Formation of “Semi”-Covalent Bonds Studied by IR Spectroscopy

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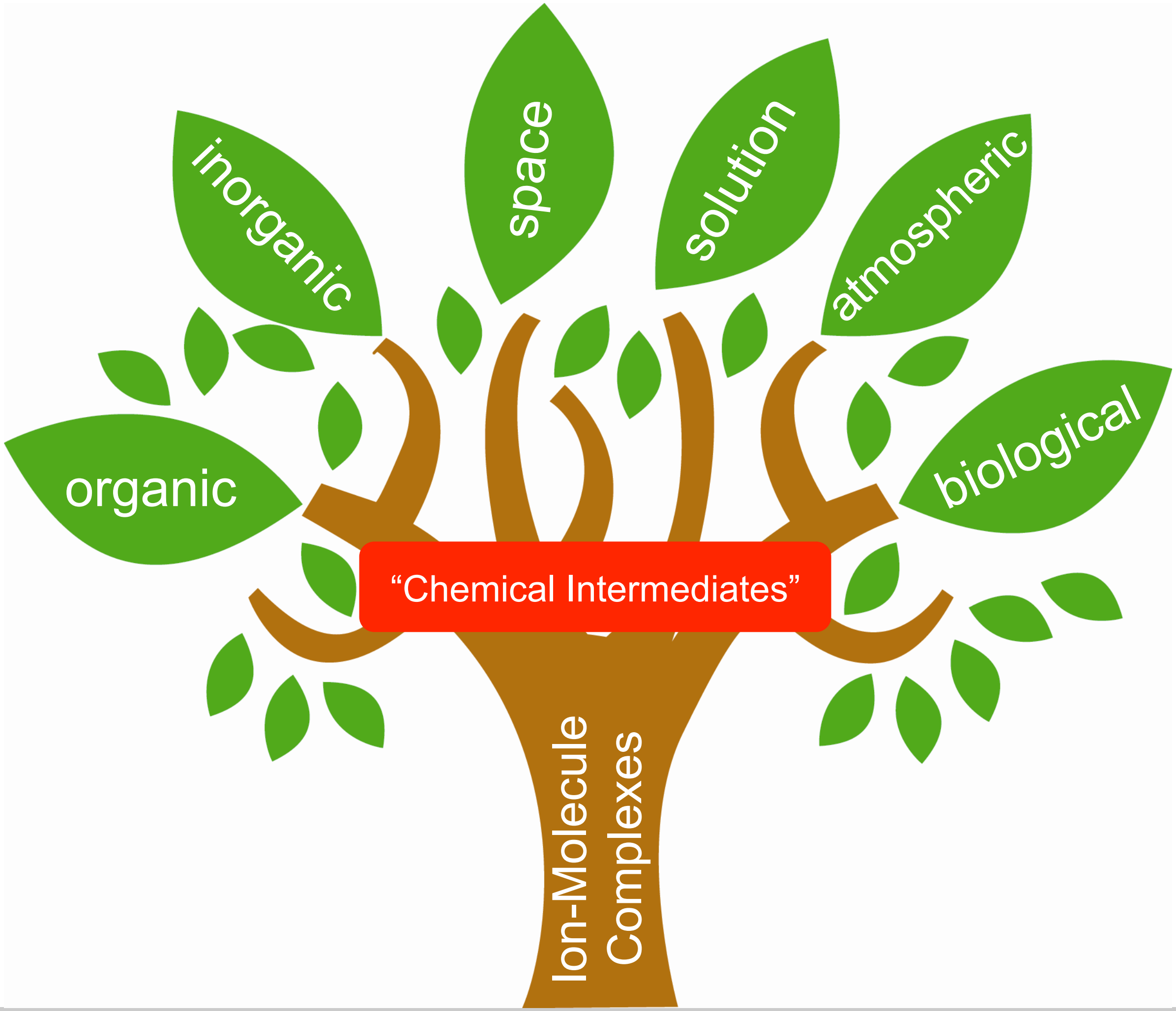
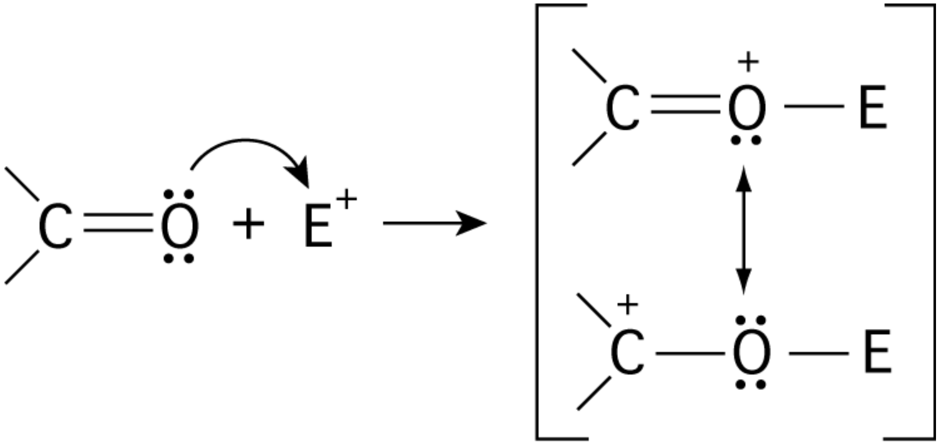
Why Ion-Molecule Complexes?



Basis of Chemistry!

Nucleophilic Additional Reactions of C=O



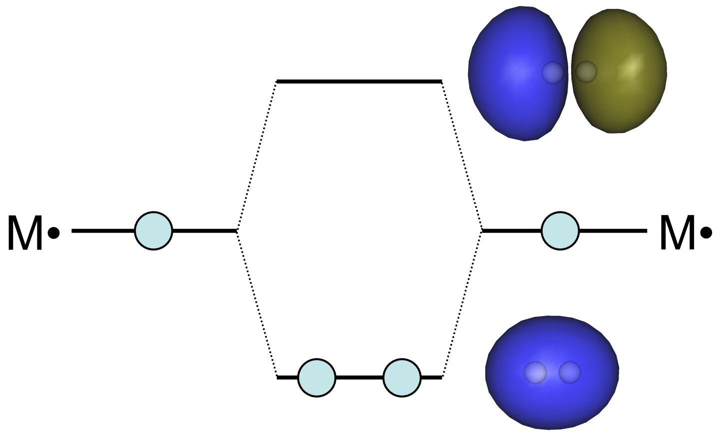
Formation of covalent bond

Primary process of nucleophilic reactions

Resonance interactions between MOs are important

Formation of Covalent Bonds (1)

Radical + Radical



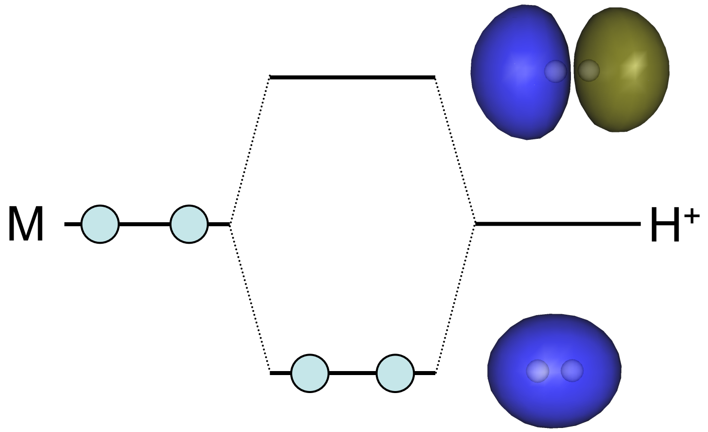
M–M

Bond order = 1

Covalent

H_2, H_2O, NH_3

Molecule + Proton



$(M–H)^+$

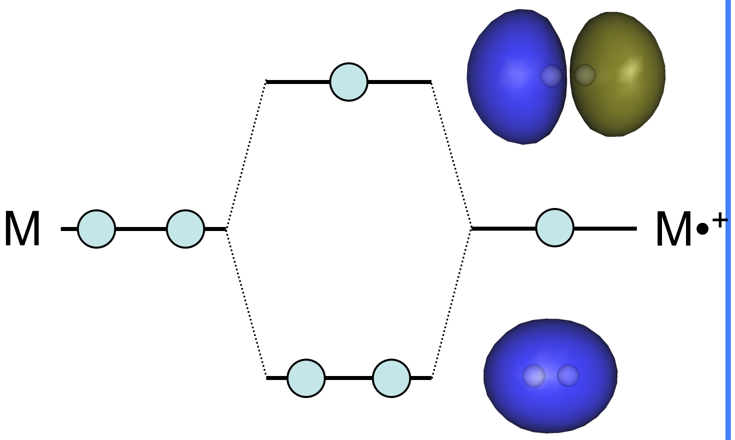
Bond order = 1

Covalent

H_3O^+, NH_4^+

Formation of Covalent Bonds (2)

Molecule + Radical Ion



$(M–H)^+$

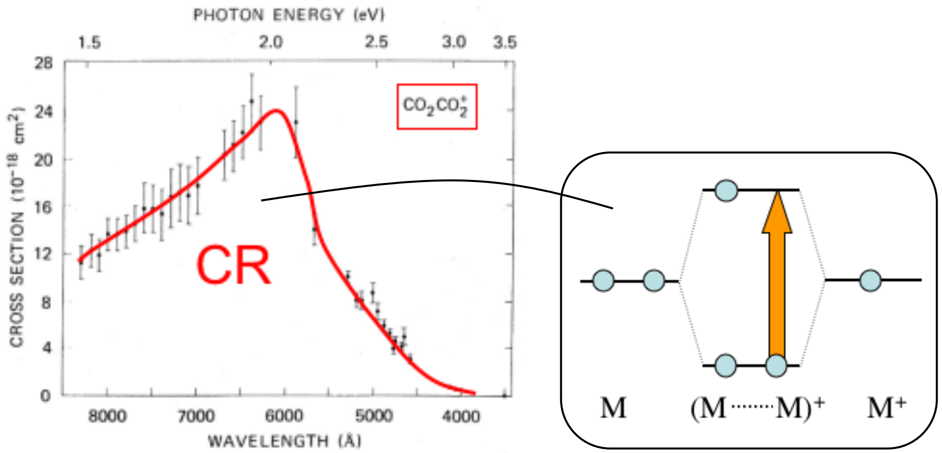
Bond order = 0.5

"Semi"-Covalent Bond

"Two-Center Three-Electron" Bond

Why IR Spectroscopy?

Electronic Spectra



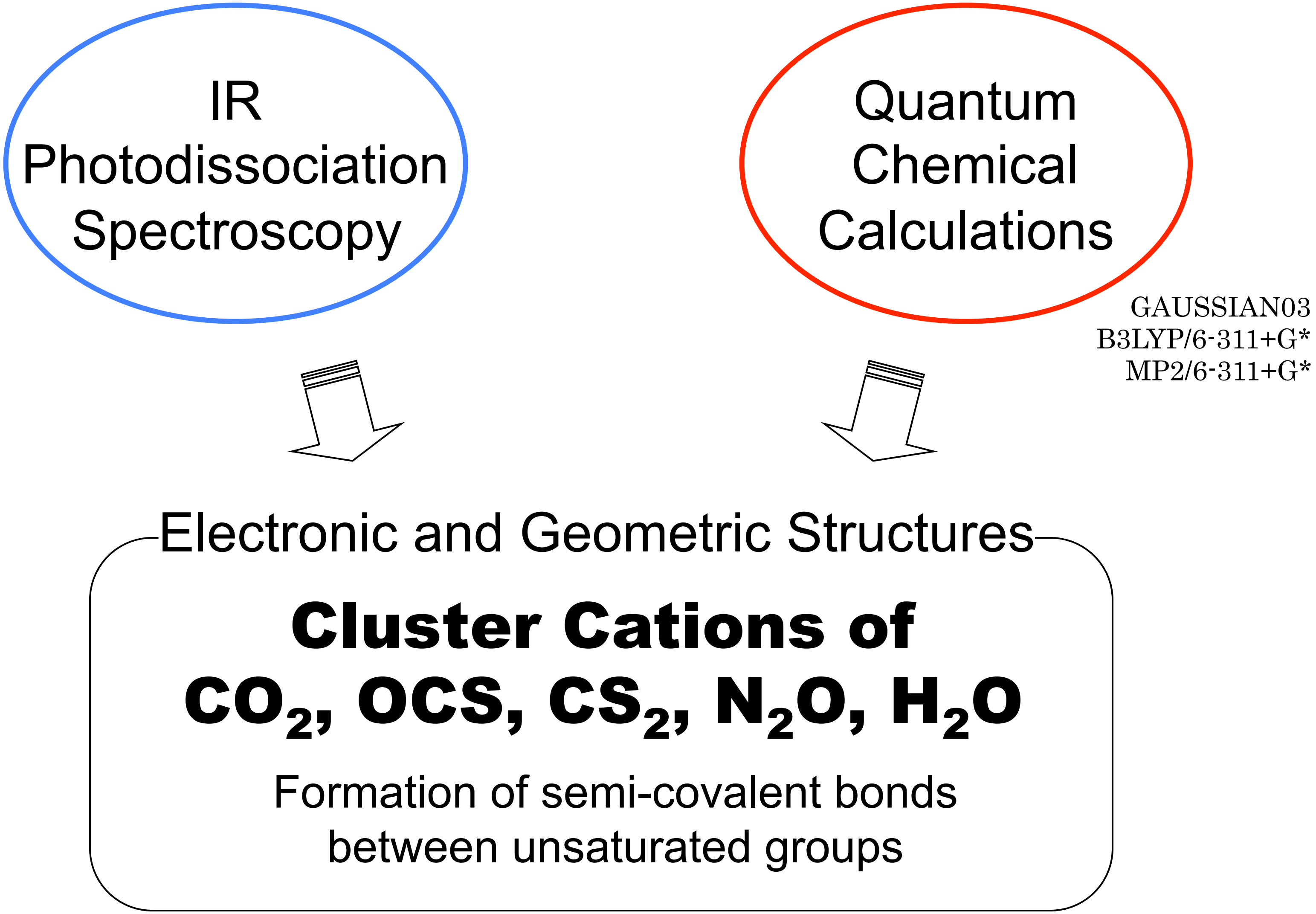
Smith and Lee, J. Chem. Phys. **69**, 5393 (1978).

