IR Photodissociation Spectroscopy

for Cluster Ions of Triatomic Molecules

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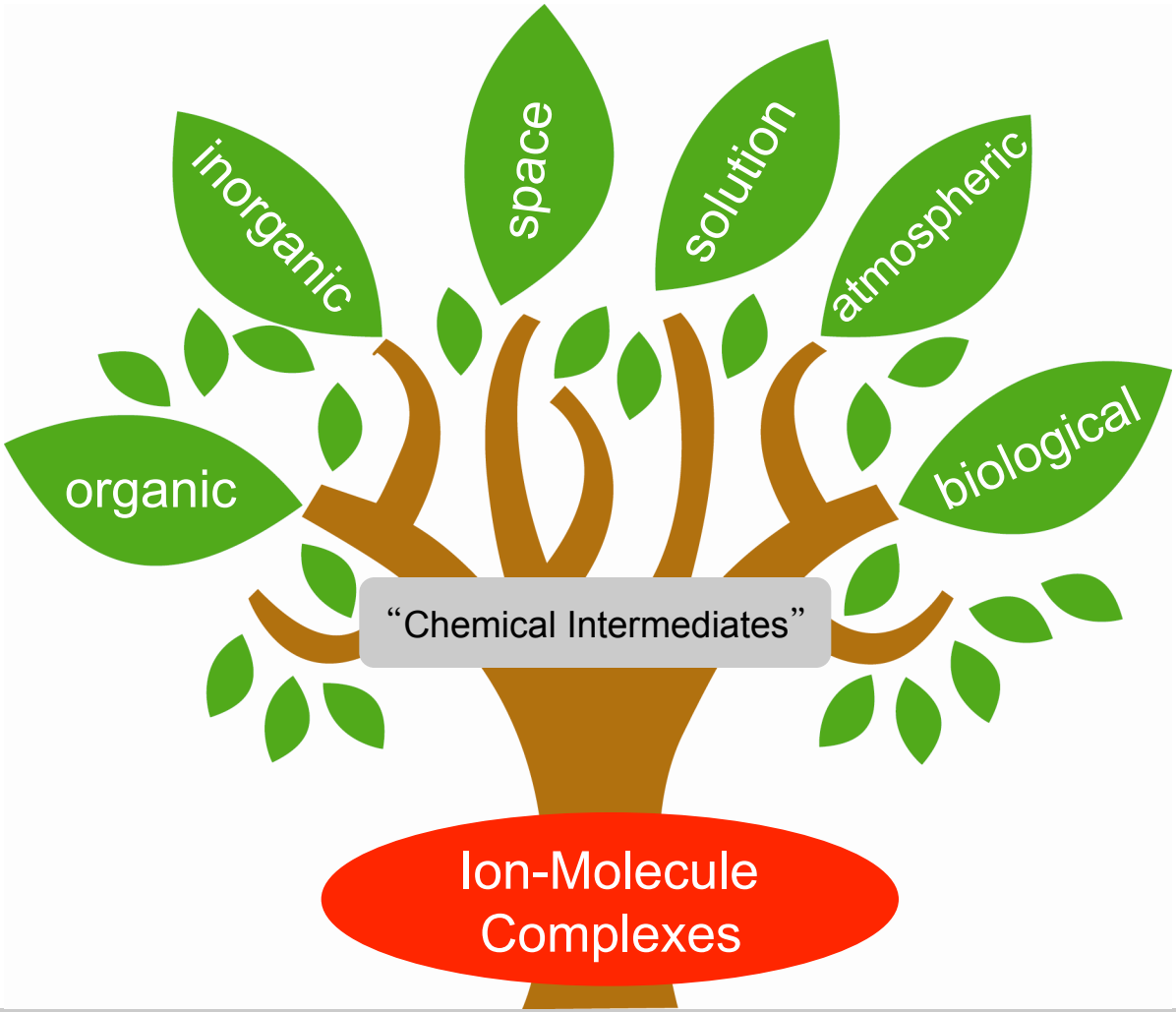
Introduction

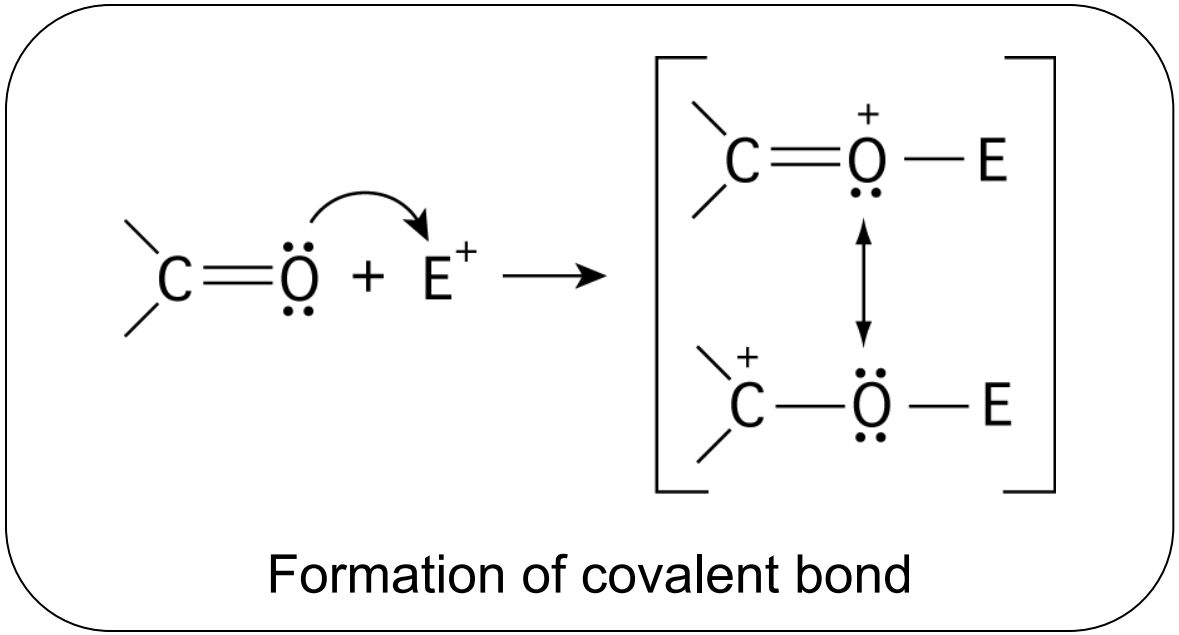
- **Why Ion-Molecule Complexes?**
- **Why IR Photodissociation Spectroscopy?**

Why Ion-Molecule Complexes?



Basis of Chemistry!

Nucleophilic Additional Reactions of C=O



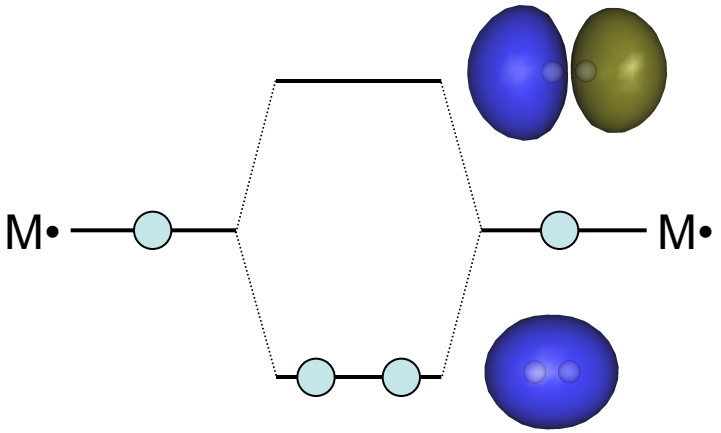
Formation of covalent bond

Primary process of nucleophilic reactions

Resonance interactions between MOs are important

Formation of Covalent Bonds (1)

