３原子分子クラスターイオン内における分子間共有結合の形成と，その電子・幾何構造の研究

（広島大学）井口佳哉，小林悠亮，江幡孝之

Summary

$(CO_2)_n^+$ $(OCS)_n^+$ $(CS_2)_n^+$

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

Cluster Size	$C_2O_4^+$	$C_2O_2S_2^+$	$C_2S_4^+$
n = 2	C_{2h}	C_2	C_{2h}
3	C_2		C_2
4	C_{2h}		
5	C_2		
6	C_{2h}		
7	C_{2h}		
8	C_{2h}		
calculation	C_{2h}	C_2	C_2

$C_2O_4^+$ changes structure with cluster size.	$C_2O_2S_2^+$ has bent (C_2) structure.	Structure in experim. and calc. different for $C_2S_4^+$.
Characteristic of solvent molecules.	Broad nature of HOMO of OCS.	Weaker intermolecular interaction.

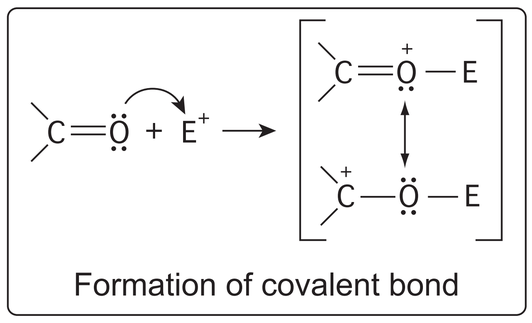
Ion Cores and Solvent Molecules

in cluster ions

Solvent Molecules: Bonded to ion core with less or no charge distributed

Ion Cores: The part in which positive charge is localized

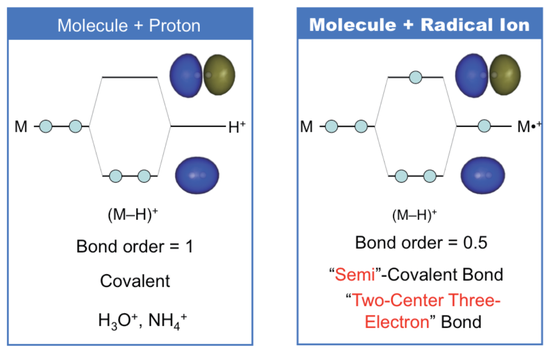
Nucleophilic Additional Reactions of C=O



Primary process of nucleophilic reactions

Resonance interactions between MOs are important

Formation of Covalent Bonds



Semi-Covalent Bonds

- Electronic and geometric characteristics not well understood.
- Involve in chemical reactions whose mechanism unclear?
- Discover new chemical reactions?

This Study

IR Photodissociation Spectroscopy

Quantum Chemical Calculations

GAUSSIAN03 B3LYP/6-311+G*

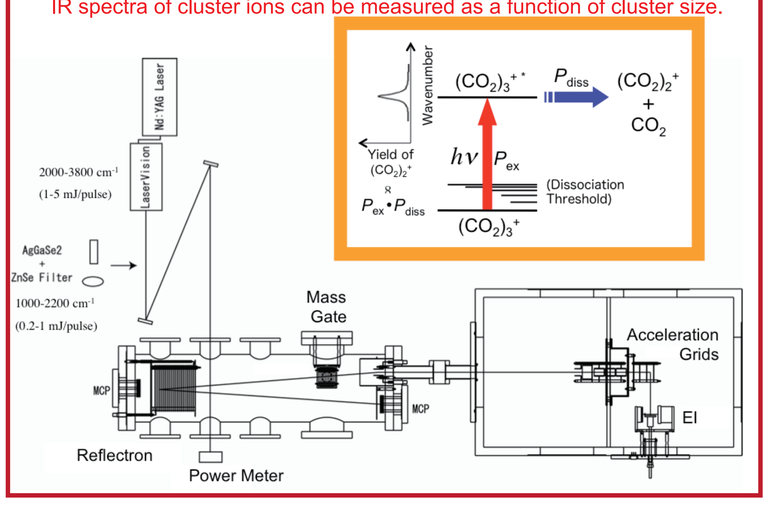
Electronic and Geometric Structures

$(CO_2)_n^+$ $(OCS)_n^+$ $(CS_2)_n^+$

Formation of semi-covalent bond expected to occur between unsaturated C=O and C=S groups