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

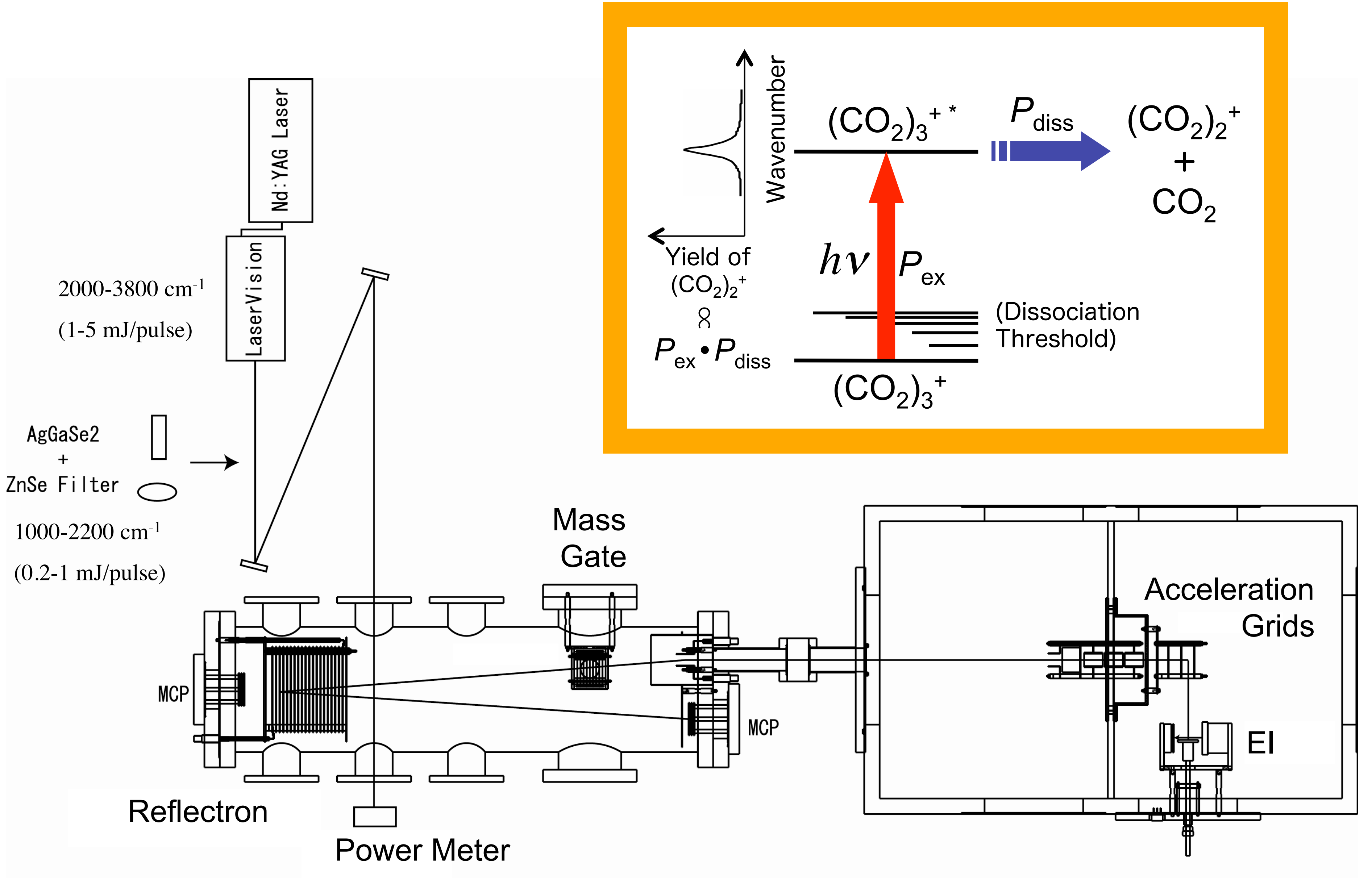
GAUSSIAN03
B3LYP/6-311+G*
MP2/6-311+G*

Electronic and Geometric Structures

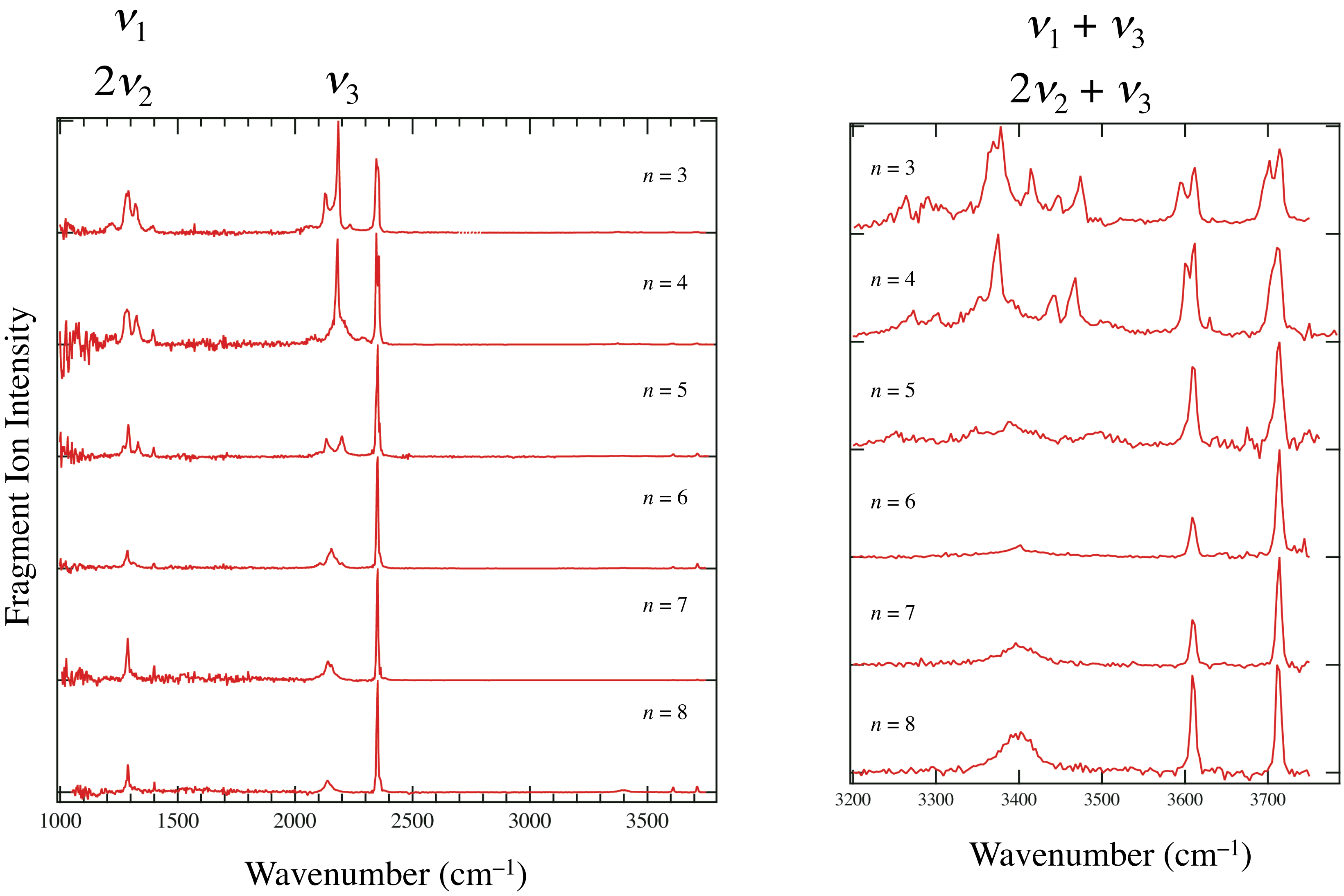
Cluster Cations of
CO_2, OCS, CS_2, N_2O, H_2O

Formation of semi-covalent bonds
between unsaturated groups

Experimental

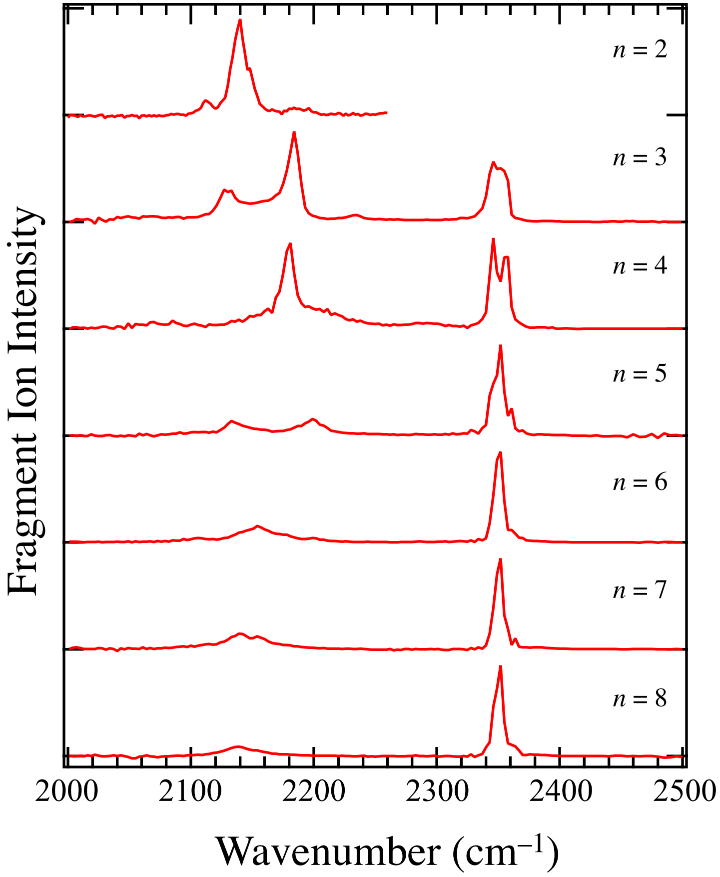


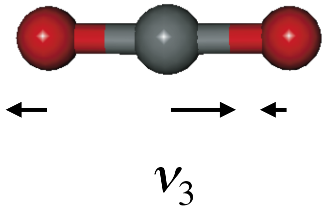
IRPD Spectra of $(CO_2)_n^+$



IRPD Spectra of $(CO_2)_n^+$

Anti-symmetric CO stretch (ν_3)

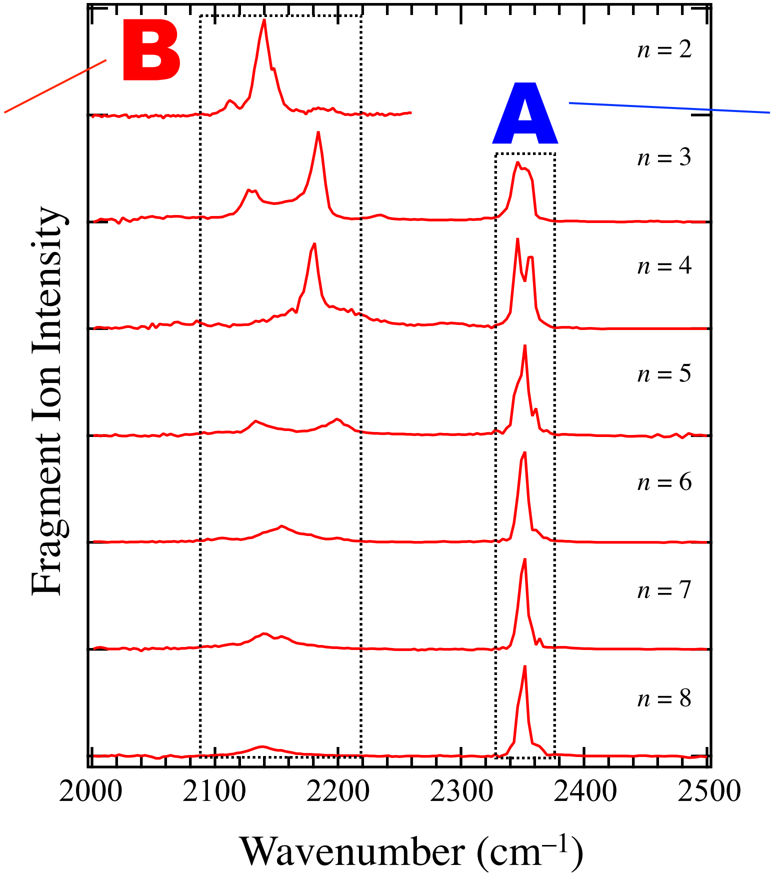




IRPD Spectra of $(CO_2)_n^+$

Intensity decreases with increasing *n*.