Radical + Radical



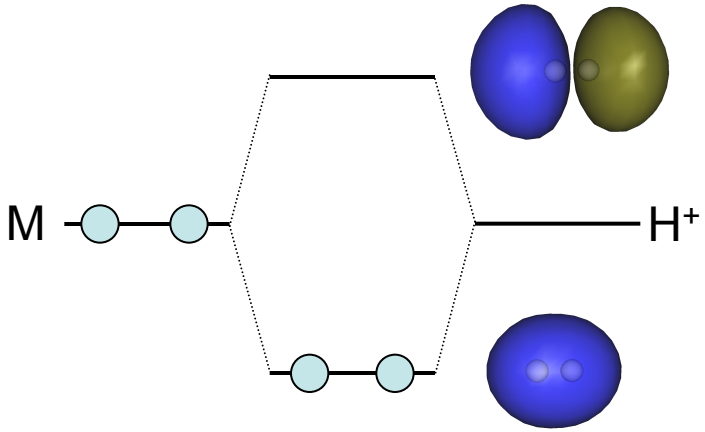
M–M

Bond order = 1

Covalent

H_2, H_2O, NH_3

Molecule + Proton



$(M–H)^+$

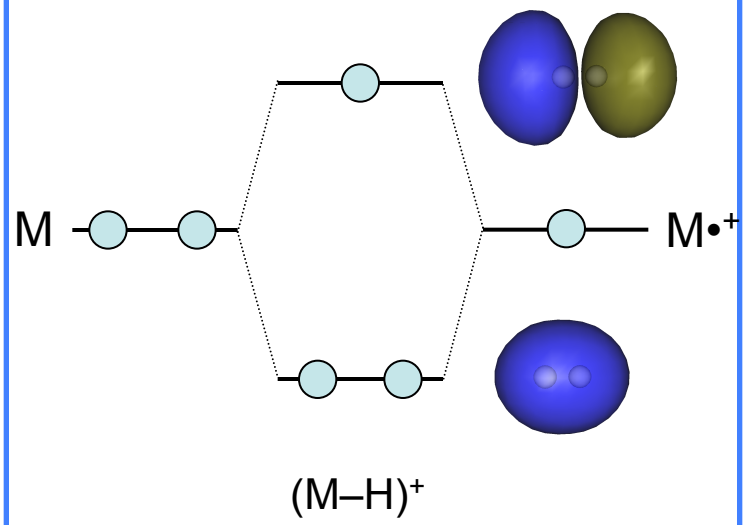
Bond order = 1

Covalent

H_3O^+, NH_4^+

Formation of Covalent Bonds (2)

Molecule + Radical Ion



$(M–H)^+$

Bond order = 0.5

"Semi" -Covalent Bond

"Two-Center Three-Electron" Bond

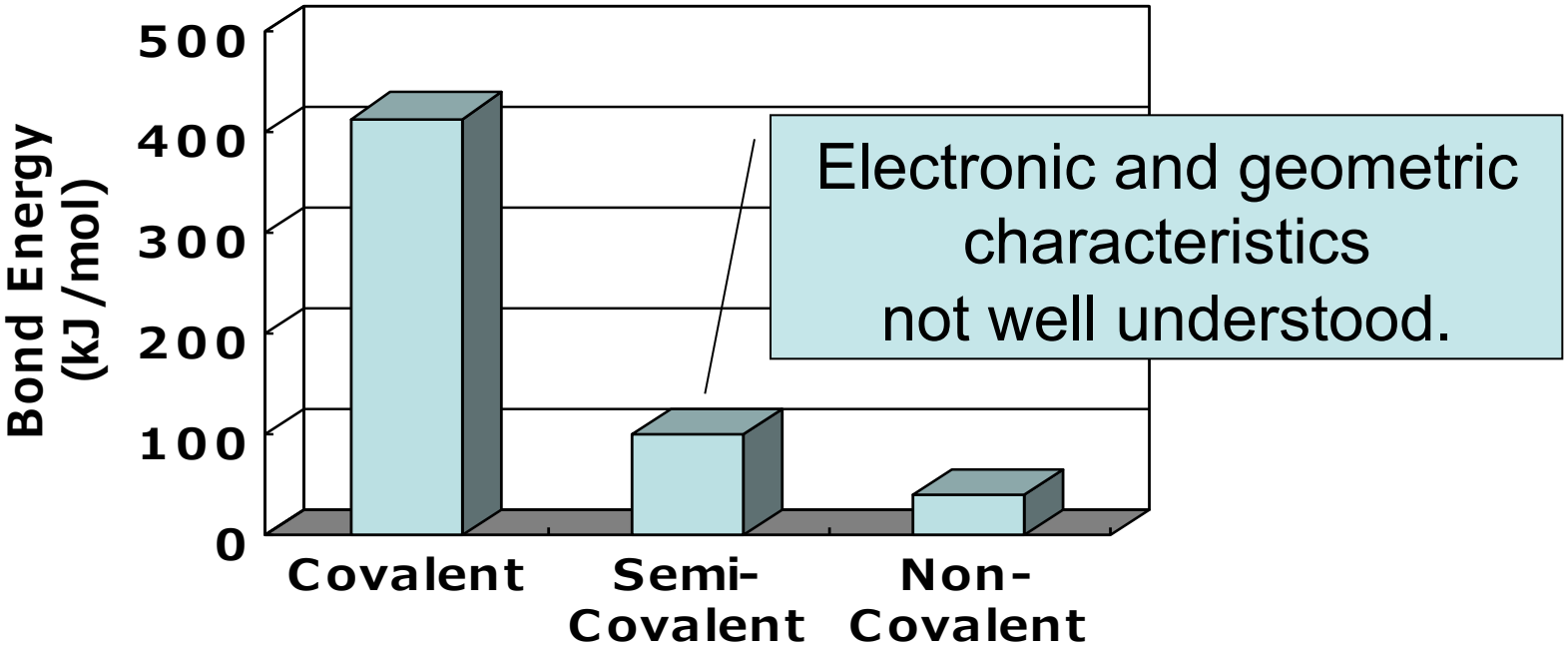
Found for

$CO_2^+ \cdots\cdots CO_2$

$C_6H_6^+ \cdots\cdots C_6H_6$

⋮

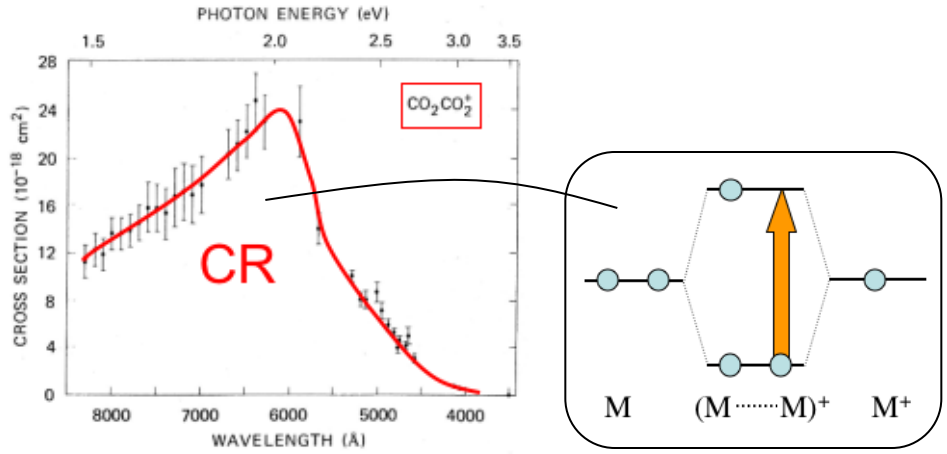
Semi-Covalent Bonds



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

Why IR Photodissociation Spectroscopy?

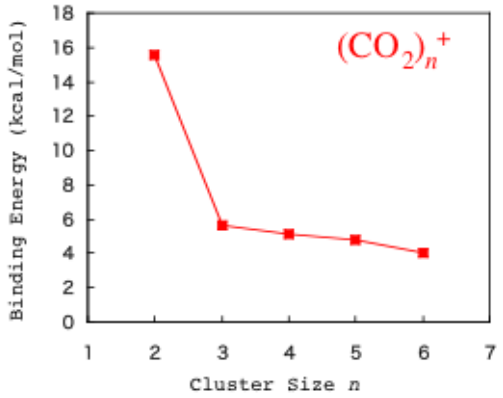
Electronic Spectra



Smith and Lee, J. Chem. Phys. **69**, 5393 (1978).

Thermochem. Measurements

High-pressure mass spectrometry



Hiraoka et al., Chem. Phys. Lett. **146**, 535 (1988).

$(CO_2)_2^+$ has higher binding E.

Resonance interaction occurs in $(CO_2)_2^+$.
No structural information.

IR Photodissociation (IRPD) Spectroscopy

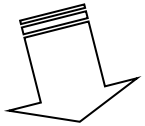
With a mass spectrometer, in the gas phase.