Experimental

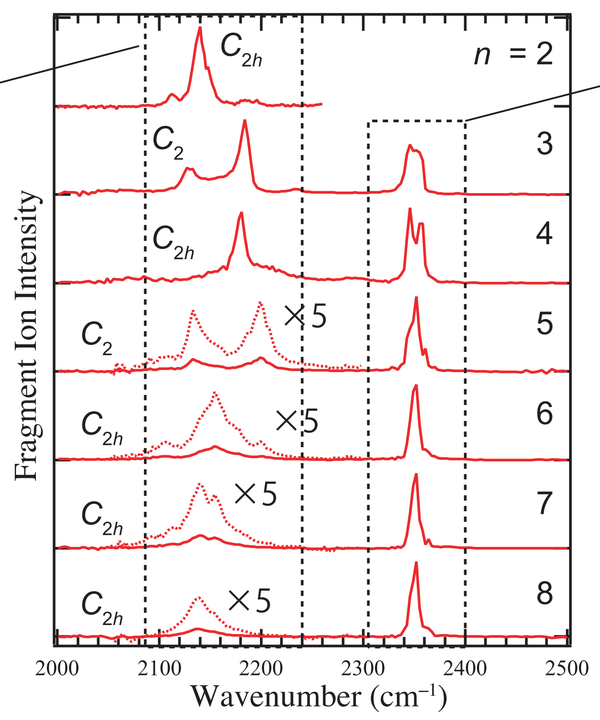
IR spectra of cluster ions can be measured as a function of cluster size.



IRPD spectra of $(CO_2)_n^+$

- Intensity decreases with increasing n.
- Band position not coincident with that of CO_2^+

