IR Photodissociation Spectroscopy
for Cluster Ions of Triatomic Molecules

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Acknowledgment

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Introduction

- Why Ion-Molecule Complexes?

- Why IR Photodissociation Spectroscopy?
Why Ion-Molecule Complexes?

"Chemical Intermediates"

Ion-Molecule Complexes

Basis of Chemistry!
Nucleophilic Additional Reactions of C=O

Resonance interactions between MOs are important

Primary process of nucleophilic reactions

Formation of covalent bond
Formation of Covalent Bonds (1)

- Radical + Radical
  - M–M
  - Bond order = 1
  - Covalent
  - H₂, H₂O, NH₃

- Molecule + Proton
  - (M–H)⁺
  - Bond order = 1
  - Covalent
  - H₃O⁺, NH₄⁺
Formation of Covalent Bonds (2)

Molecule + Radical Ion

\[ (M-H)^+ \]

Bond order = 0.5

“Semi” - Covalent Bond

“Two-Center Three-Electron” Bond

Found for

\[ CO_2^+ \quad \cdots \quad CO_2 \]

\[ C_6H_6^+ \quad \cdots \quad C_6H_6 \]
Semi-Covalent Bonds

- Involve in chemical reactions whose mechanism not clear?
- Discover new chemical reactions?

Electronic and geometric characteristics not well understood.
Why IR Photodissociation Spectroscopy?

Resonance interaction occurs in (CO\textsubscript{2})\textsuperscript{2+}. No structural information.

IR Photodissociation (IRPD) Spectroscopy
With a mass spectrometer, in the gas phase.

Electronic Spectra

Thermochem. Measurements


(CO\textsubscript{2})\textsuperscript{2+} has higher binding E.
This Study

IR Photodissociation Spectroscopy

Quantum Chemical Calculations

Electronic and Geometric Structures

\((\text{CO}_2)_n^+ \ (\text{OCS})_n^+ \ (\text{CS}_2)_n^+\)

Formation of semi-covalent bonds between unsaturated C=O and C=S groups

GAUSSIAN03
B3LYP/6-311+G*
Experimental

$$\text{EI} \quad \text{Acceleration Grids}$$

$$\text{Mass Gate}$$

$$\text{Reflectron}$$

$$\text{Power Meter}$$

$$\text{Experimental (CO}_2\text{)}_3^{+ \ast} + \text{CO}_2$$

$$\text{(Dissociation Threshold)}$$

$$h\nu P_{\text{ex}} P_{\text{diss}}$$

$$\text{Nl: YAG Laser}$$

$$\text{LaserVision}$$

$$\text{AgGaSe}_2 + \text{ZnSe Filter}$$

$$2000-3800 \text{ cm}^{-1}$$

(1-5 mJ/pulse)

$$1000-2200 \text{ cm}^{-1}$$

(0.2-1 mJ/pulse)
Ion Cores and Solvent Molecules

In cluster ions

**Ion Cores**
The part in which positive charge is localized.

**Solvent Molecules**
Bonded to ion core with less or no charge distributed.
IRPD Spectra of $(\text{CO}_2)_n^+$

Anti-symmetric CO stretch ($\nu_3$)

Wavenumber (cm$^{-1}$)

Fragment Ion Intensity

$n = 2$
$n = 3$
$n = 4$
$n = 5$
$n = 6$
$n = 7$
$n = 8$
IRPD Spectra of $(\text{CO}_2)_n^+$

- Band position almost the same as that of CO$_2$.
- Solvent CO$_2$ molecules
- Intensity decreases with increasing $n$. 
  - Ion core
- Fragment Ion Intensity
- Wavenumber (cm$^{-1}$)
What is Ion Core of $(\text{CO}_2)_n^+$?

$\text{CO}_2^+$ or $\text{C}_2\text{O}_4^+$?

$\text{CO}_2^+$ or $\text{C}_2\text{O}_4^+$?

Ion core of $(\text{CO}_2)_n^+$

$\text{C}_2\text{O}_4^+$

$\times$

$\text{CO}_2^+$

$\text{CO}_2^+$ ion core

$(\text{CO}_2)_n^+$ have $\text{C}_2\text{O}_4^+$ ion core.
Structure of $\text{C}_2\text{O}_4^+$ is controlled by overlap between HOMOs.
IRPD Spectra of $(\text{CO}_2)_n^+$

Band number alternately changes.

Structural change of $\text{C}_2\text{O}_4^+$ part? or whole cluster?
Structure of $(\text{CO}_2)_2^+$ and $(\text{CO}_2)_3^+$

Change of $\text{C}_2\text{O}_4^+$ band number for $(\text{CO}_2)_n^+$

$\rightarrow$ Structural change of $\text{C}_2\text{O}_4^+$ ion core
In-Phase and Out-of-Phase Combinations

The number of IR bands indicates the planarity.

<table>
<thead>
<tr>
<th>Point Group</th>
<th>$C_{2h}$ (planar)</th>
<th>$C_2$ (bent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-phase</td>
<td>inactive</td>
<td>active (weak)</td>
</tr>
<tr>
<td>Out-of-phase</td>
<td>active</td>
<td>active (strong)</td>
</tr>
</tbody>
</table>

(a) in-phase combination
(b) out-of-phase combination

IR activity of dimer ions

The number of IR bands indicates the planarity.
IRPD Spectra of \((\text{CO}_2)_n^+\)

Number of \(\text{C}_2\text{O}_4^+\) core band changes alternately.