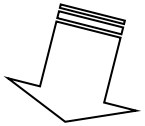
This Study

IR Photodissociation Spectroscopy

Quantum Chemical Calculations

GAUSSIAN03
B3LYP/6-311+G*



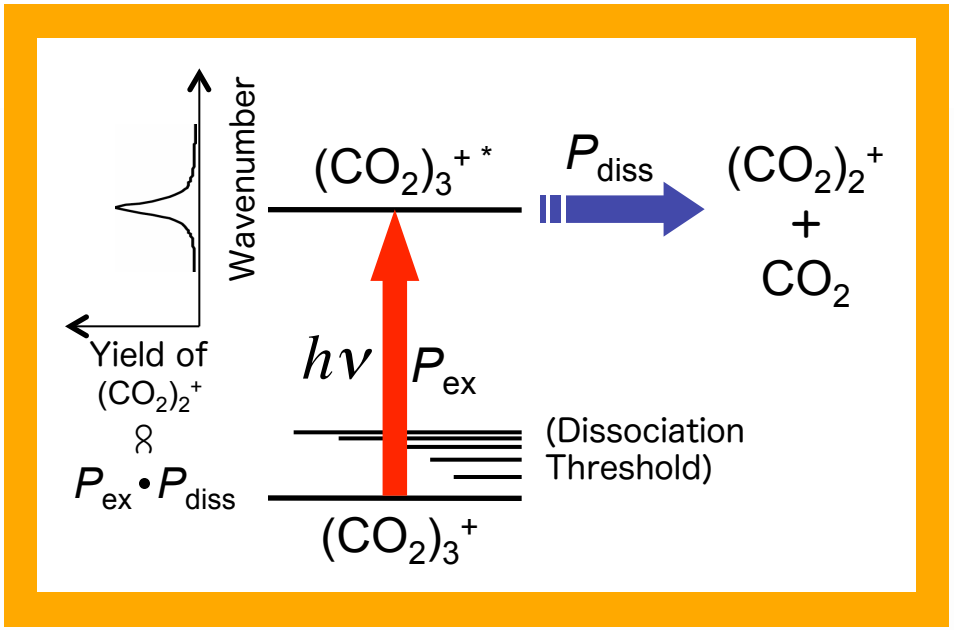


Electronic and Geometric Structures

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

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

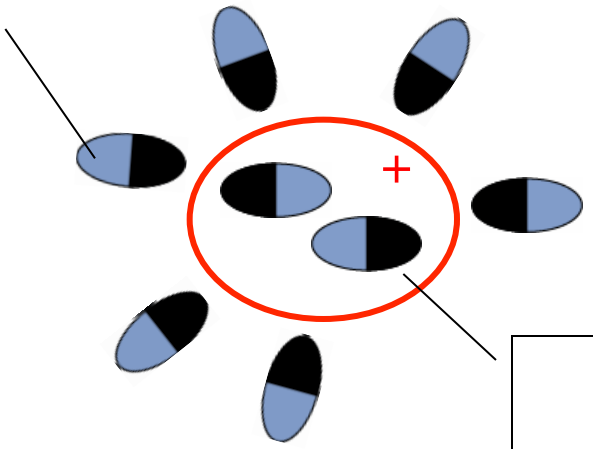
Experimental



Ion Cores and Solvent Molecules

in cluster ions

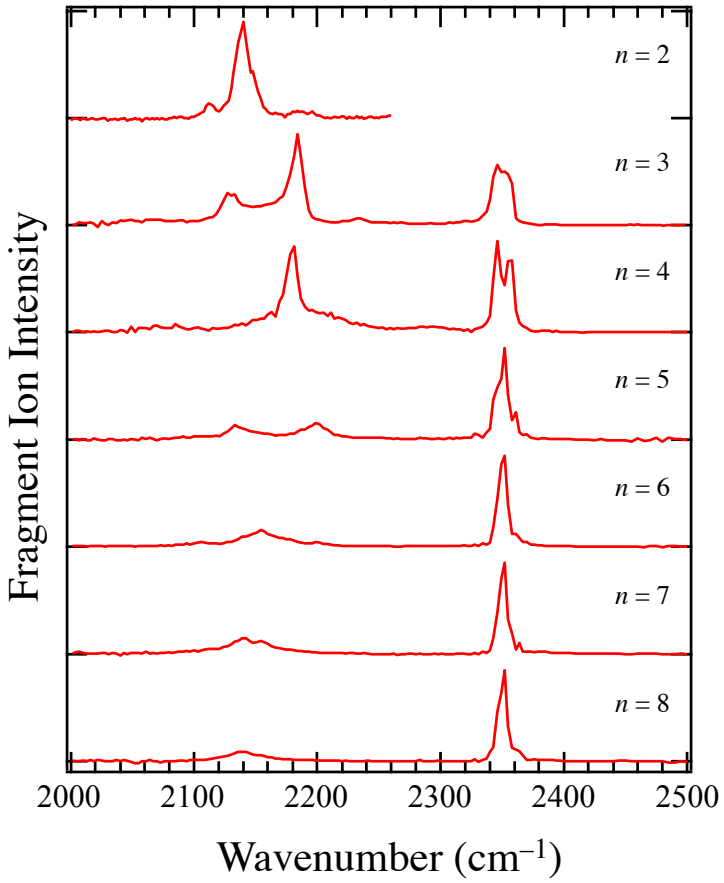
Solvent Molecules
Bonded to ion core with less or no charge distributed.

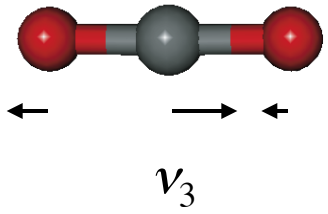


Ion Cores
The part in which positive charge is localized.

IRPD Spectra of $(CO_2)_n^+$

Anti-symmetric CO stretch (ν_3)



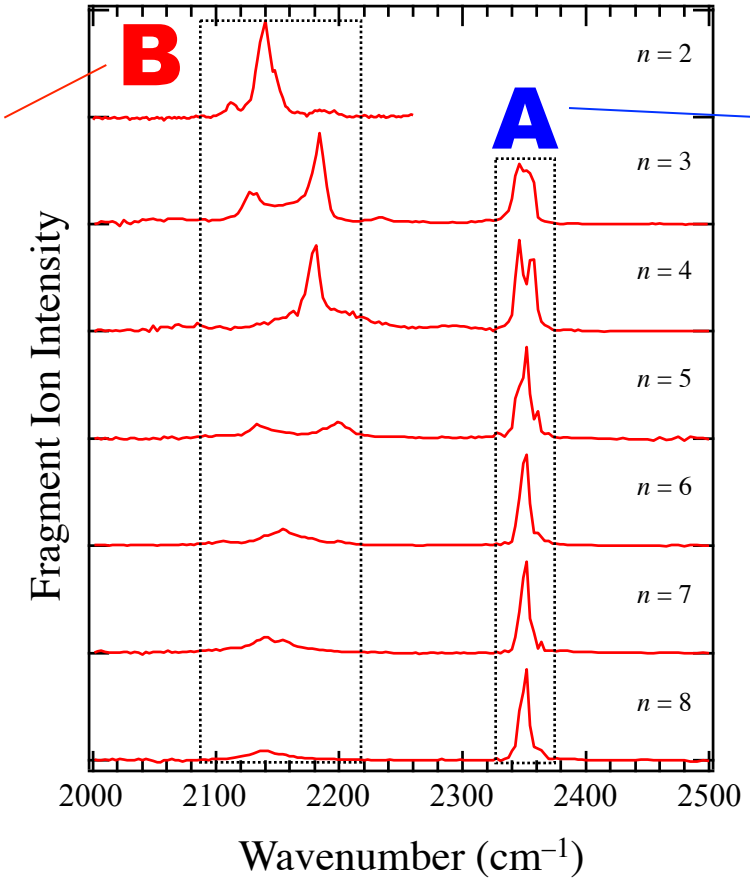


IRPD Spectra of $(CO_2)_n^+$

Intensity decreases with increasing *n*.

⇩

Ion core



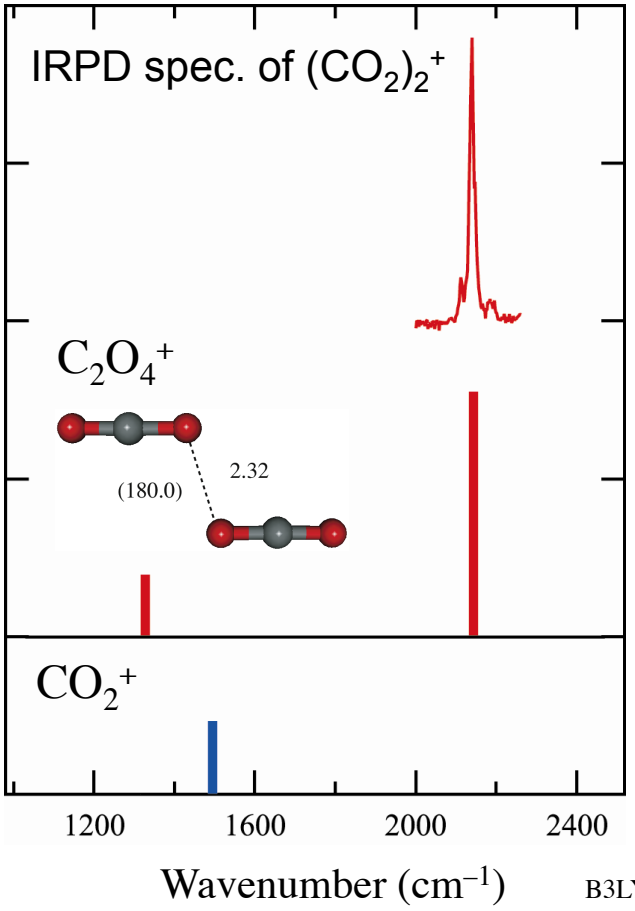
Band position almost the same as that of CO_2.