Ion core

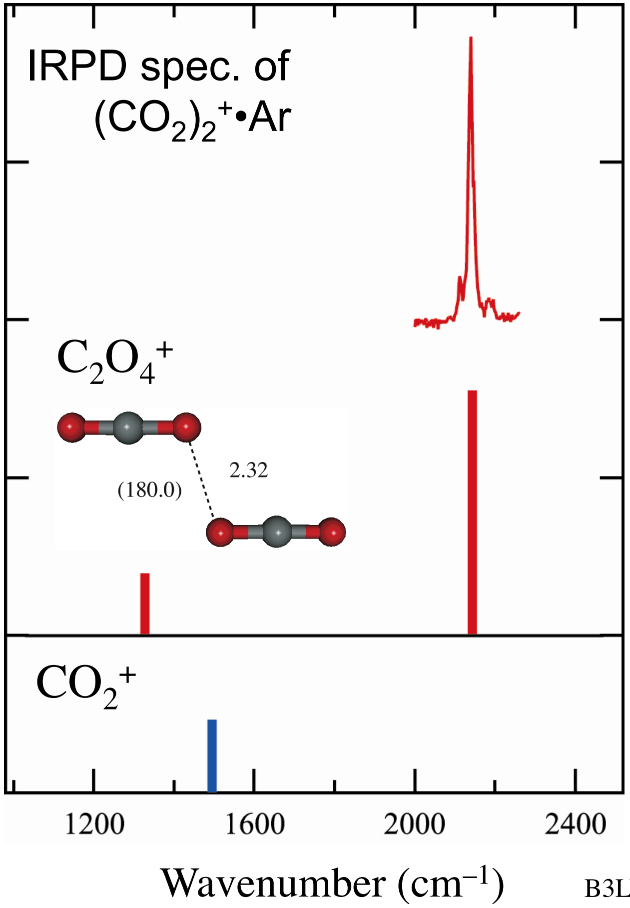


Band position almost the same as that of CO_2.

Solvent CO_2 molecules

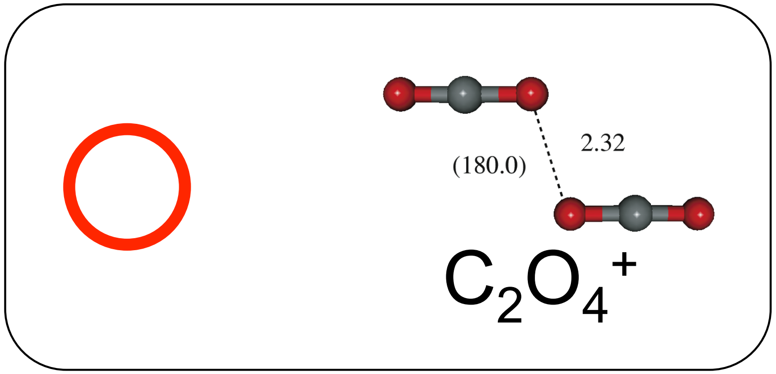
What is Ion Core of $(CO_2)_n^+$?

CO_2^+ or $C_2O_4^+$?

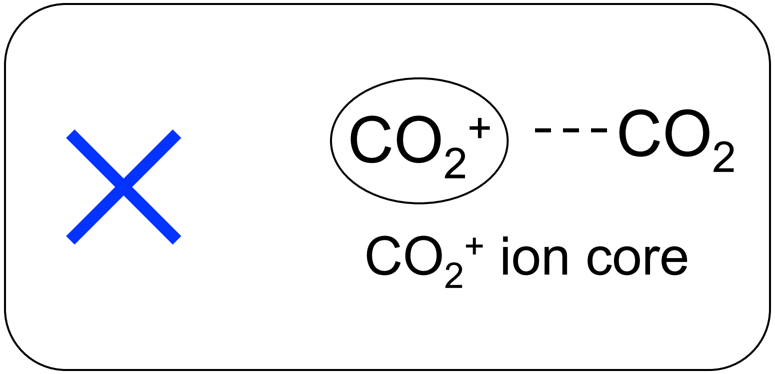


B3LYP/6-311+G*

Ion core of $(CO_2)_n^+$



$C_2O_4^+$

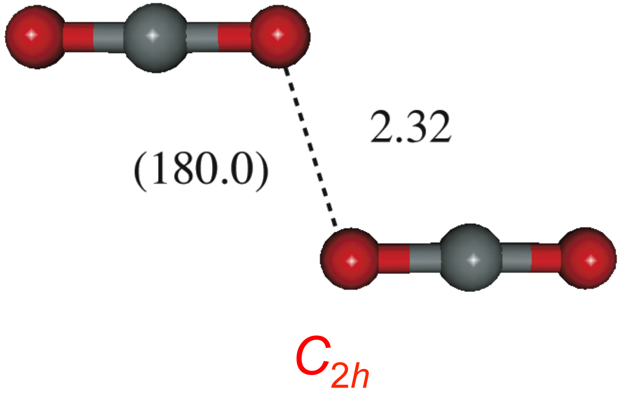


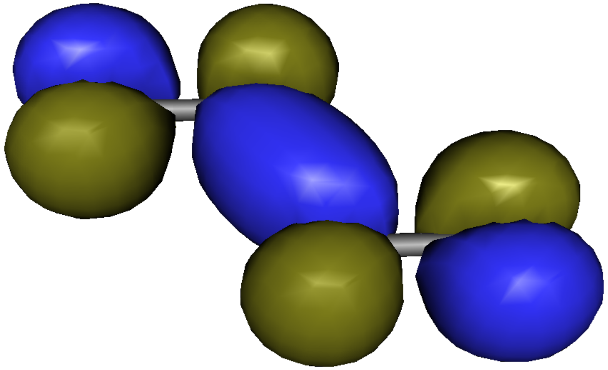
CO_2^+ ---CO_2

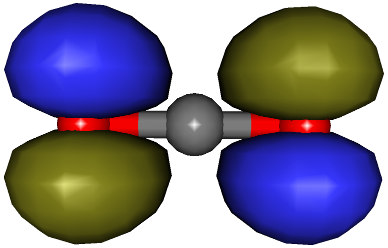
CO_2^+ ion core

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

Structure of $C_2O_4^+$







HOMO of CO_2

B3LYP/6-311+G*

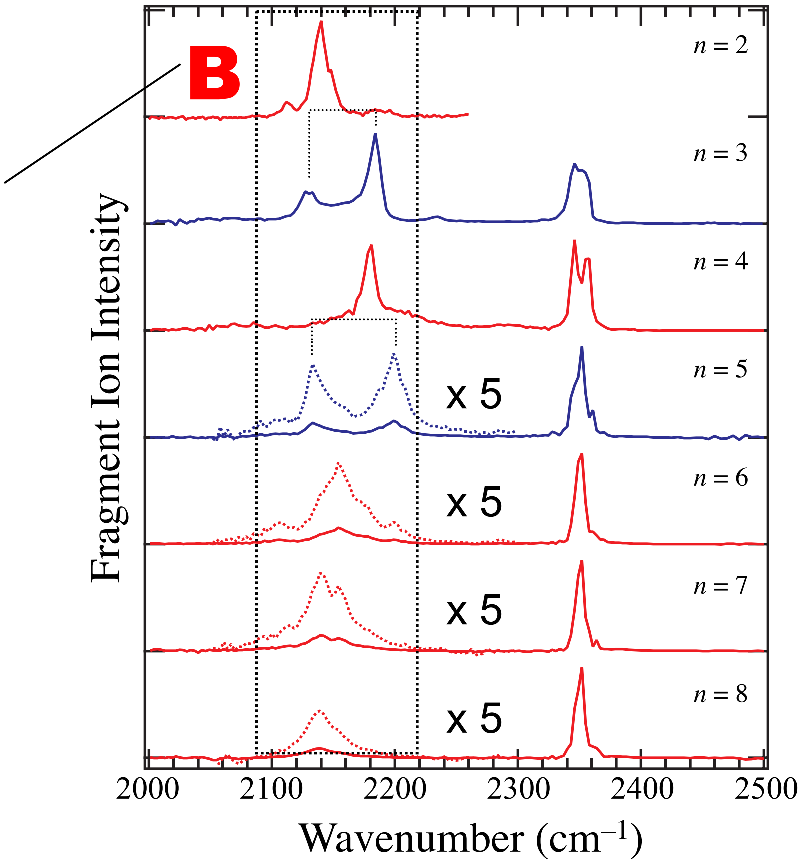
Structure of $C_2O_4^+$ is controlled by overlap between HOMOs.

IRPD Spectra of $(CO_2)_n^+$

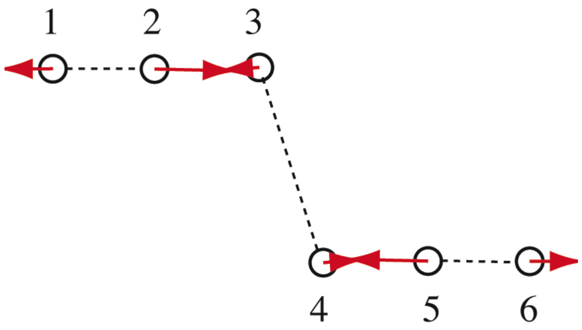
Band number alternately changes.

↓

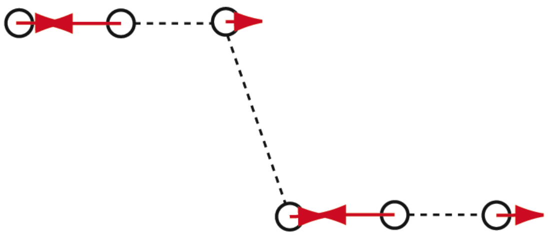
Structural change of $C_2O_4^+$ part



In-Phase and Out-of-Phase Combinations



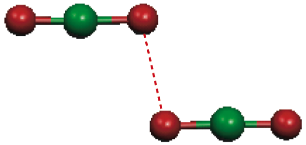
(a) in-phase combination

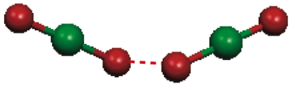


(b) out-of-phase combination

IR activity of dimer ions

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



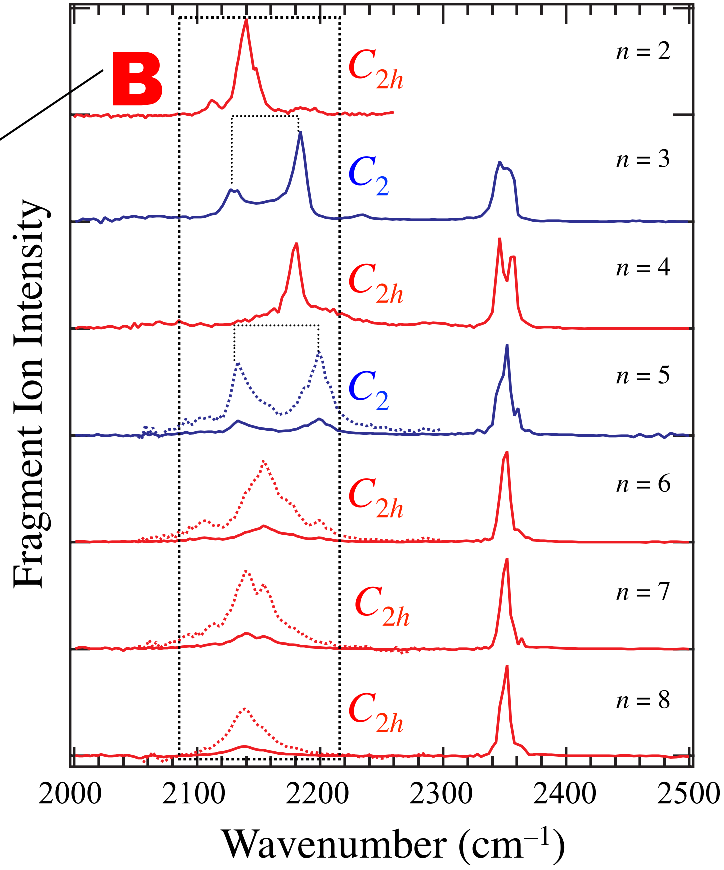


The number of IR bands indicates the planarity.

IRPD Spectra of $(CO_2)_n^+$

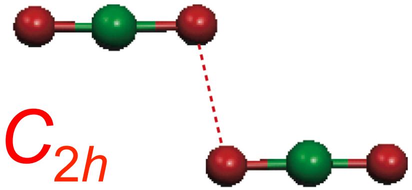
Number of $C_2O_4^+$ core band changes alternately.

Structure of $C_2O_4^+$ core changes alternately.

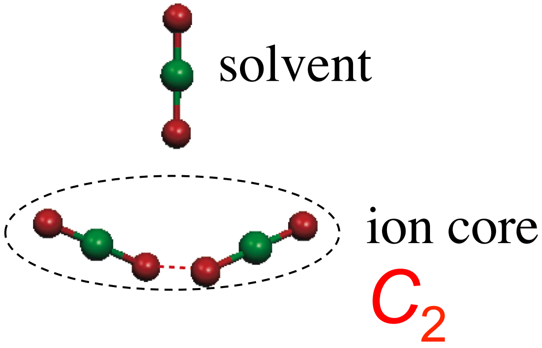


Bare $C_2O_4^+$ ion has planar (C_{2h}) structure.
Structure of $C_2O_4^+$ depends on cluster size.

