# IR Photodissociation (IRPD) Spectroscopy of Ion-Molecule Complexes as Chemical Intermediates

Yoshiya INOKUCHI (*Hiroshima University*)

## Summary

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

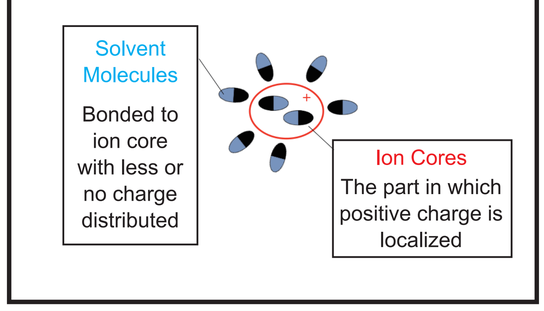
- Dimer ion core structure.
- The semi-covalent bond formed in dimer ion core.

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

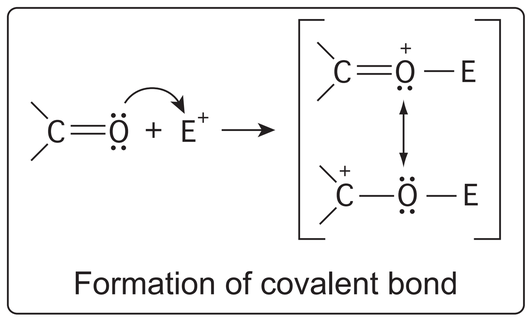
| $C_2O_4^+$ changes structure with cluster size. | $C_2O_2S_2^+$ has bent ($C_2$) structure. | Structure in experim. and calc. different for $C_2S_4^+$. |
|---|---|---|
| Characteristic of solvent molecules. | Broad nature of HOMO of OCS. | Weaker intermolecular interaction. |