⇩

Solvent CO_2 molecules

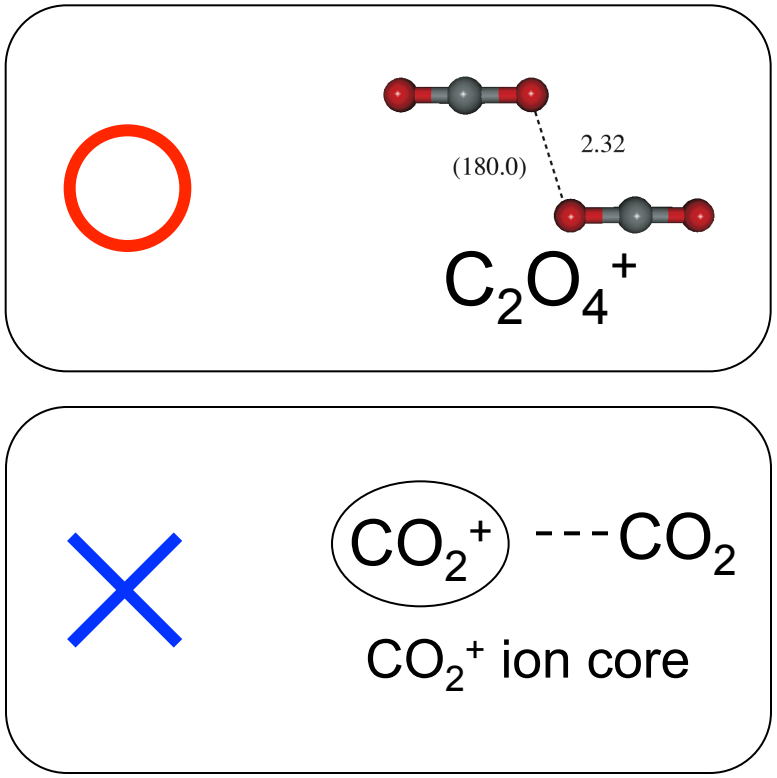
What is Ion Core of $(CO_2)_n^+$?

CO_2^+ or $C_2O_4^+$?



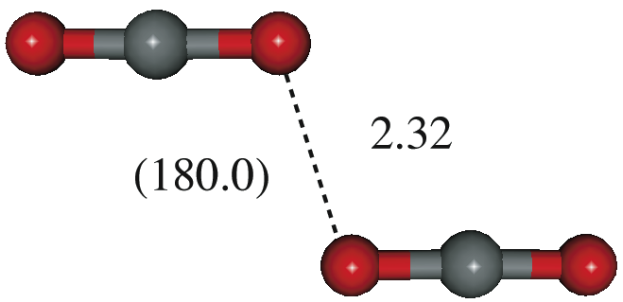
B3LYP/6-311+G*

Ion core of $(CO_2)_n^+$

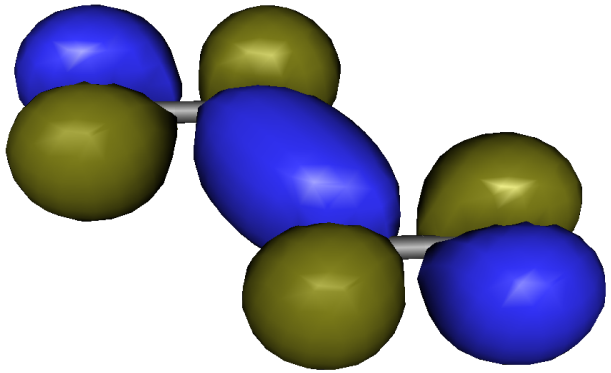


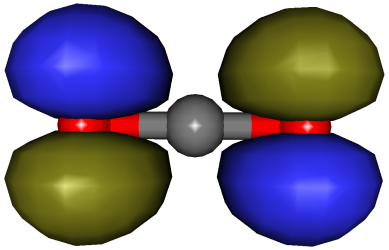
$(CO_2)_n^+$ have $C_2O_4^+$ ion core.

Structure of $C_2O_4^+$



C_{2h}





HOMO of CO_2

B3LYP/6-311+G*

Structure of $C_2O_4^+$ is controlled by overlap between HOMOs.

IRPD Spectra of $(CO_2)_n^+$

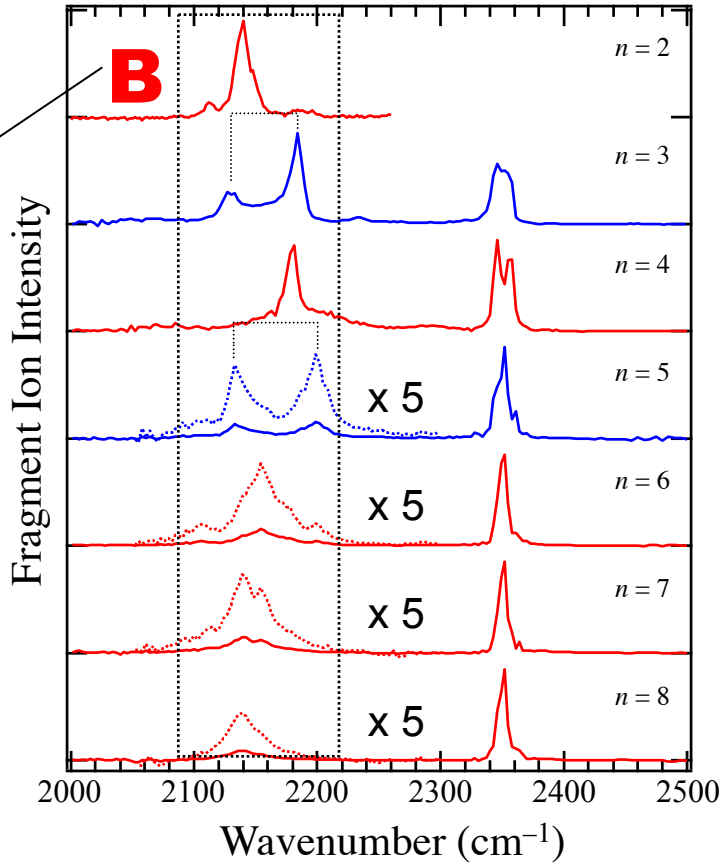
Band number alternately changes.

Structural change of

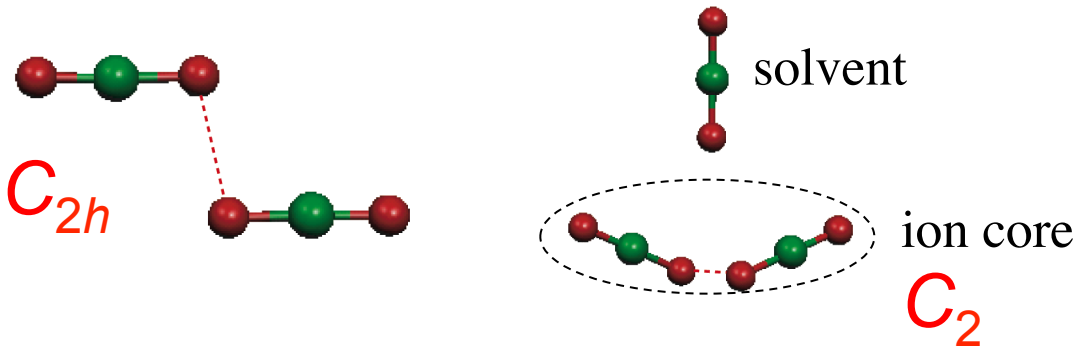
$C_2O_4^+$ part ?

or

whole cluster ?