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



$(CO_2)_2^+$

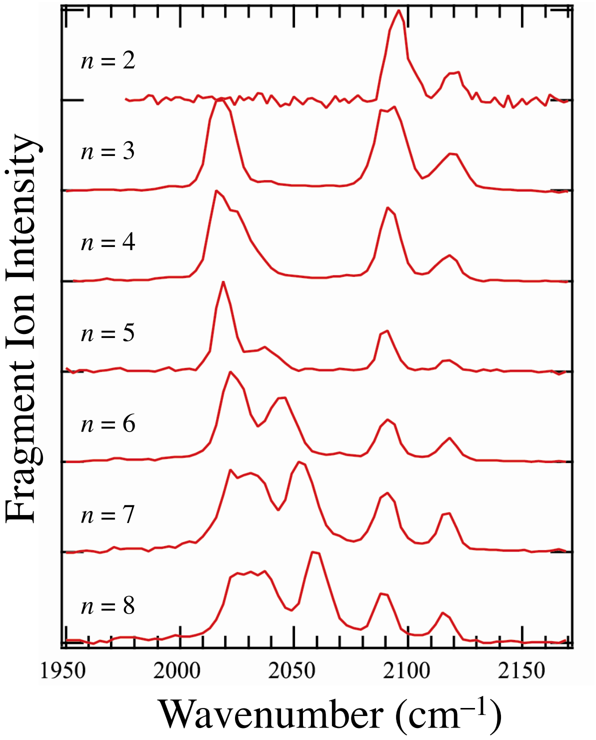


$(CO_2)_3^+$

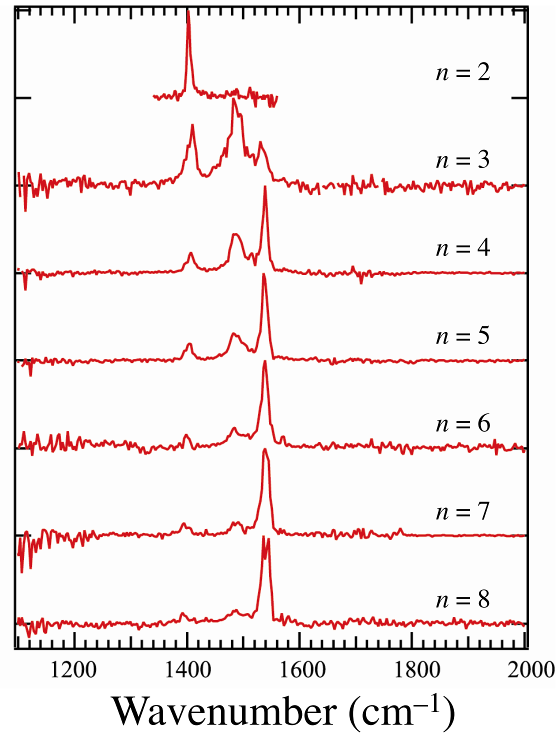
Change of $C_2O_4^+$ band number for $(CO_2)_n^+$
→ Structural change of $C_2O_4^+$ ion core

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

$(OCS)_n^+$

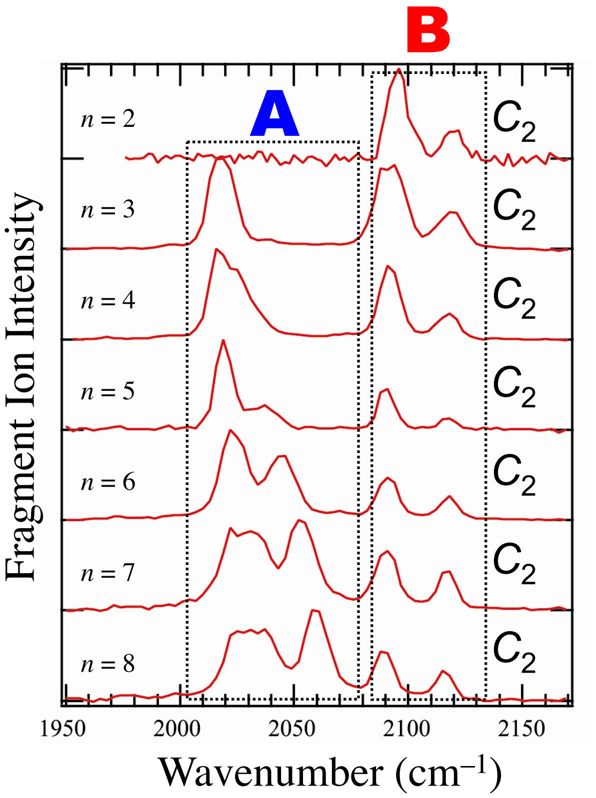


$(CS_2)_n^+$

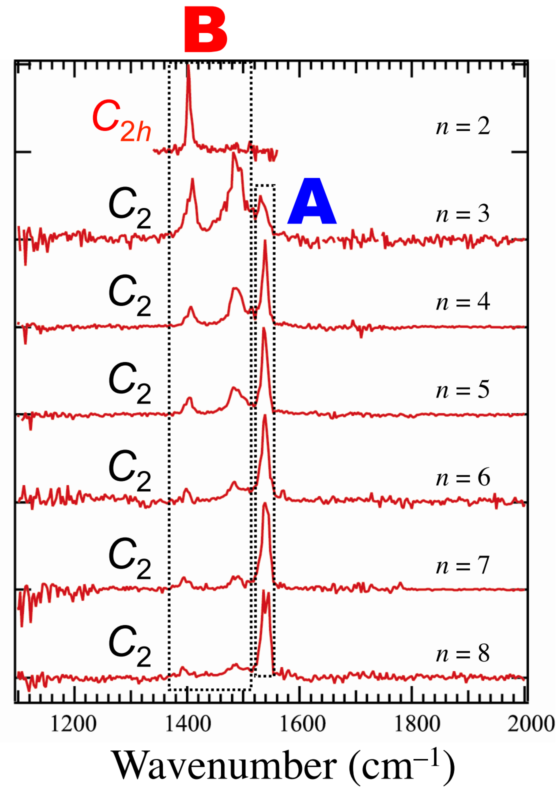


IRPD Spectra of $(OCS)_n^+$ and $(CS_2)_n^+$

$(OCS)_n^+$



$(CS_2)_n^+$



A

Solvent molecules

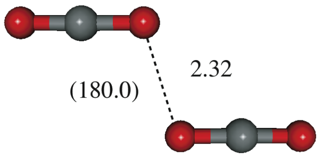
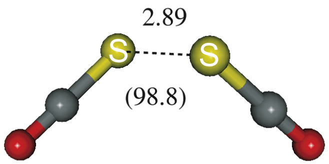
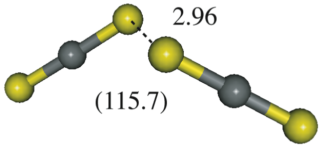
B

Dimer ion core

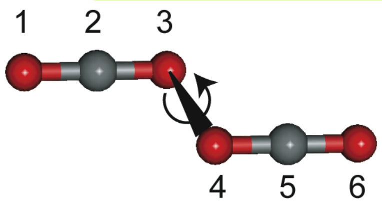
$(OCS)_n^+$ and $(CS_2)_n^+$ $\longrightarrow$ dimer ion core.

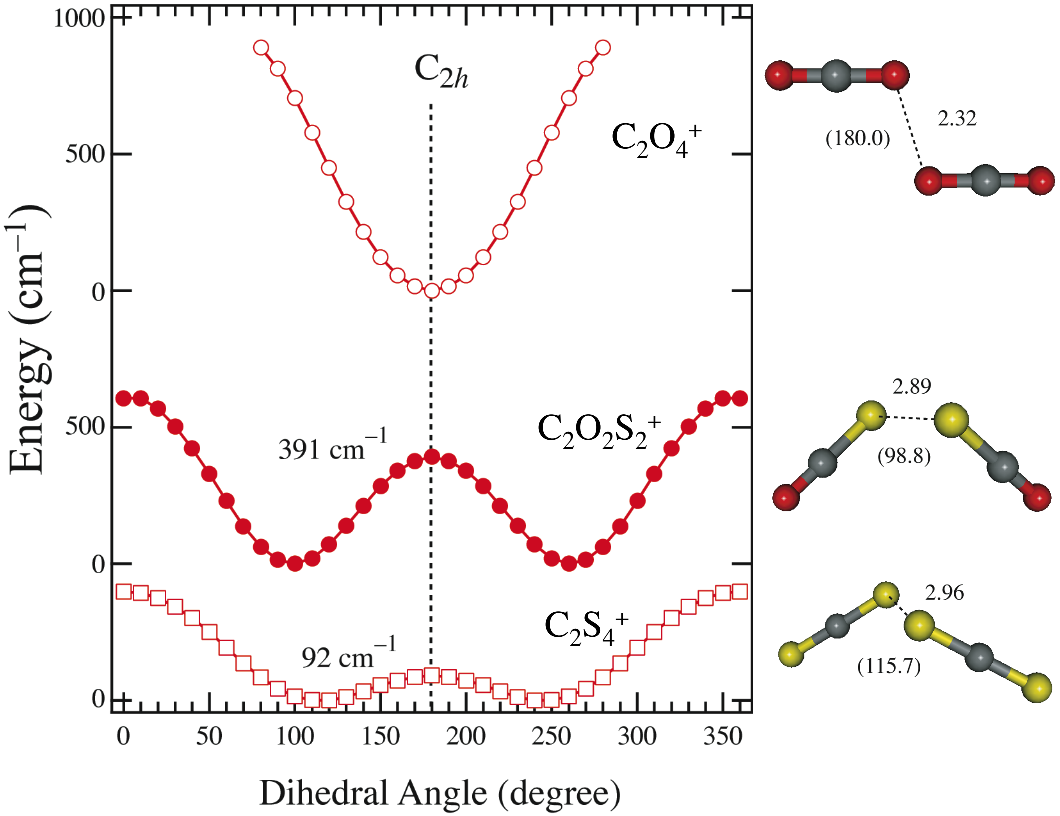
Core structure not so change, different from $(CO_2)_n^+$.

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

Is $C_2O_4^+$ So Floppy?





PES along out-of-plane torsional motion

@B3LYP/6-311+G*

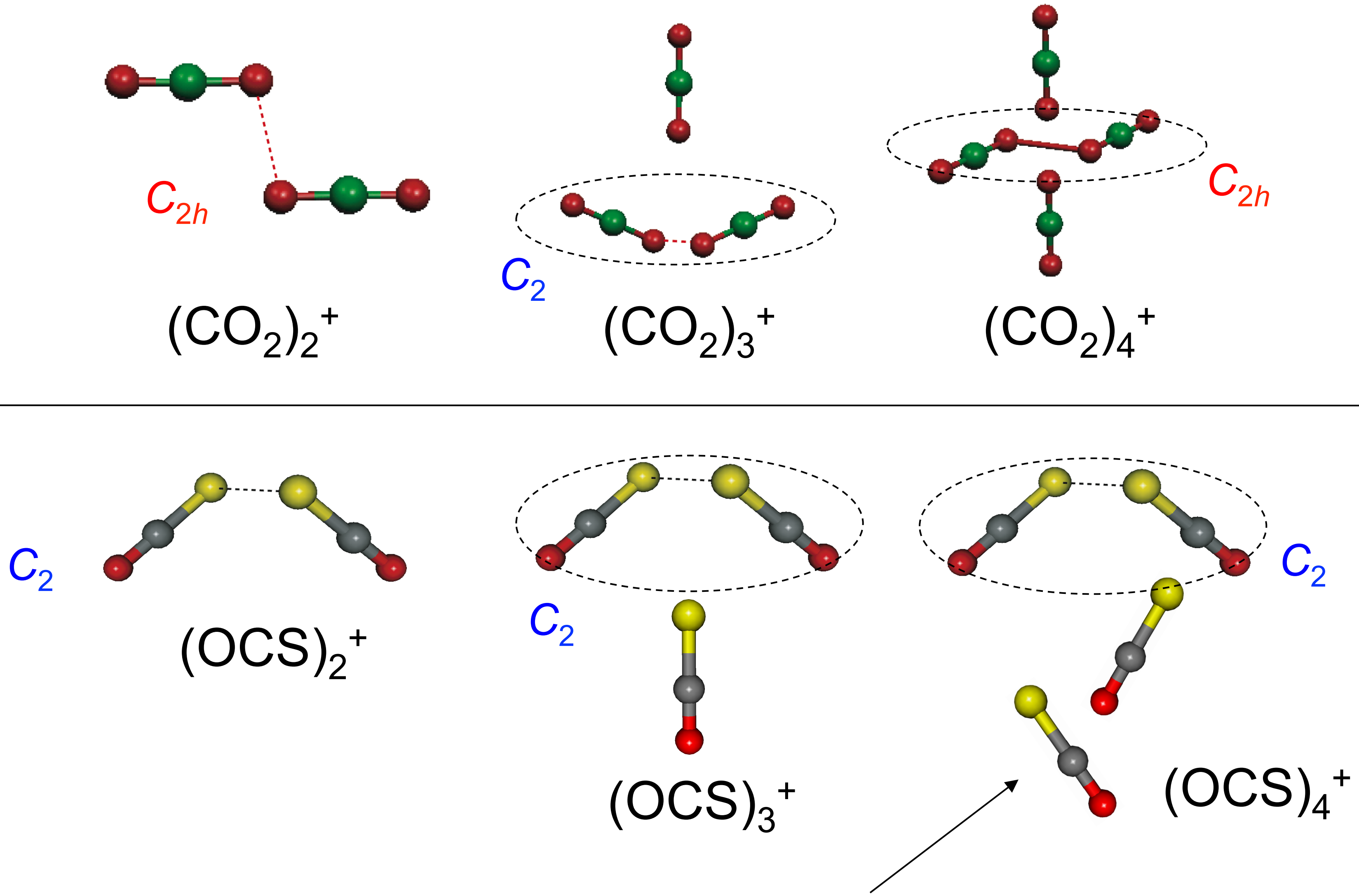
A.