### Ion Cores and Solvent Molecules

in cluster ions

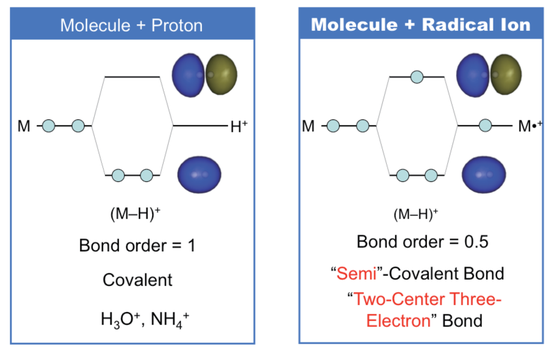



### Nucleophilic Additional Reactions of C=O




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*

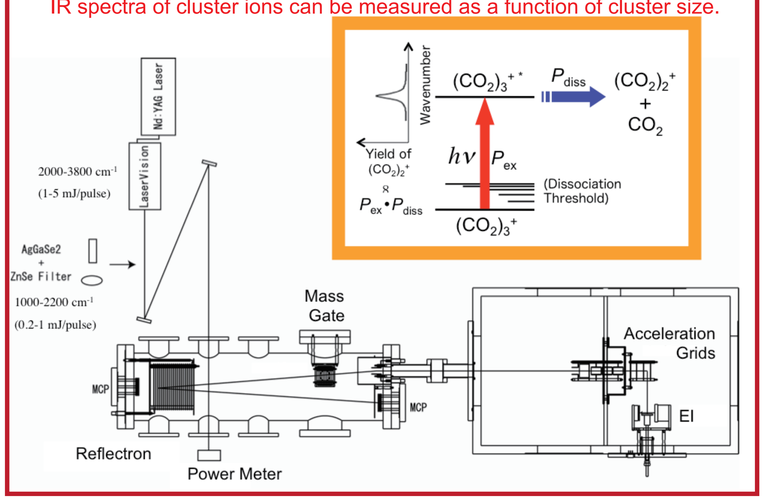
**Electronic and Geometric Structures**

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

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

### Experimental

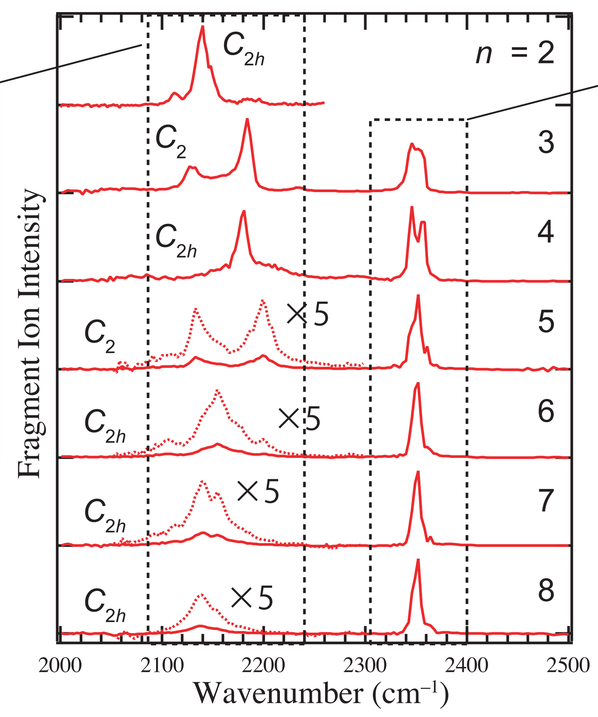
IR spectra of cluster ions can be measured as a function of cluster size.




## 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

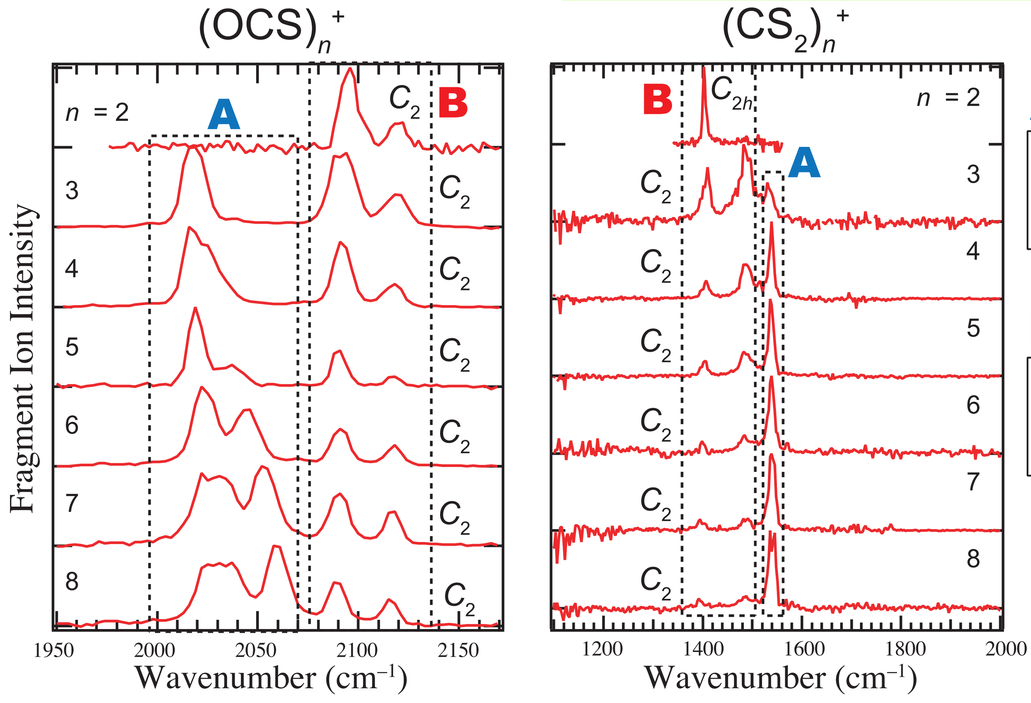



Band position almost the same as that of $CO_2$.

→ Solvent $CO_2$ molecules

*Anti-symmetric C=O stretching*

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



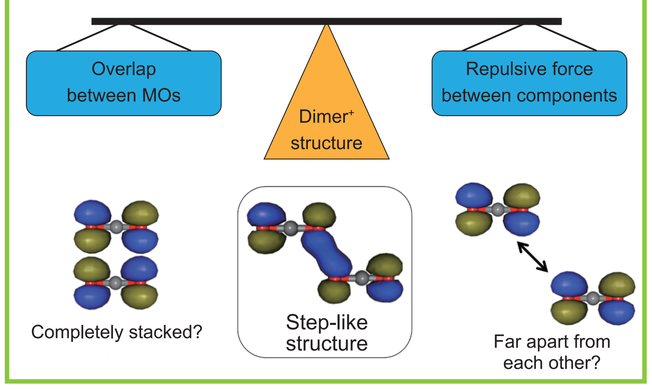

*C=O stretching* *Anti-symmetric C=S stretching*

**A** Solvent molecules

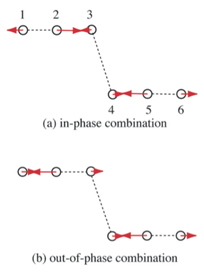
**B** Dimer ion core

### 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 | $C_2O_4^+$ | $C_2O_2S_2^+$ | $C_2S_4^+$ |
|---|---|---|---|
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| 3 | $C_2$ | | |
| 4 | $C_{2h}$ | | |
| 5 | $C_2$ | $C_2$ | $C_2$ |
| 6 | $C_{2h}$ | | |
| 7 | $C_{2h}$ | | |
| 8 | $C_{2h}$ | | |
| $n$ = 2 calculation | $C_{2h}$ (180.0, 2.32) | $C_2$ (2.89, 98.8) | $C_2$ (2.96, 115.7) |