→ $C_2O_4^+$ ion core

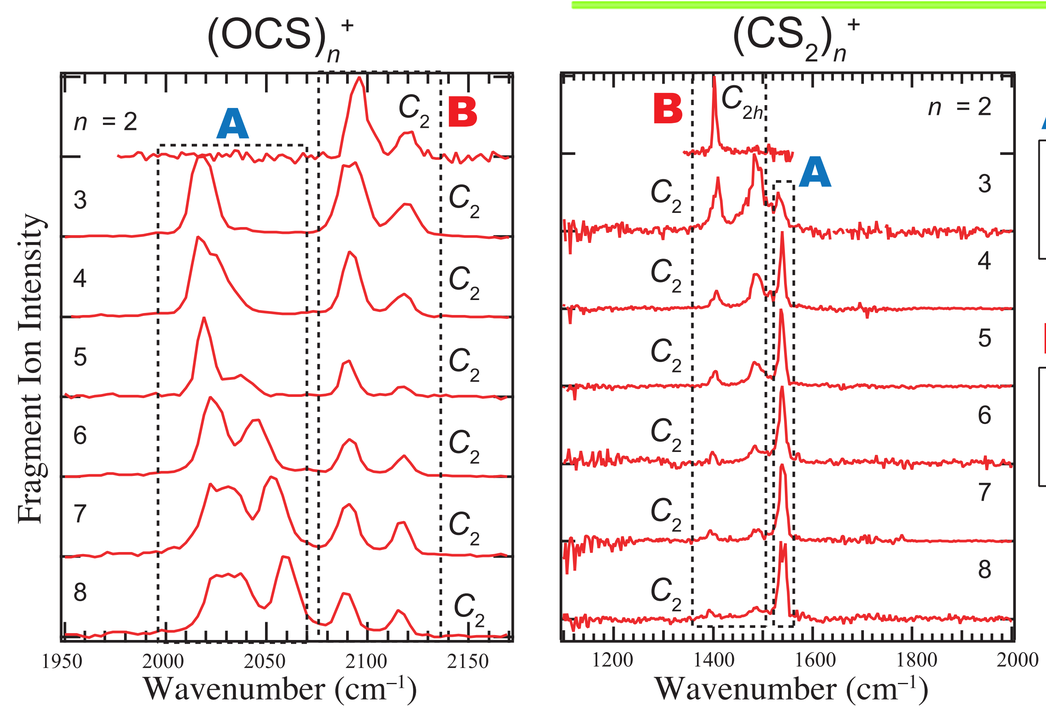


Band position almost the same as that of CO_2.

→ Solvent CO_2 molecules

Anti-symmetric C=O stretching

IRPD spectra of $(OCS)_n^+$ and $(CS_2)_n^+$



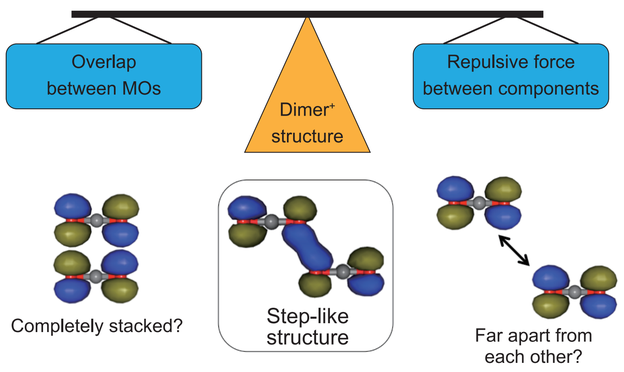
C=O stretching *Anti-symmetric C=S stretching*

A Solvent molecules

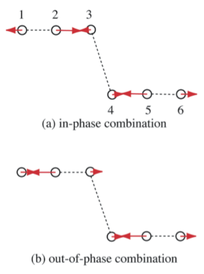
B Dimer ion core

Structure of $C_2O_4^+$

Structure of dimer$^+$ is determined by balance between two factors.



Structure and Band Number for Dimer$^+$



IR activity of dimer ions

Point Group	C_{2h} (planar)	C_2 (bent)
In-phase	inactive	active (weak)
Out-of-phase	active	active (strong)

The number of IR bands indicates the planarity.

Structure of Dimer Ion Core

Cluster Size	$C_2O_4^+$	$C_2O_2S_2^+$	$C_2S_4^+$
n = 2	C_{2h}	C_2	C_{2h}
3	C_2		C_2
4	C_{2h}		
5	C_2		
6	C_{2h}		
7	C_{2h}		
8	C_{2h}		
n = 2 calculation	C_{2h}	C_2	C_2

Q1: Why structure of $C_2O_4^+$ alternately changes?

Q2: Why bare $C_2O_2S_2^+$ has bent (C_2) structure?

Q3: Why structure different bentween exp. and calc. for $C_2S_4^+$?

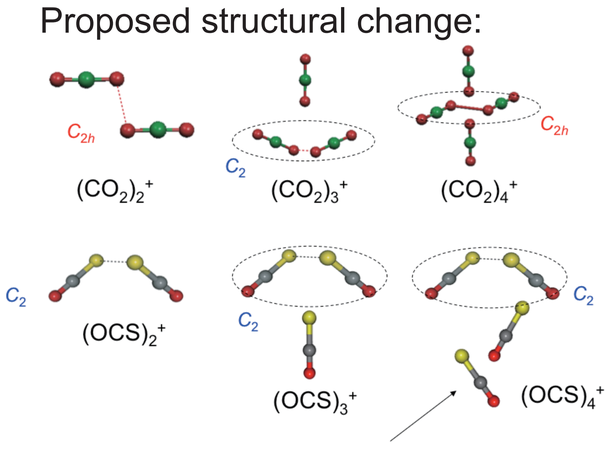
A1: Rather $C_2O_4^+$ has hardest structure.