- 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 interaction between solvent molecules

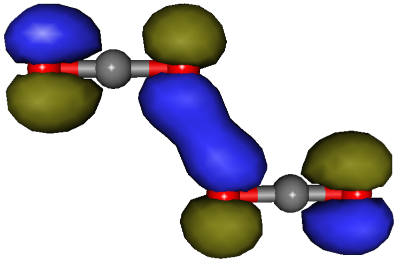
Proposed Structural Change



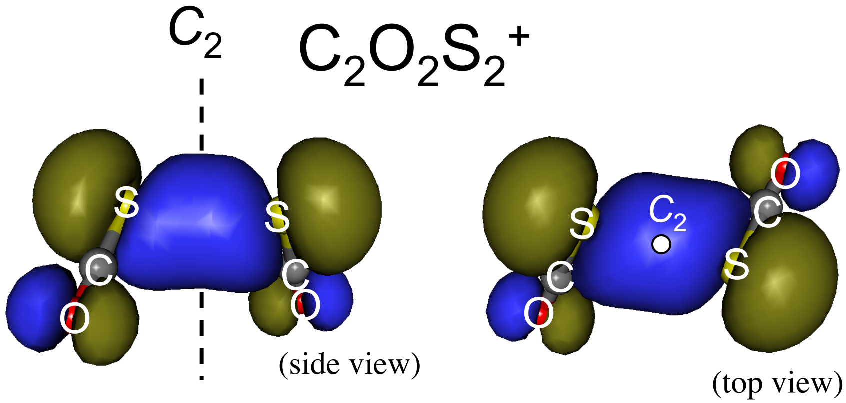
Intermol.bonds formed between solvent mols.
Solvent complex bonded asymmetrically to ion core.

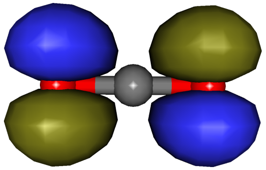
Why $C_2O_2S_2^+$ bent?

$C_2O_4^+$

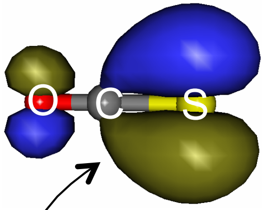


$C_2O_2S_2^+$





CO_2



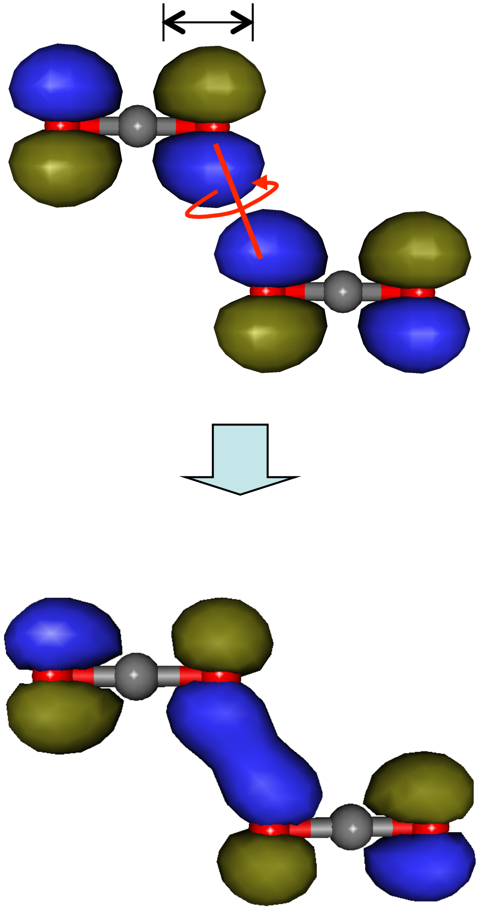
OCS

HOMO

Contains 2p component of C atom

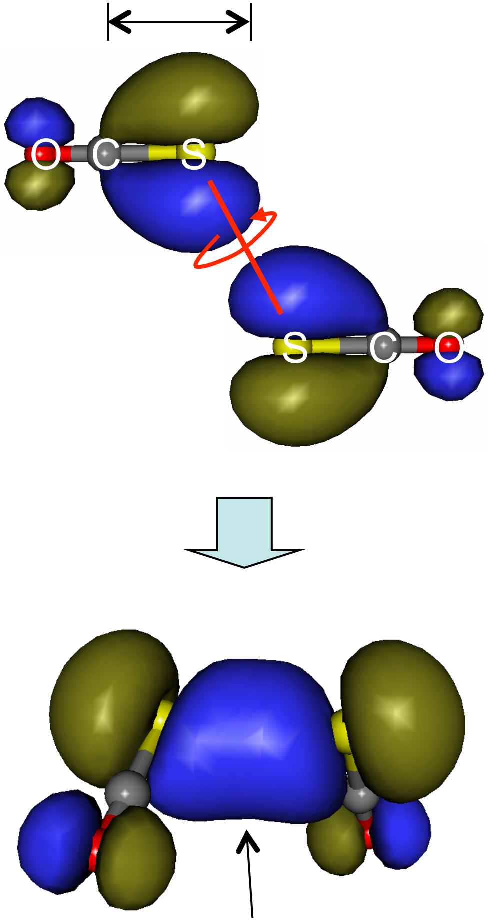
Why $C_2O_2S_2^+$ bent?

$C_2O_4^+$



Minimizes repulsive force.

$C_2O_2S_2^+$



Overlap increases
with decreasing the angle.

A. Bent structure originates from broad nature of HOMO.

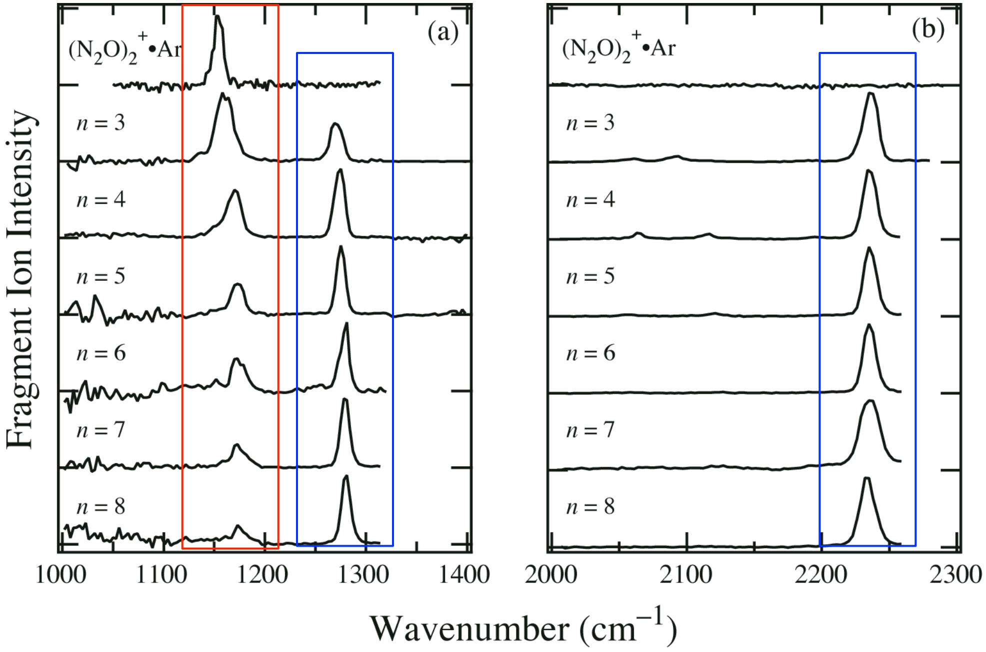
$(CO_2)_n^+$ $(OCS)_n^+$ $(CS_2)_n^+$

- 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

Kobayashi et al., J Chem. Phys., **2008**, *128*, 164319.
Inokuchi et al., J. Chem. Phys., **2008**, *129*, 044308.