**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 $C_2S_4^+$?**

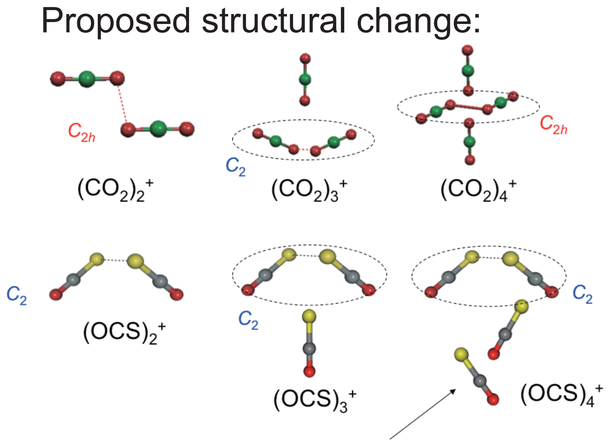
**A1:** Rather $C_2O_4^+$ has hardest structure.

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

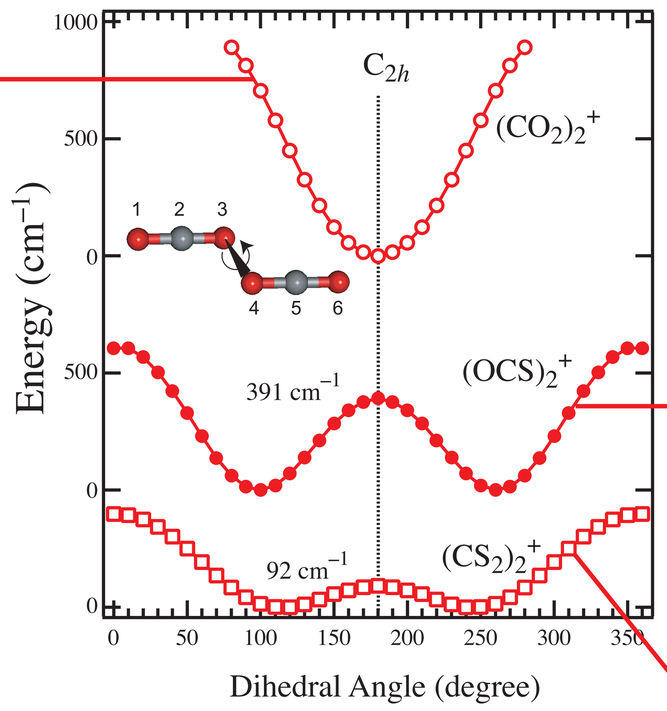
× structural weakness of $C_2O_4^+$

○ characteristics of solvation

Proposed structural change:

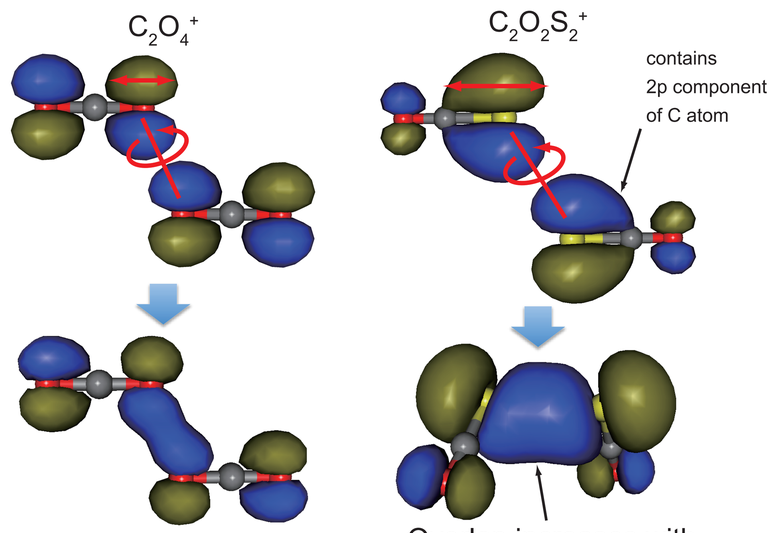



Intermol. bonds formed between solvent mols.
Solvent complex bonded asymmetrically to ion core.




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.