Structure of $(CO_2)_2^+$ and $(CO_2)_3^+$

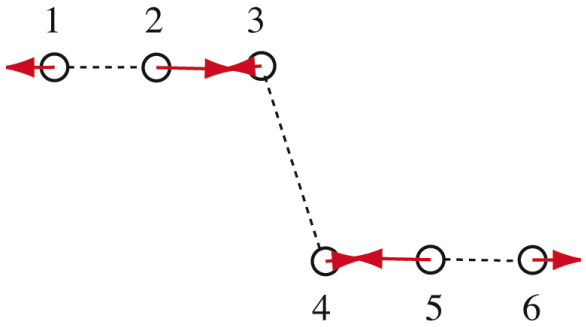


$(CO_2)_2^+$ $(CO_2)_3^+$

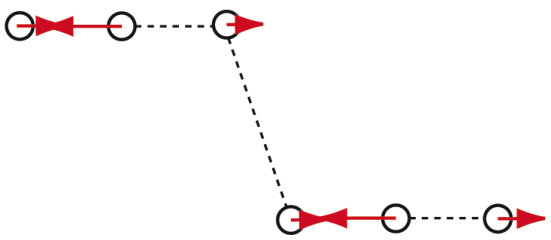
Change of $C_2O_4^+$ band number for $(CO_2)_n^+$

→ Structural change of $C_2O_4^+$ ion core

In-Phase and Out-of-Phase Combinations



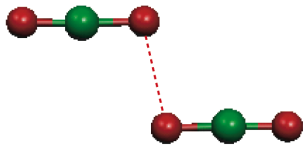
(a) in-phase combination

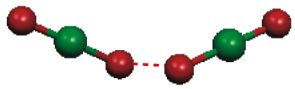


(b) out-of-phase combination

IR activity of dimer ions

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



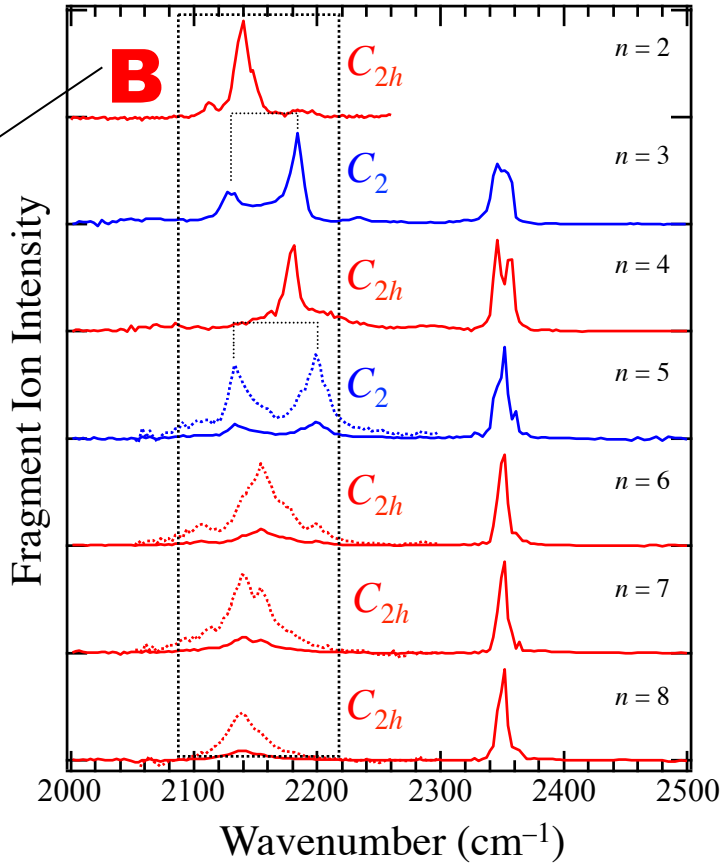


The number of IR bands indicates the planarity.

IRPD Spectra of $(CO_2)_n^+$

Number of $C_2O_4^+$ core band changes alternately.

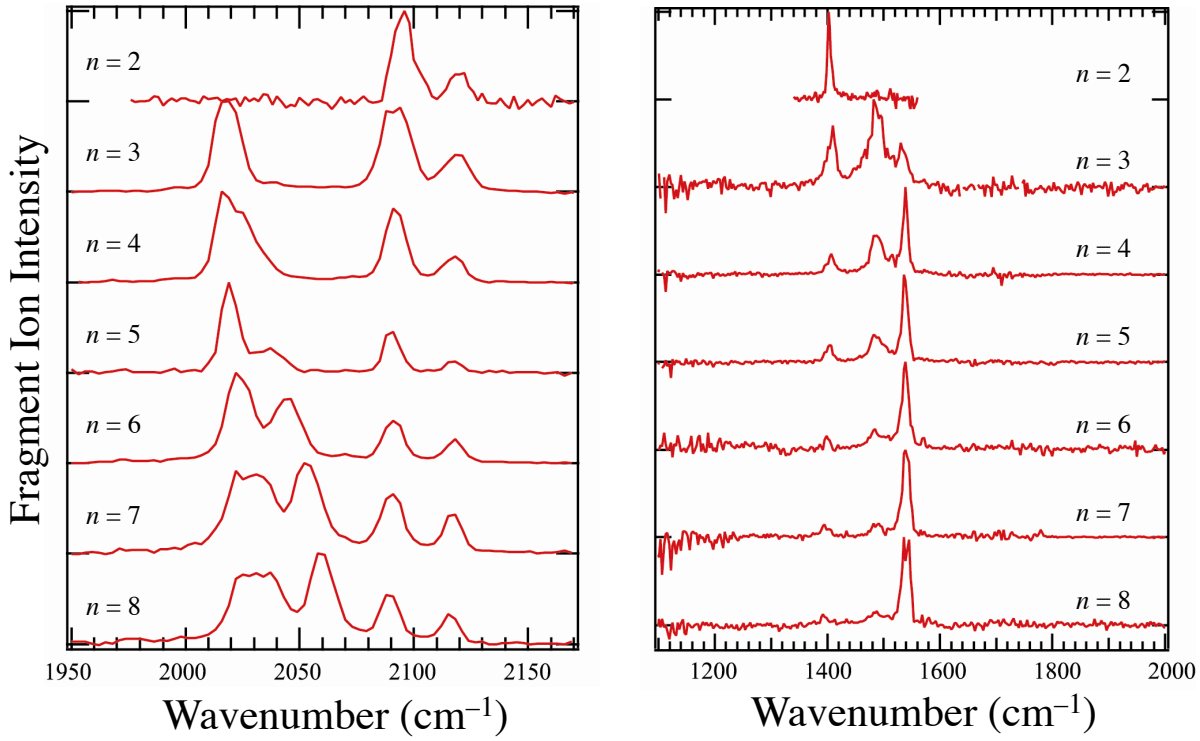
Structure of $C_2O_4^+$ core changes alternately.



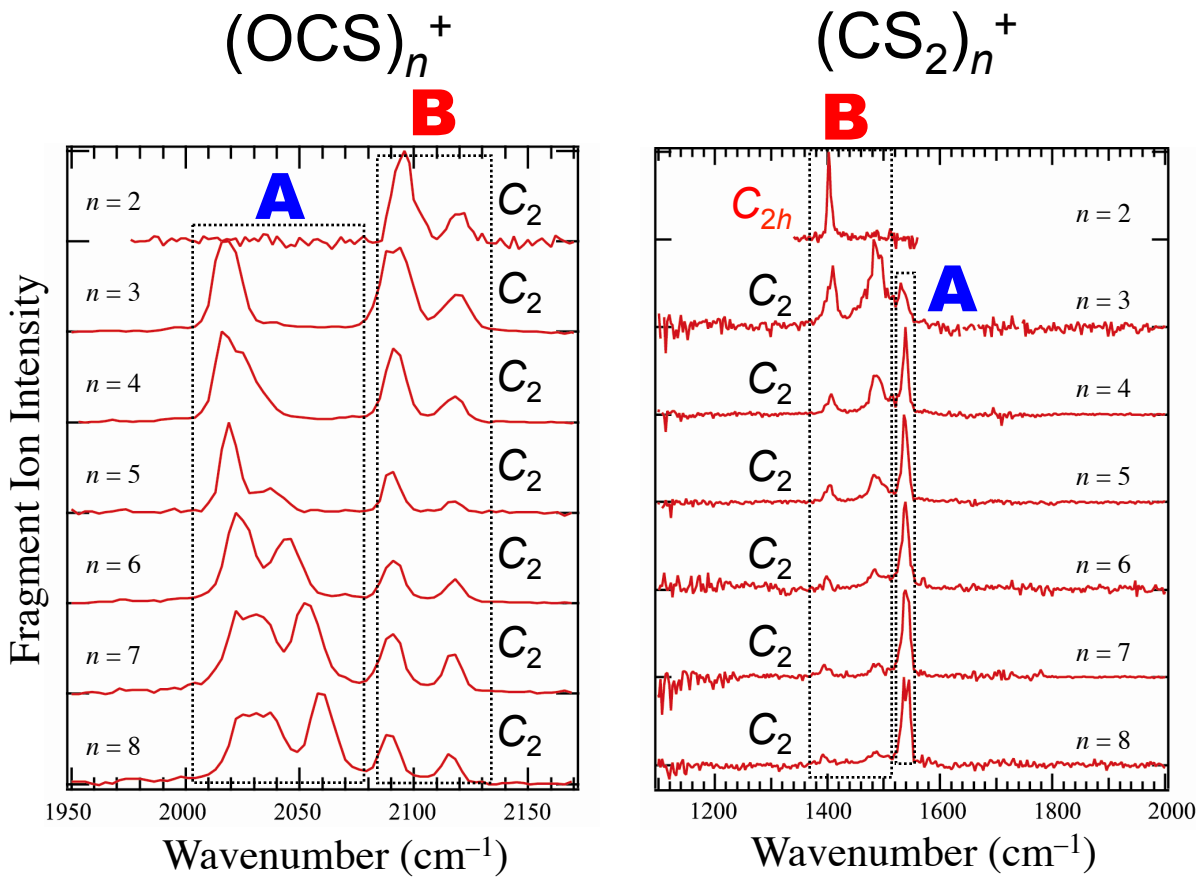
Bare $C_2O_4^+$ ion has planar (C_{2h}) structure.
Structure of $C_2O_4^+$ depends on cluster size.