IRPD Spectra of $(N_2O)_n^+$



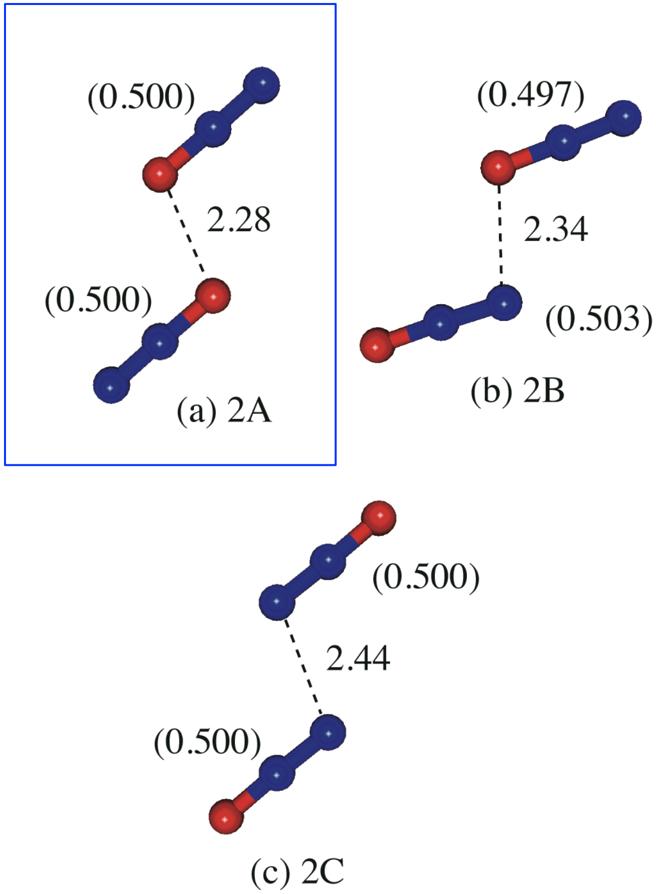
A

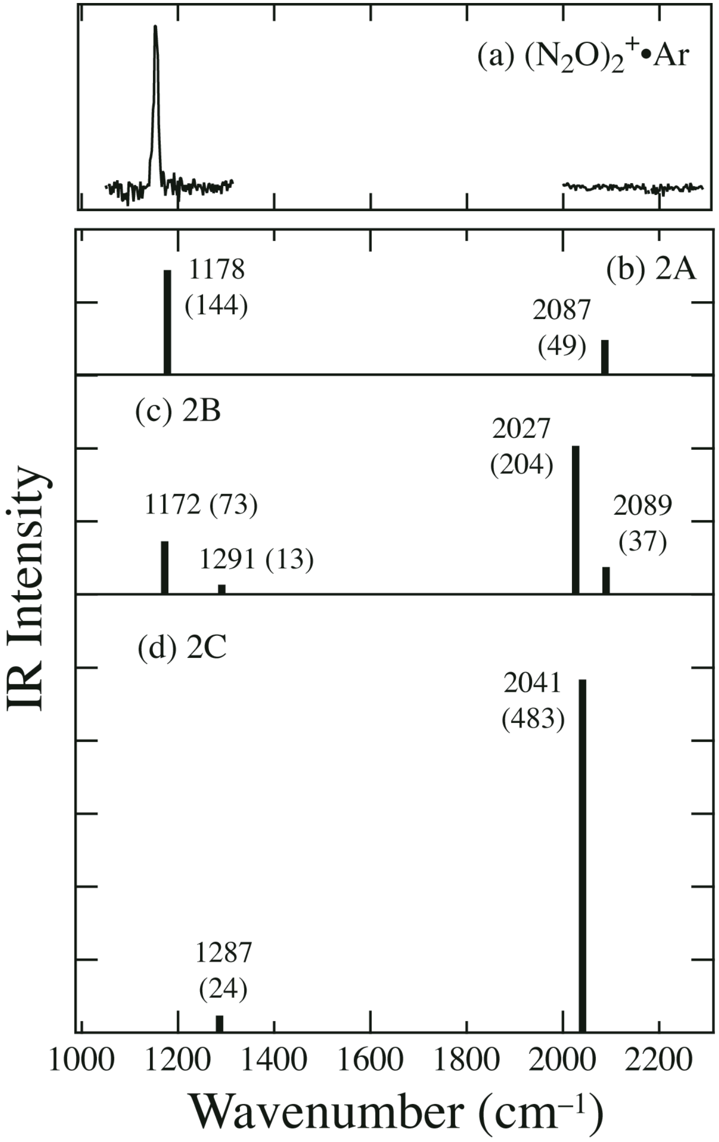
Solvent molecules

B

Dimer ion core

Structure of $(N_2O)_2^+$

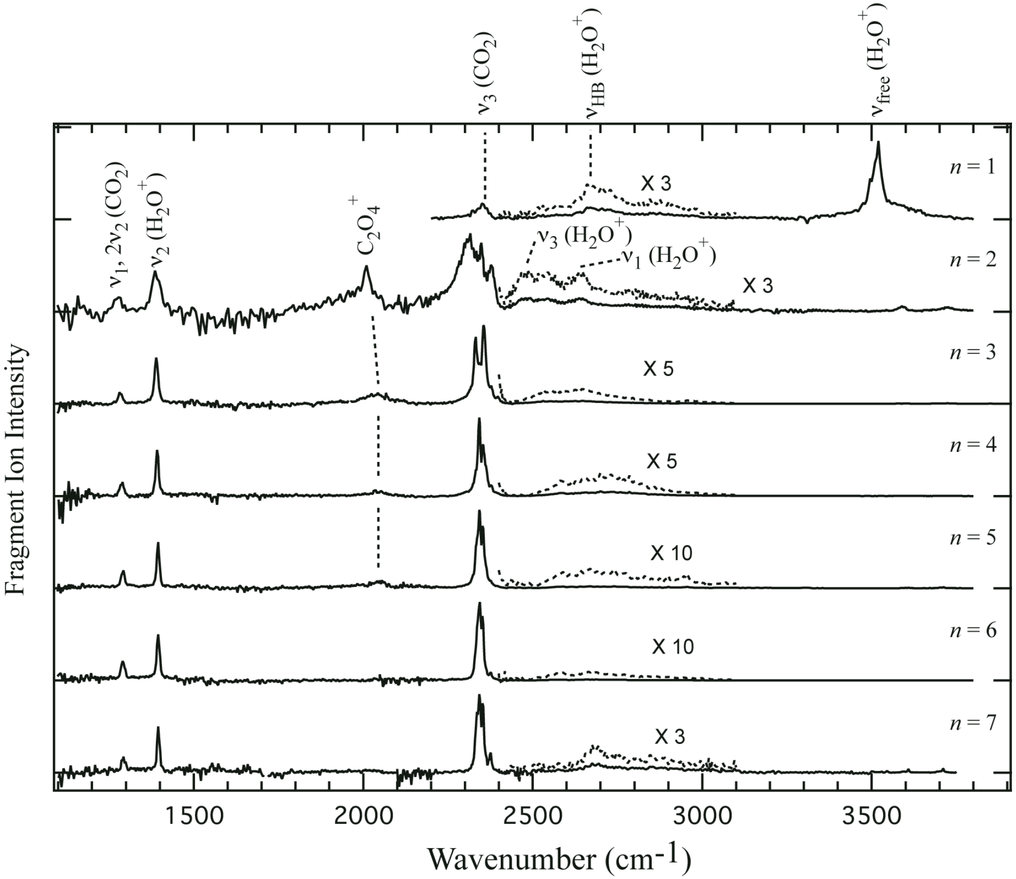


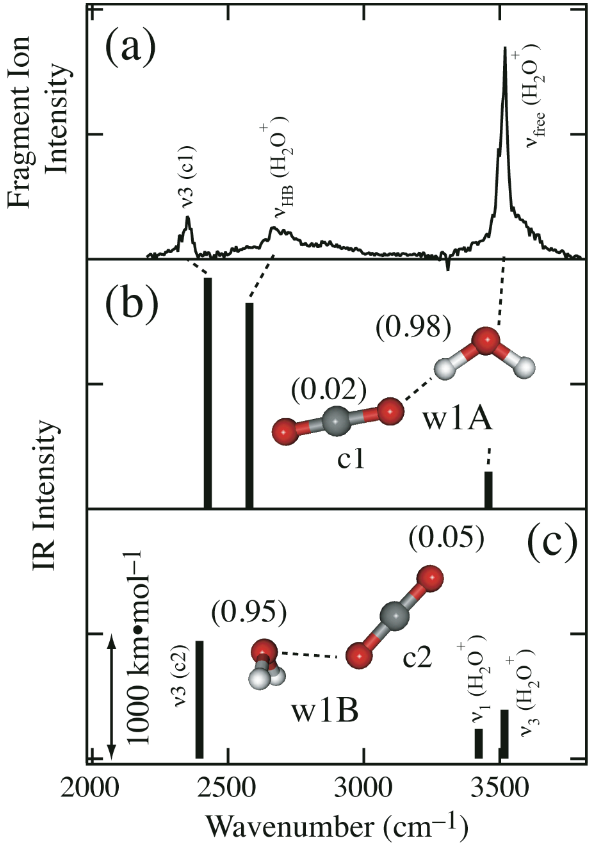


Inokuchi et al., J. Chem. Phys., **2009**, *131*, 044325.

Introduction of H_2O to $(CO_2)_n^+$

IRPD spectra of $[H_2O(CO_2)_n]^+$



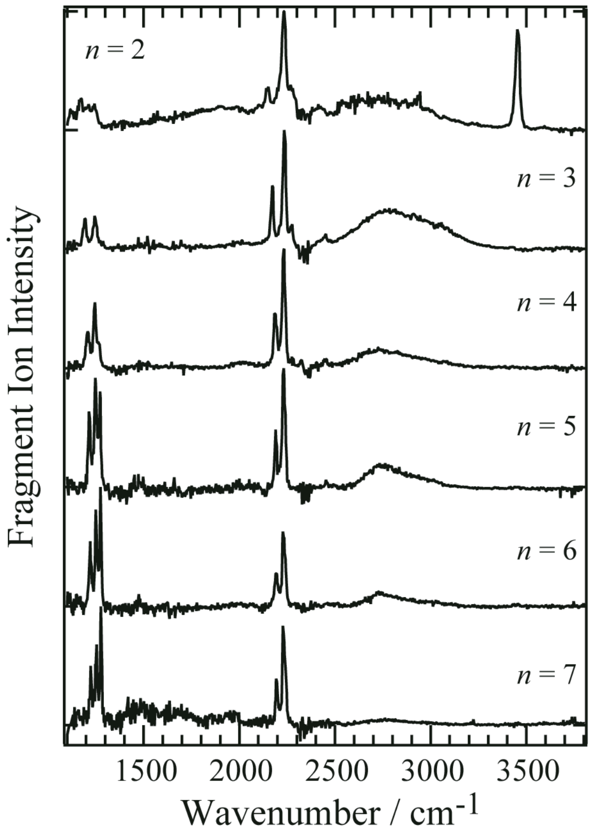


Inokuchi et al., J. Chem. Phys., **2009**, *130*, 154304.

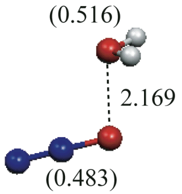
$[H_2O(CO_2)_n]^+$ clusters have an H_2O^+ ion core.

Introduction of H_2O to $(N_2O)_n^+$

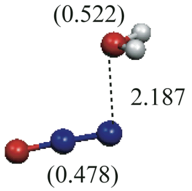
IRPD spectra of $[H_2O(N_2O)_n]^+$



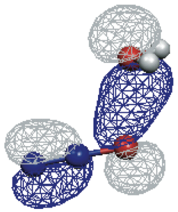
The $n = 1$ ion not dissociated.



(a) 1A ($\Delta E = 0$ cm^{-1})



(b) 1B ($\Delta E = 760$ cm^{-1})



(c) 1A

Matsushima et al., J. Phys. Chem. A, in press.

$[H_2O(N_2O)_n]^+$ clusters have an $[H_2O\text{–}ON_2]^+$ ion core.

Introduction of H_2O to $(CO_2)_n^+$ and $(N_2O)_n^+$

M	Ionization Potential (eV)	Ion Core of $[H_2O\bullet M_n]^+$ Clusters
CO_2	13.78	H_2O^+
N_2O	12.89	$[H_2O–ON_2]^+$
H_2O	12.62	–

IPs of components control the charge distribution and the formation of semi-covalent bonds.

Summary

- Ion core species and their structure
- The formation of intermolecular covalent bonds

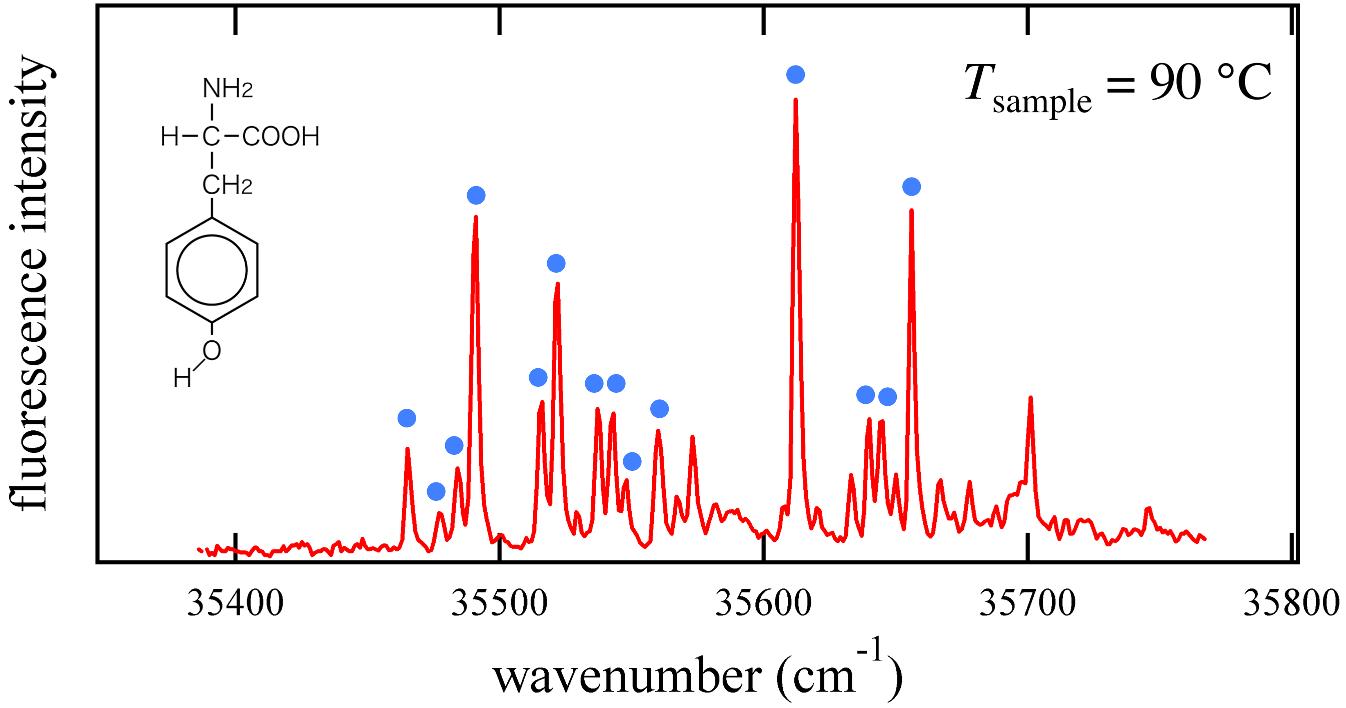
highly depend on

◆ the shape of MO
◆ the ionization potential

What about anions ?

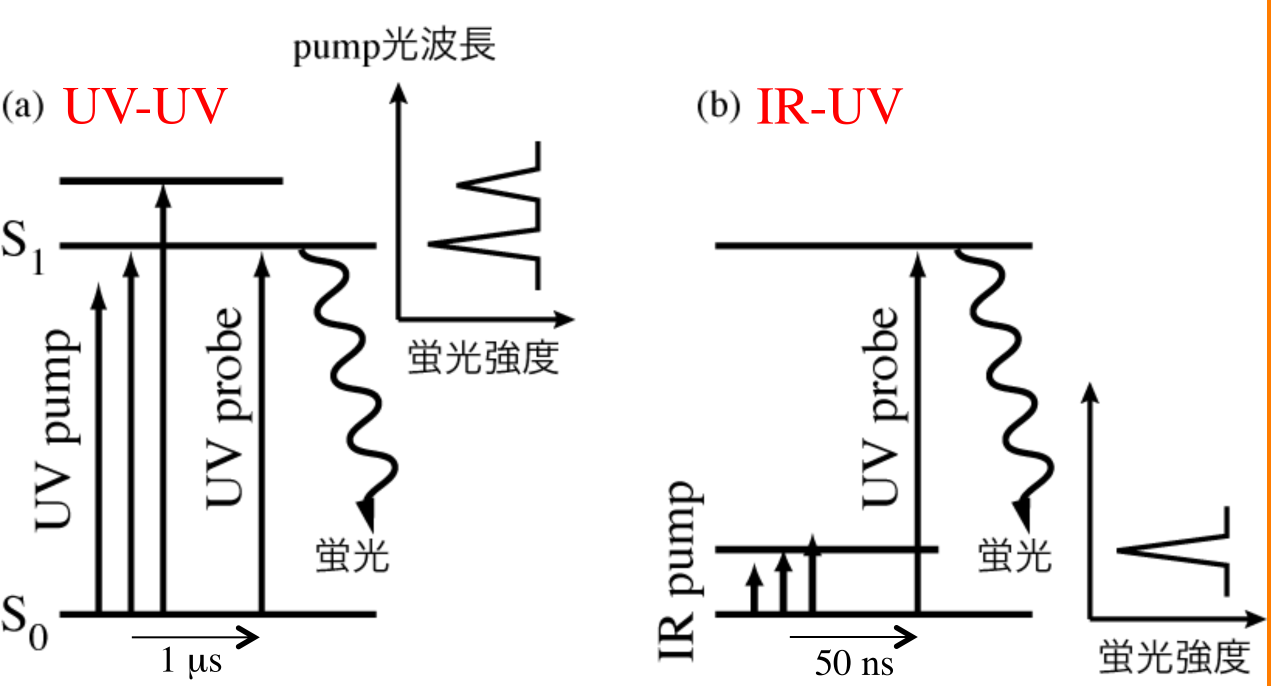
Muraoka et al., J. Chem. Phys., **2005**, *122*, 094303.
Muraoka et al., J. Phys. Chem. A, **2008**, *112*, 4906.
Kobayashi et al., J. Chem. Phys. **2008**, *128*, 164319.
Muraoka et al., J. Phys. Chem. A, **2009**, *113*, 8942.