Structural change of $C_2O_4^+$ in $(CO_2)_n^+$

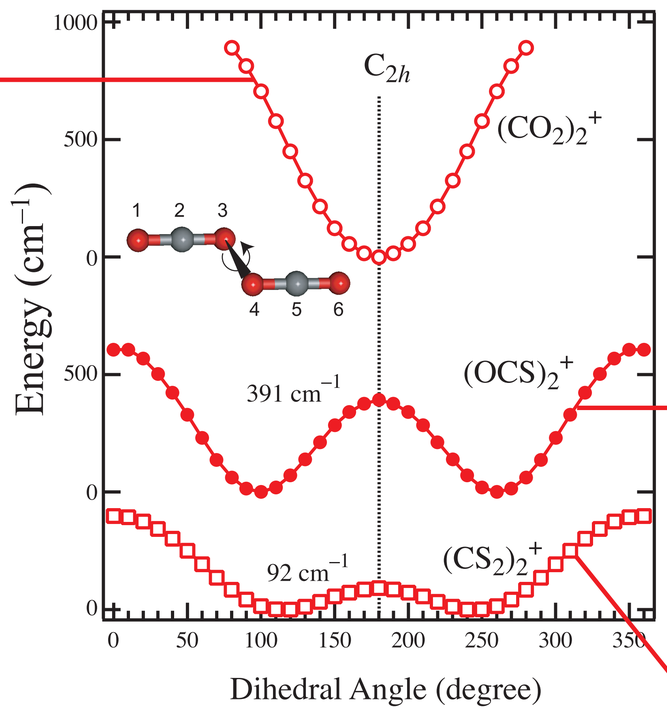
× structural weakness of $C_2O_4^+$

○ characteristics of solvation

Proposed structural change:

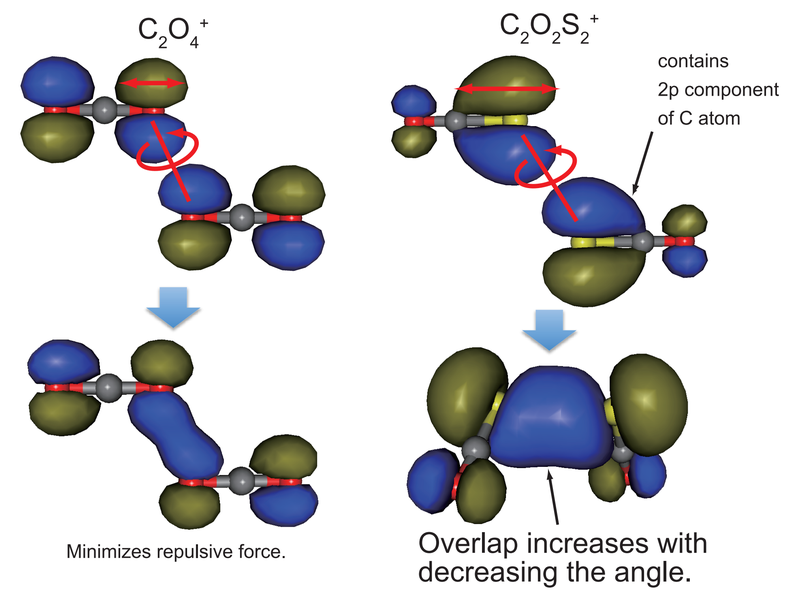


Intermol. bonds formed between solvent mols.
Solvent complex bonded asymmetrically to ion core.



PES along out-of-plane torsional motion

A2: Due to broad nature of HOMO of OCS.



A3: Due to weaker interaction in $C_2S_4^+$.

PES shallow → weaker intermolecular interaction
Calculation cannot reproduce correctly the PES.