletion spectra consistent with that published by Duncan et al. (J. Chem. Phys., 2004, Vol. 120(21), pg. 10037)

(ii) We can successfully induce IR-driven processes!
IRMPD Experiments on V\(^+\)-(CO\(_2\))\(_n\) Clusters

IRMPD Spectra of the V\(^+\)-(CO\(_2\))\(_9\), VO\(^+\)-(CO\(_2\))\(_9\) and VCO\(^+\)-(CO\(_2\))\(_9\) Clusters

Two features observed at ca. 2350 cm\(^{-1}\) and 2376 cm\(^{-1}\):

- Feature at 2350 cm\(^{-1}\) due to second-sphere CO\(_2\) molecules. \(v_2\) of free CO\(_2\) = 2349 cm\(^{-1}\) – appears in all three IRMPD spectra.
- Feature at 2376 cm\(^{-1}\) due to directly co-ordinated CO\(_2\) molecules, hence the blue-shift. However, feature has appeared to red-shift upon addition of O atom to V\(^+\)!

Interesting feature arising at ca. 2398 cm\(^{-1}\) due to V\(^{2+}\)-C\(_2\)O\(_4\)\(^-\) ion pair formation disappears in the VO\(^+\)-(CO\(_2\))\(_9\) spectrum!

Why? Addition of O atom to V\(^+\) precludes formation of the ion pair!

What now?

(i) Perform DFT calculations in order to provide further insight into ligand effects **(CURRENTLY IN PROGRESS!)**

(ii) Prepare manuscript on findings.
## Project Milestones

Goals and Timelines from EPSRC Proposal

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### Scientific (S) and Technical (T) Milestones

**S11** – Preliminary IRMPD of CO-decorated clusters.

**S12** – VMI Study of H₂ binding to charged metal clusters.

**S13** – VMI of IR-driven cluster surface reactions.

**S14** – H₂ binding energies to metal oxide clusters.

**S15** – Testing of new crossed beam experiment with e.g. Rh⁺ + N₂O and FeO⁺ + H₂

**S16** – Multi-mass imaging of metal ion / cluster reactions.

**T15** – Integration of PlmMS sensor to crossed beam apparatus for metal ion / cluster expts.

**T16 & T17** – Modification & optimization of ion optics of VMI instrument for charged clusters.

**T18** – Design and construction of crossed beam imaging spectrometer for metal ion/cluster expts.
Crossed Molecular Beam Studies – $M + O_2$

Previous Work

$\text{Mo}(a^7S_3) + O_2 (X^3\Sigma_g^-) \rightarrow \text{MoO} (X^5\Pi) + O (^3P_J), \Delta_r H_0^0 = -31.3 \text{ kJ mol}^{-1}$

- Reaction between Mo atoms and $O_2$ studied at 3 different kinetic energies (controlled via seeding the metal atom carrier gas).
- Vibrationally-excited MoO formed upon reaction.

Topic II: Product branching ratios in IR-driven cluster surface reactions

**ONE PG FOCUS:** \( M_nN_2O^+ + mh\nu (IR) \rightarrow M_nO^+ + N_2 \) or \( M_n^+ + N_2O \)

**Topics of Interest in Project**

Project Breakdown

Topics of Interest in Project
What are we interested in?

**Topic I: $M_n^{+/L}$ Binding Energies and Cluster Fragmentation Dynamics**

**Previous Example: IR Photodissociation Spectrum of Ag$^+$-H$_2$**

Upper-limit to $D_o$ given at band centre ($< 3755.5 \text{ cm}^{-1}$)

(i) IR photodissociation only occurs if $V_{HH} > D_o$.

(ii) VMI can be used to accurately determine $D_o$ values for Ag$^+$-H$_2$ and other complexes of interest!


**IDEA:** Use VMI to determine dissociation energies of rare-gas atoms and ligands to clusters
Conclusions from Calcs:

(i) Linear form is more stable than T-Shaped form.

(ii) \(V^+\) binds to Oxygen rather than Carbon.

(iii) 2 (or more!) IR-photons @ the CO\(_2\) asym. stretch to dissociate the \(V^+-\text{O}\) bond.
IRMPD Experiments on Au$^+$-L(CO$_2$)$_n$ Clusters

Mass Spectrum of Au$^+$-(CO$_2$)$_n$, AuO$^+$-(CO$_2$)$_n$ and AuCO$^+$-(CO$_2$)$_n$ Clusters

15% CO$_2$/Ar Mix
(Backing Pressure = 6 bar)
VMI Experiments on $M_n^{+}$-L/RG Clusters

From these Simulations:

(i) Can separate out small clusters by 1 amu. A little bit trickier for Au$^+$ clusters and their H$_2$ complexes though…

(ii) **PROBLEM:** Clusters gain a significant amount of KE upon being separated via the Wiley-McLaren Mass Spectrometer (ca. 300 eV!). This can affect images further down stream.

**SOLUTION:** Float VMI spectrometer at some potential so as to make the charged cluster “walk up a potential ramp” and slow them down.
IRMPD Experiments on $\text{Co}^+-(\text{H}_2)_n$ Clusters

Mass Spectrum of $\text{Co}^+-(\text{H}_2)_n$

$D_0 = 6365 \text{ cm}^{-1}$

VMI Experiments on $M_n^{+}$-L/RG Clusters

Current Experimental Setup for M-RG Dimers and $M_2$ Clusters

Need to install some form of mass separation here for our proposed VMI Experiments on charged metal clusters!
Polar Onion-Peeling Algorithm

Theory of the POP algorithm

Seeks to “peel” φ dependence along the x-direction away from the image (assuming Cylindrical symmetry around φ).

Start from the outside and peel away φ with decreasing x.