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

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



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



A

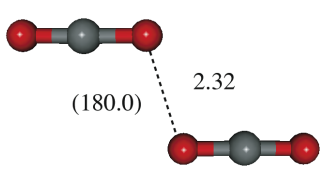
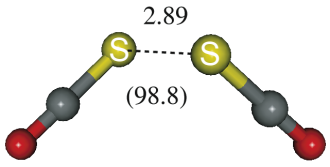
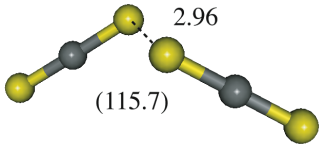
Solvent molecules

B

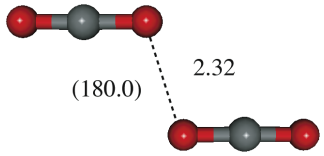
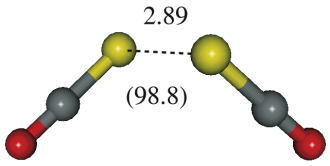
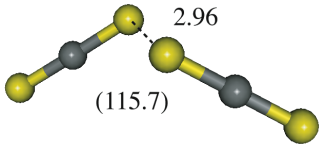
Dimer ion core

$(OCS)_n^+$ and $(CS_2)_n^+$ ⟶ dimer ion core.
Core structure not so change, different from $(CO_2)_n^+$.

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

Structure of Dimer Ion Core

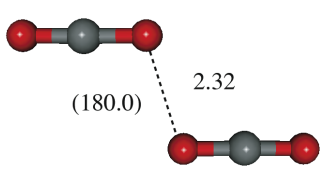
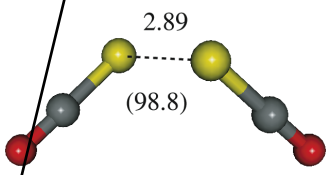
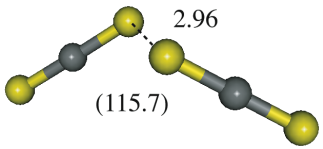
Cluster Size	$C_2O_4^+$	$C_2O_2S_2^+$	$C_2S_4^+$
n = 2	C_{2h}	C_2	C_{2h}
	C_2		C_2
	C_{2h}		
	C_2		
	C_{2h}		
	C_{2h}		
8	C_{2h}		
n = 2 calculation	 C_{2h}	 C_2	 C_2

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

↓

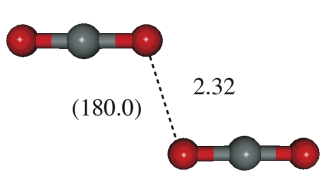
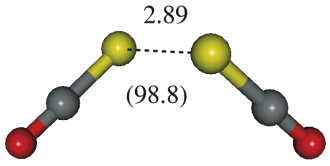
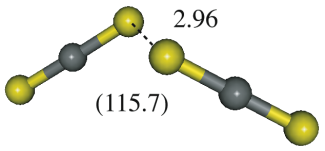
$C_2O_4^+$ so floppy?

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_2	 C_2

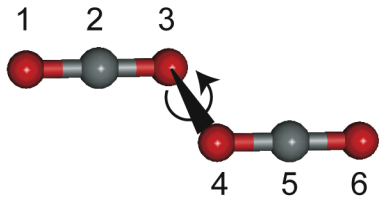
Q2.
Why bare $C_2O_2S_2^+$ has bent (C_2) structure?

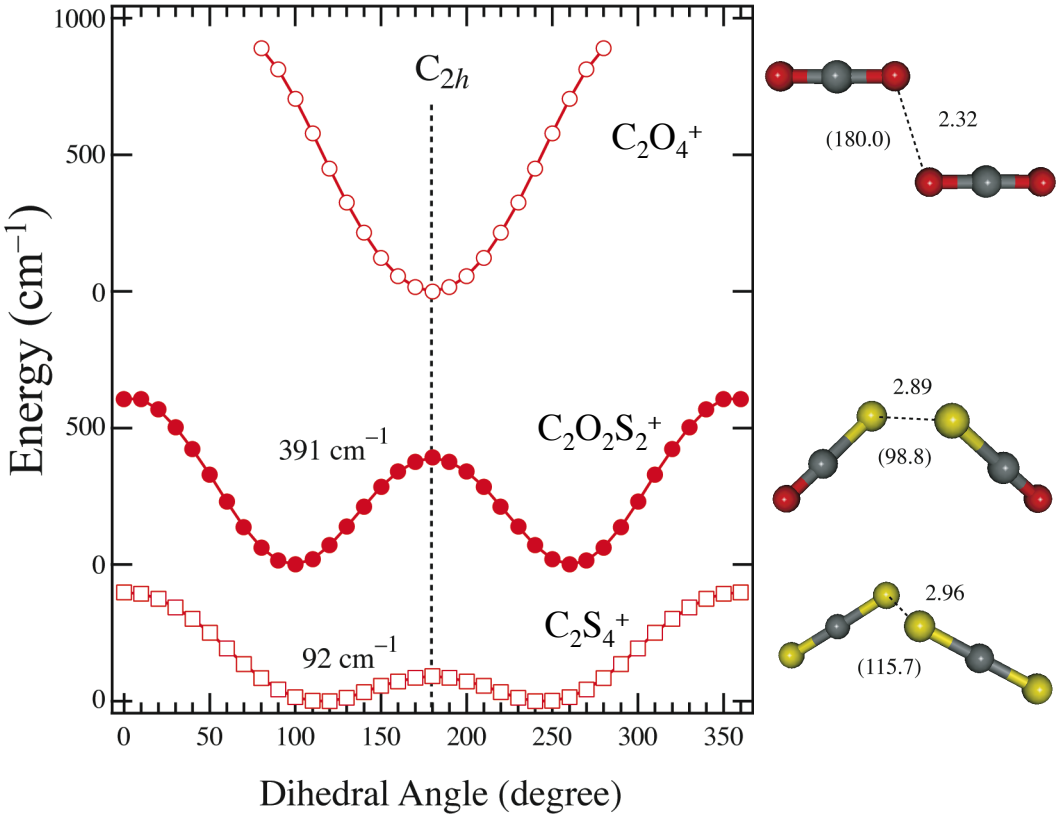
Structure of Dimer Ion Core

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

Q3.
Why structure different between experiment and calc. for $C_2S_4^+$?

Q1. Is $C_2O_4^+$ So Floppy?





PES along out-of-plane torsional motion

@B3LYP/6-311+G*

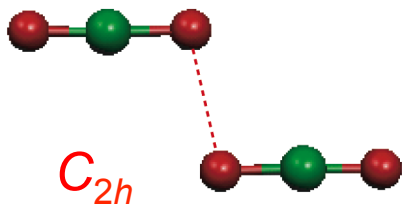
A.