LIF spectrum of jet-cooled tyrosine



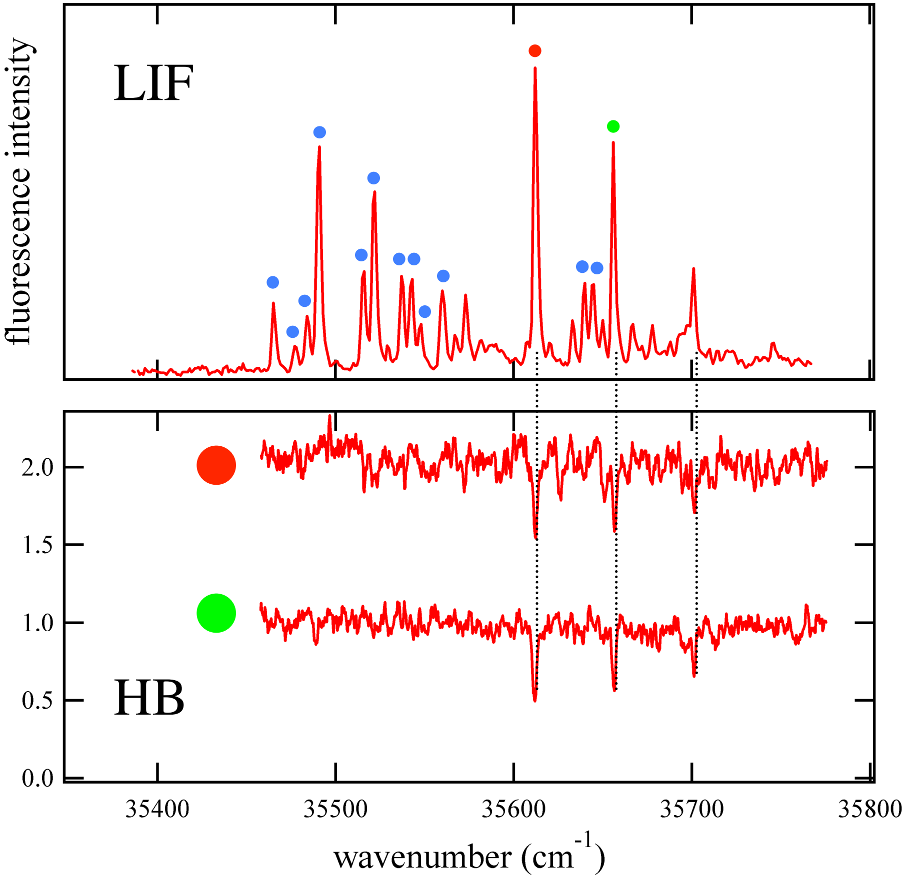
How many isomers ?

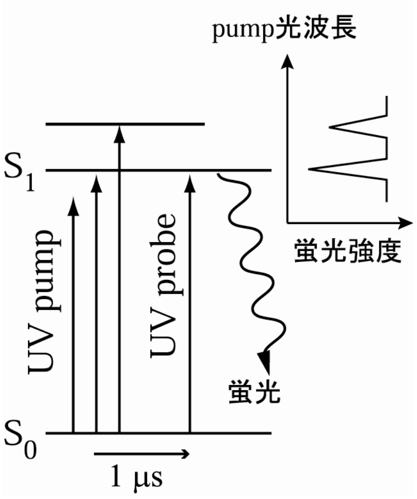
Experiment

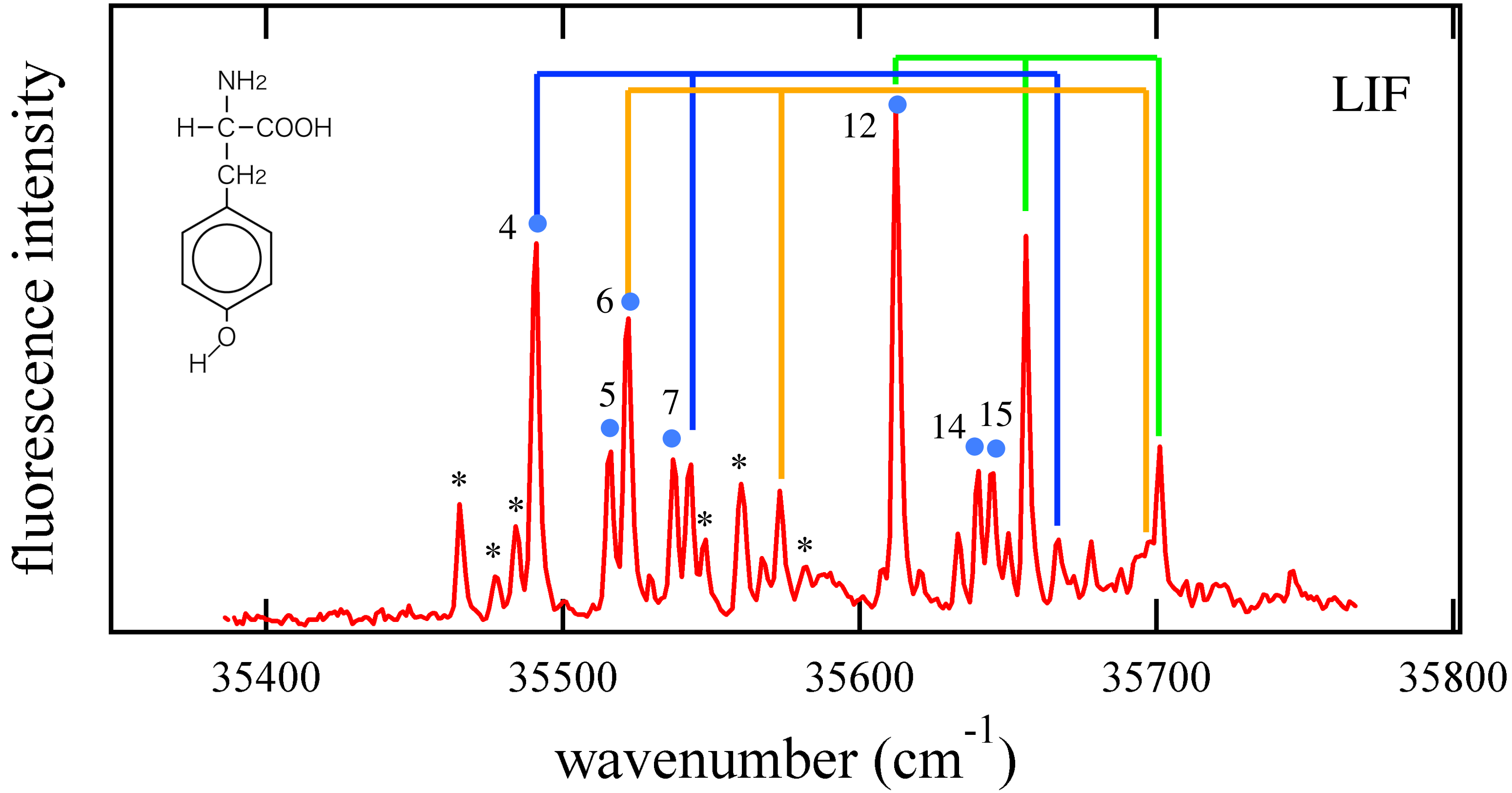


(a) UV-UV
pump光波長
S1
S0
UV pump
UV probe
蛍光
蛍光強度
1 μs
(b) IR-UV
IR pump
UV probe
蛍光
蛍光強度
50 ns

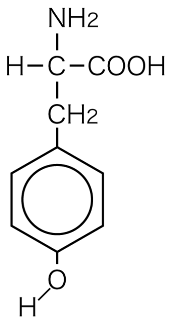
UV-UV Hole-Burning (HB) Spectra

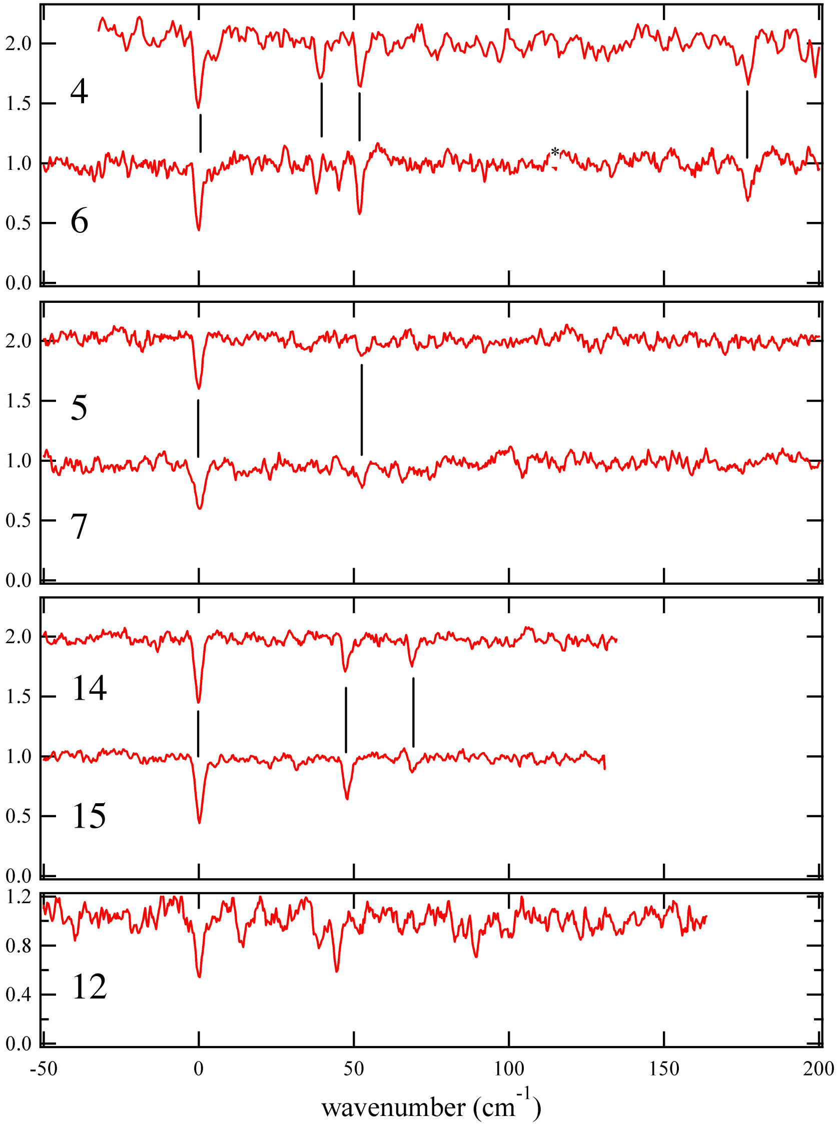





LIF
fluorescence intensity
wavenumber (cm^{-1})
35400
35500
35600
35700
35800
4
5
6
7
12
14
15
*
NH2
H-C-COOH
CH2
O
H