Structure of \(\text{C}_2\text{O}_4^+\) core changes alternately.

Bare \(\text{C}_2\text{O}_4^+\) ion has planar \((\text{C}_2\text{h})\) structure. Structure of \(\text{C}_2\text{O}_4^+\) depends on cluster size.
IRPD Spectra of \((\text{OCS})_n^+\) and \((\text{CS}_2)_n^+\)

**Fragment Ion Intensity**

**Wavenumber (cm\(^{-1}\))**

- **\((\text{OCS})_n^+\)**
  - \(n = 2\)
  - \(n = 3\)
  - \(n = 4\)
  - \(n = 5\)
  - \(n = 6\)
  - \(n = 7\)
  - \(n = 8\)

- **\((\text{CS}_2)_n^+\)**
  - \(n = 2\)
  - \(n = 3\)
  - \(n = 4\)
  - \(n = 5\)
  - \(n = 6\)
  - \(n = 7\)
  - \(n = 8\)
IRPD Spectra of $(OCS)_n^+$ and $(CS_2)_n^+$

$(OCS)_n^+$ and $(CS_2)_n^+$

(Dimer ion core)

Core structure not so change, different from $(CO_2)_n^+$. 

Solvent molecules
## Structure of Dimer Ion Core

<table>
<thead>
<tr>
<th>Cluster Size</th>
<th>( \text{C}_2\text{O}_4^+ )</th>
<th>( \text{C}_2\text{O}_2\text{S}_2^+ )</th>
<th>( \text{C}_2\text{S}_4^+ )</th>
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<tr>
<td>( n = 2 ) calculation</td>
<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
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## Structure of Dimer Ion Core

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**Q1.** Why structure of C$_2$O$_4^+$ alternately changes?  
C$_2$O$_4^+$ so floppy?

For $n = 2$ calculation:
- C$_2$O$_4^+$: 2.32 Å (180.0°), 2.89 Å (98.8°)  
- C$_2$O$_2$S$_2^+$: 2.96 Å (115.7°)  
- C$_2$S$_4^+$: 2.96 Å (115.7°)
Structure of Dimer Ion Core

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$n = 2$ calculation

Q2. Why bare $\text{C}_2\text{O}_2\text{S}_2^+$ has bent ($\text{C}_2$) structure?
## Structure of Dimer Ion Core

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$n = 2$ calculation

- $C_{2h}$
- $C_2$
- $C_2$

**Q3.** Why structure different between experiment and calc. for $\text{C}_2\text{S}_4^+$?
Q1. Is $C_2O_4^+$ So Floppy?

- Rather $C_2O_4^+$ has hardest structure.
- Structural change of $C_2O_4^+$ in $(CO_2)_n^+$
  - structural weakness of $C_2O_4^+$
  - characteristics of solvent molecules
Proposed Structural Change

Intermol. bonds formed between solvent mols.
Solvent complex bonded asymmetrically to ion core.
Q2. Why $\text{C}_2\text{O}_2\text{S}_2^+$ bent?

$\text{C}_2\text{O}_2\text{S}_2^+$ has deep double-minimum potential.

Calc. results agree with experimental result.

<table>
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Q2. Why $\text{C}_2\text{O}_2\text{S}_2^+$ bent?

Contains 2p component of C atom

$\text{C}_2\text{O}_4^+$

$\text{C}_2\text{O}_2\text{S}_2^+$ (side view)

$\text{C}_2\text{O}_2\text{S}_2^+$ (top view)

$\text{CO}_2$

$\text{OCS}$

HOMO
Q2. Why $\text{C}_2\text{O}_2\text{S}_2^+$ bent?

- Overlap between MOs
- Repulsive force between components

Completely stacked?

Step-like structure

Far apart from each other?
Q2. Why $\text{C}_2\text{O}_2\text{S}_2^+$ bent?

A. Bent structure originates from broad nature of HOMO.

Minimizes repulsive force.

Overlap increases with decreasing the angle.
Q3. Why Structure in Experiment and Calculation Different for $\text{C}_2\text{S}_4^+$?

$\text{C}_2\text{O}_4^+$ has shallow PES $\rightarrow$ so floppy

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@B3LYP/6-311+G*

A. Intermol. interaction weaker for $\text{C}_2\text{S}_4^+$. Higher-level calculations needed.
Summary

$(\text{CO}_2)_n^+$  $(\text{OCS})_n^+$  $(\text{CS}_2)_n^+$

- Dimer ion core structure.
- The semi-covalent bond formed in dimer ion core.

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$\text{C}_2\text{O}_4^+$ changes structure with cluster size.

$\text{C}_2\text{O}_2\text{S}_2^+$ has bent $(\text{C}_2)$ structure.

Structure in experim. and calc. different for $\text{C}_2\text{S}_4^+$.

Characteristic of solvent molecules.

Broad nature of HOMO of OCS.

Weaker intermolecular interaction.