- Rather $C_2O_4^+$ has hardest structure.
- Structural change of $C_2O_4^+$ in $(CO_2)_n^+$

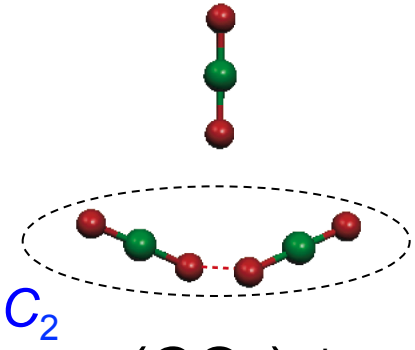
structural weakness of $C_2O_4^+$

characteristics of solvent molecules

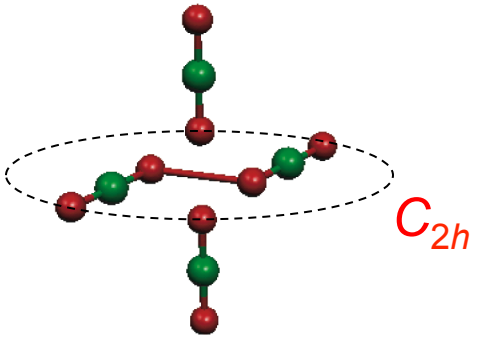
Proposed Structural Change



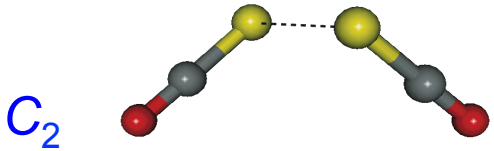
$(CO_2)_2^+$



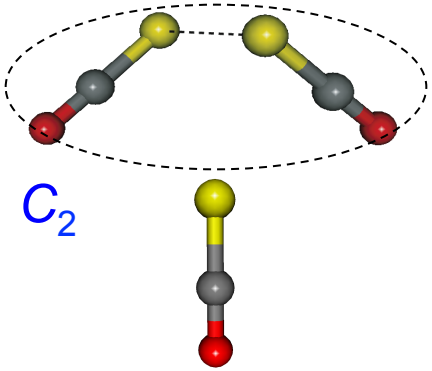
$(CO_2)_3^+$



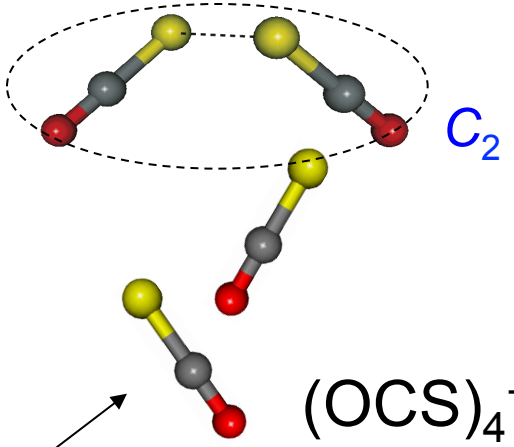
$(CO_2)_4^+$



$(OCS)_2^+$



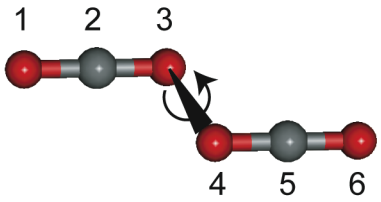
$(OCS)_3^+$

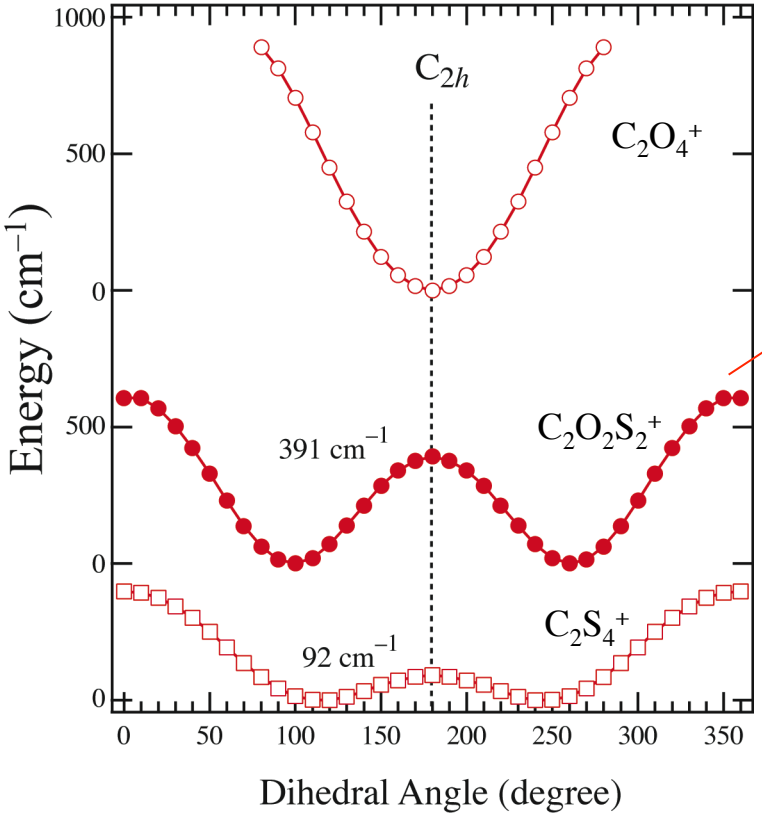


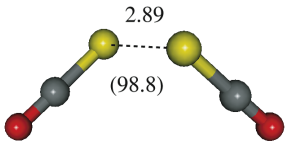
$(OCS)_4^+$

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

Q2. Why $C_2O_2S_2^+$ bent?







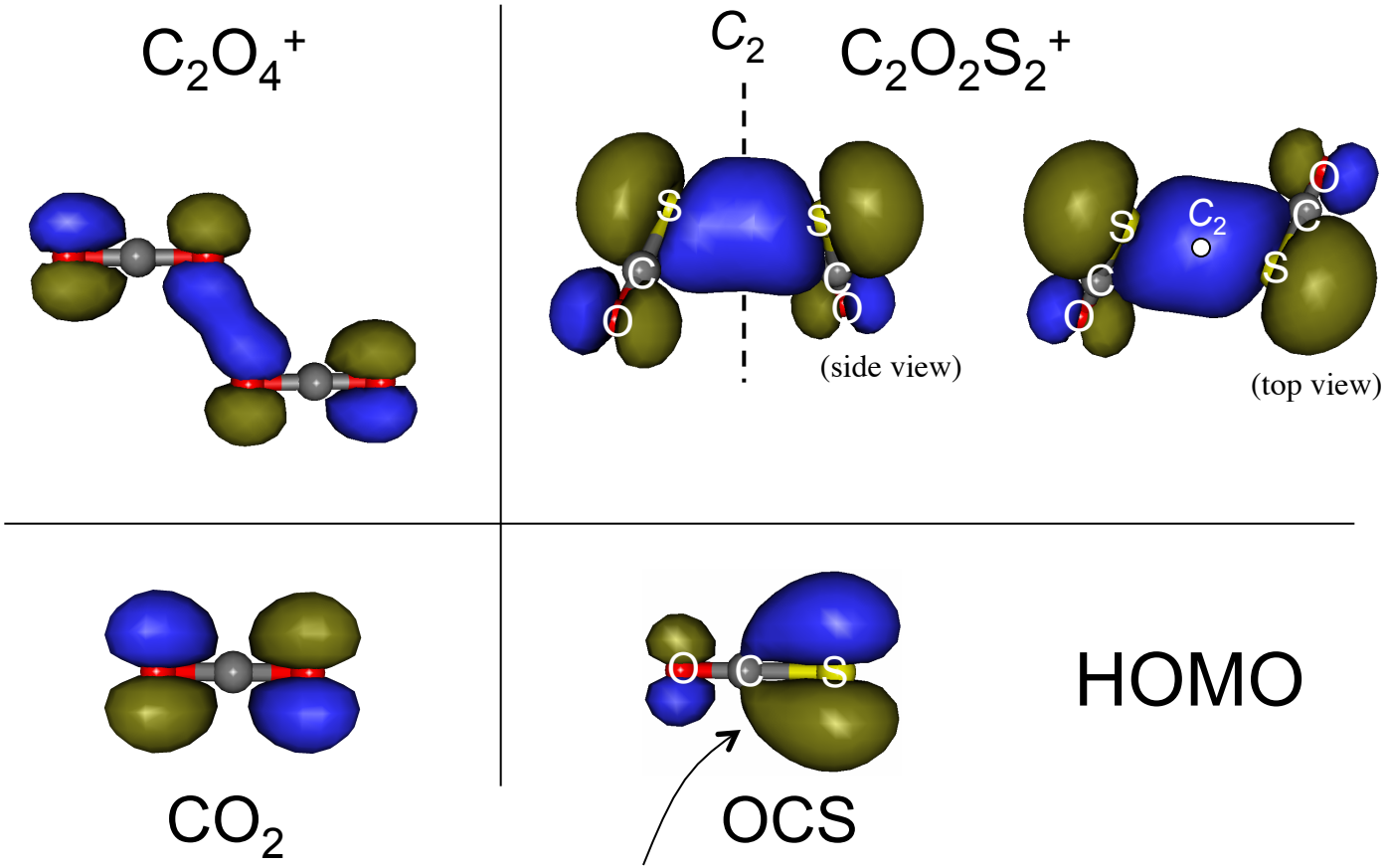
PES along out-of-plane torsional motion

$C_2O_2S_2^+$ has deep double-minimum potential.

Calc. results agree with experimental result.

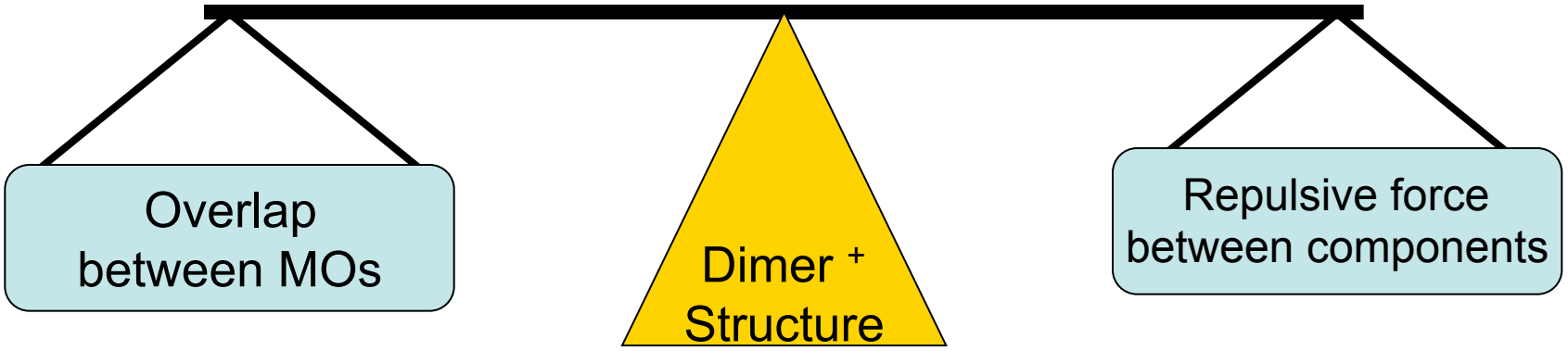
	$C_2O_2S_2^+$
experiment	C_2
calculation	C_2

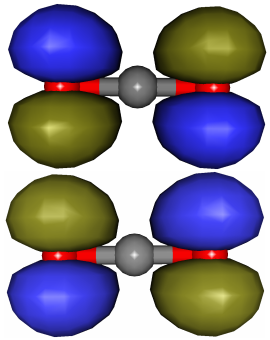
Q2. Why $C_2O_2S_2^+$ bent?



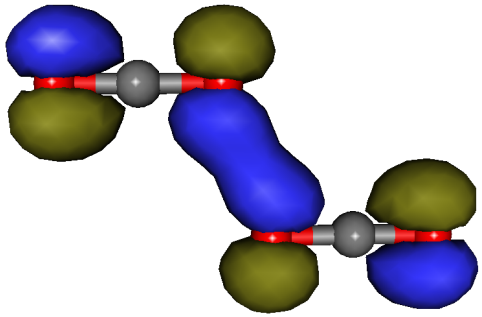
Contains 2p component of C atom

Q2. Why $C_2O_2S_2^+$ bent?

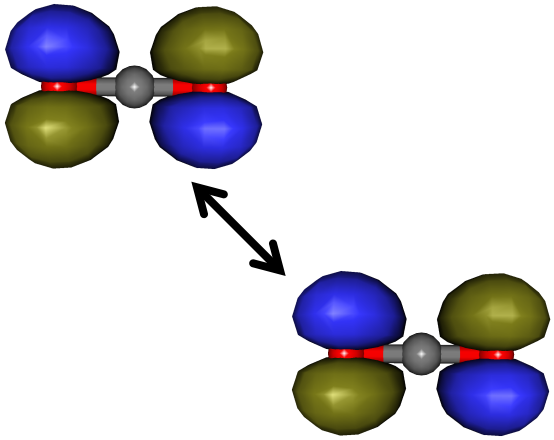




Completely stacked?



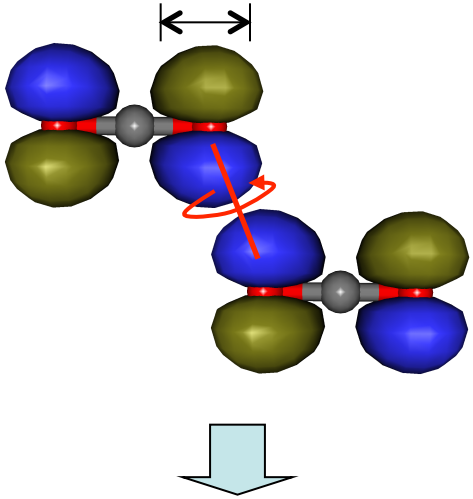
Step-like
structure

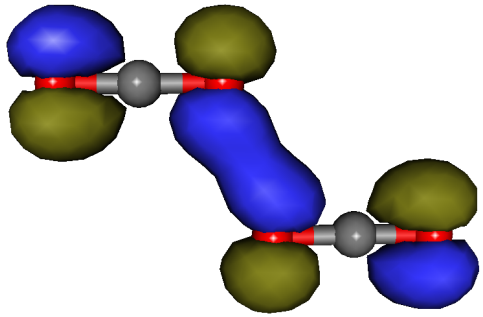


Far apart from each other?

Q2. Why $C_2O_2S_2^+$ bent?

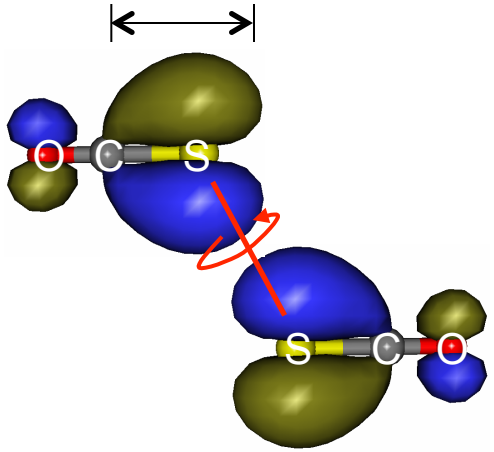
$C_2O_4^+$

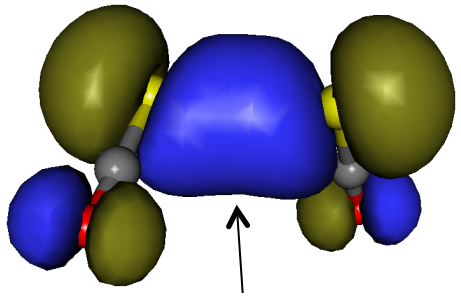




Minimizes repulsive force.

$C_2O_2S_2^+$

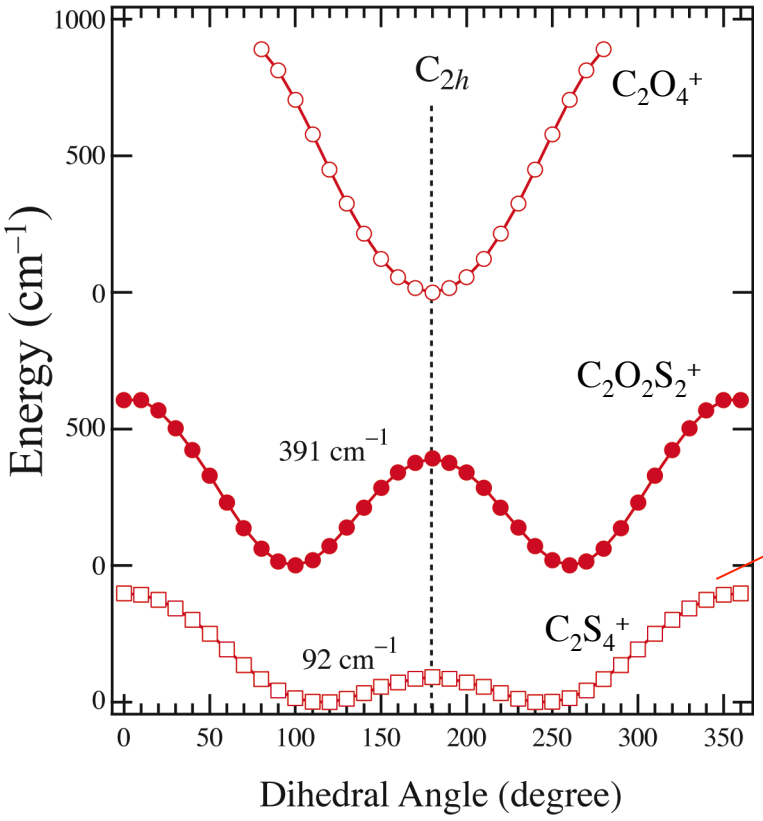




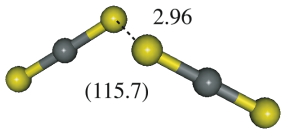
Overlap increases
with decreasing the angle.

A. Bent structure originates from broad nature of HOMO.

Q3. Why Structure in Experiment and Calculation Different for $C_2S_4^+$?



@B3LYP/6-311+G*



	$C_2S_4^+$
experiment	C_{2h}
calculation	C_2

$C_2S_4^+$ has shallow PES
→ so floppy

A. Intermol. interaction weaker for $C_2S_4^+$.
Higher-level calculations needed.

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.