Comparison of S_1 vibronic structure in HB spectra

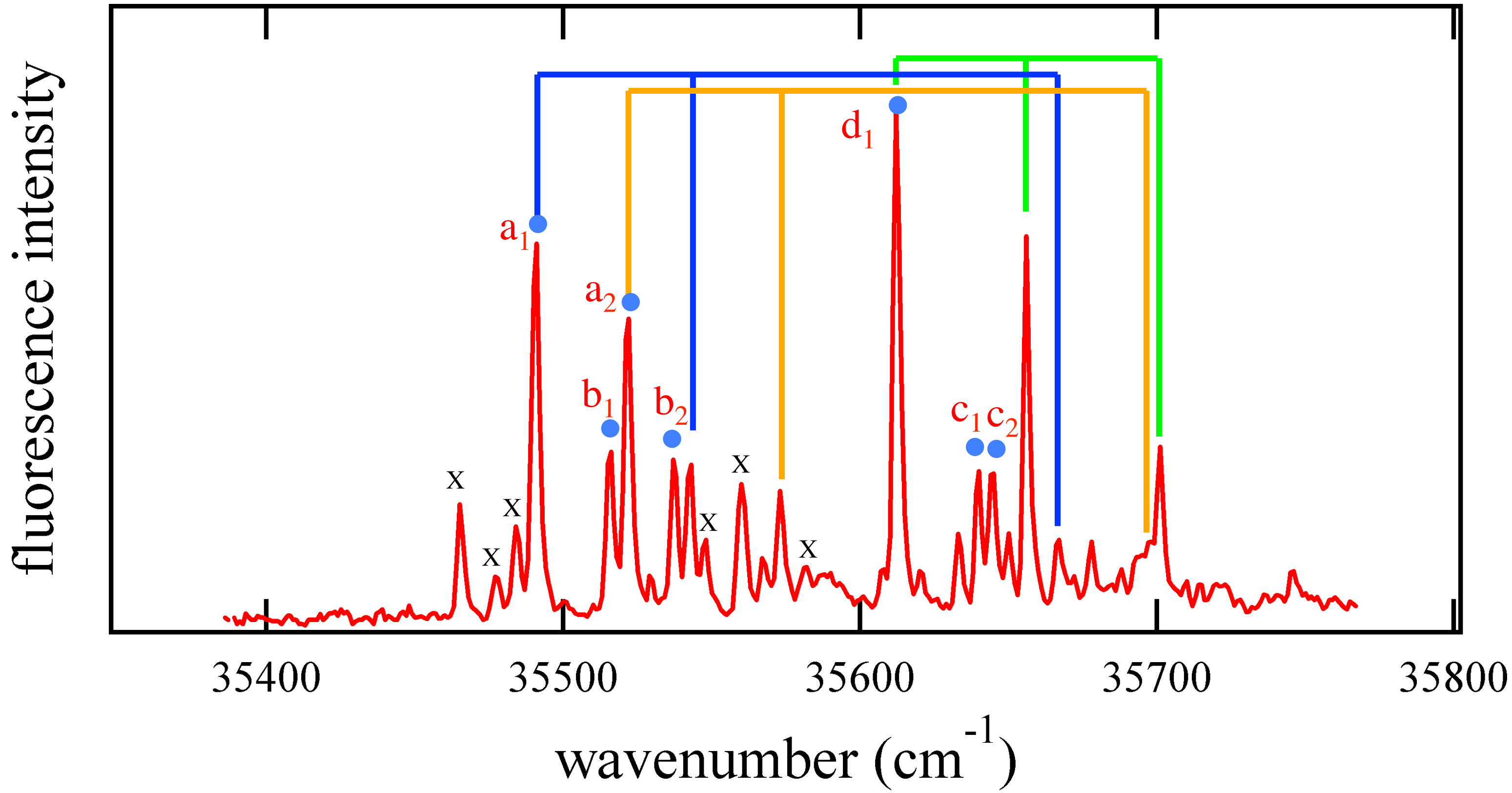




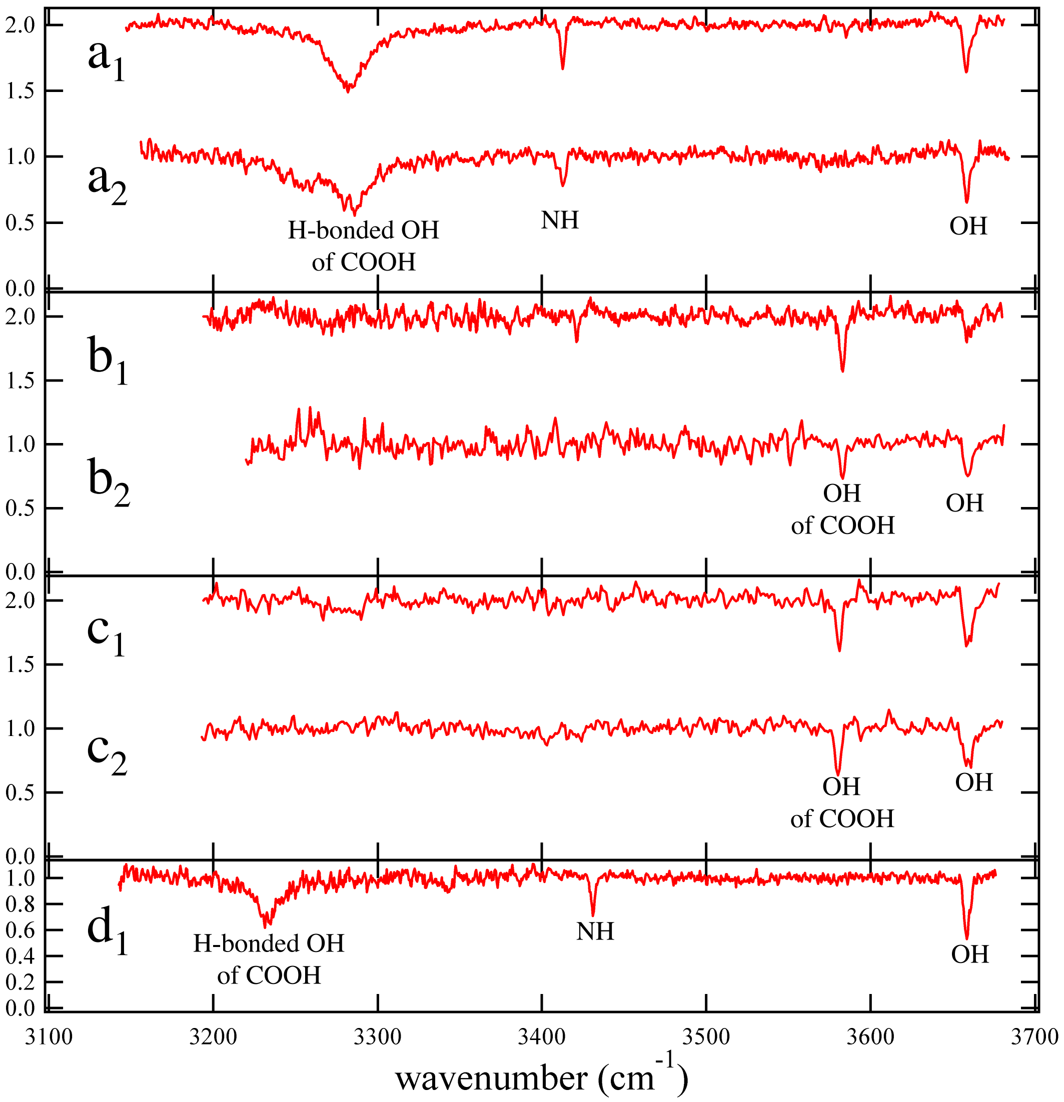
Different species
but
similar vibronic structure

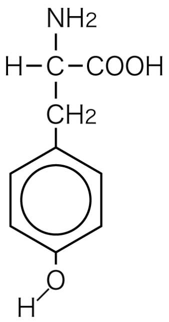
Rotational isomers
for the phenolic OH group

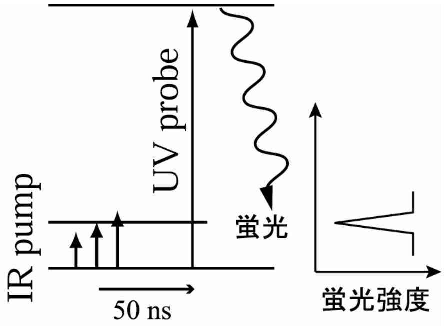
Rotational isomers of tyrosine



S_0 IR-UV spectra



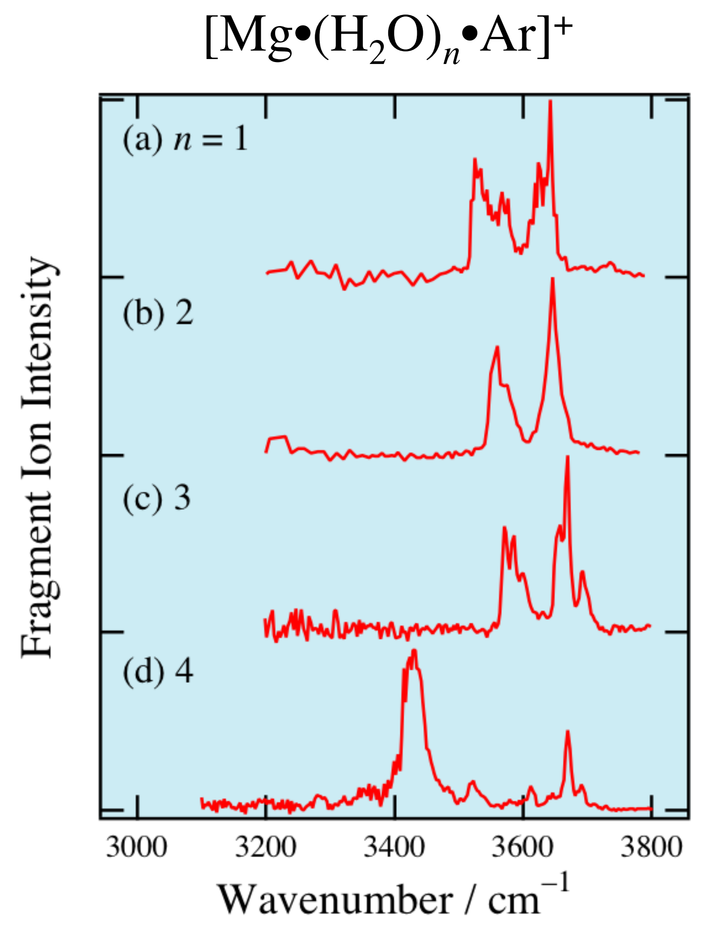


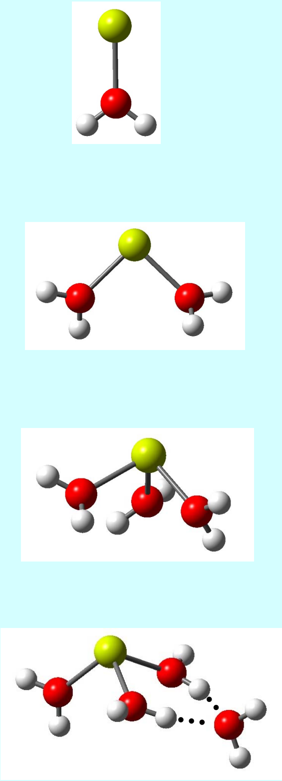


Jet-cooled tyrosine has
at least 7 (probably 8) isomers.

Inokuchi et al., J Phys. Chem. A, **2007**, *111*, 3209.

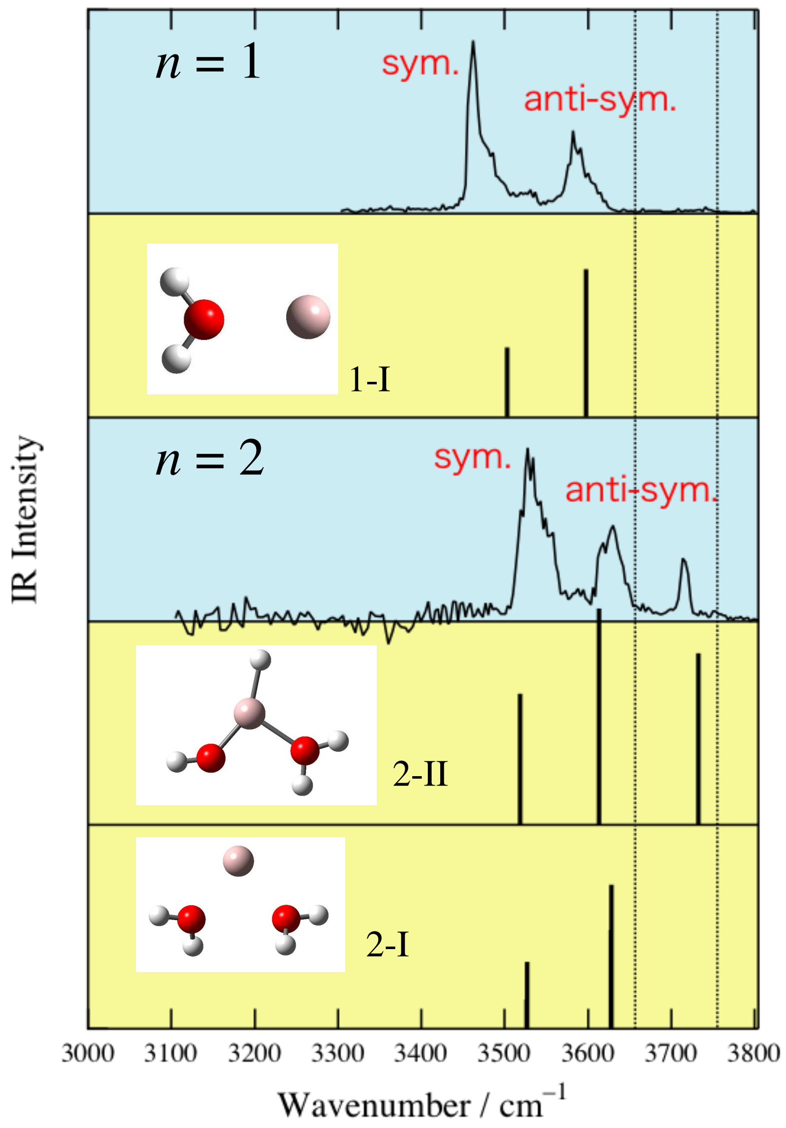
$[Mg \cdot (H_2O)_{1-4} \cdot Ar]^+$ IRPD Spectra





Inokuchi et al., J Phys. Chem. A, **2004**, *108*, 5034.

$[Al \cdot (H_2O)_{1,2} \cdot Ar]^+$ IRPD Spectra



$[H\text{–}Al\text{–}O\text{–}H]^+$ ion core!

Inokuchi et al.,
Chem Phys. Lett., **2004**, *390*, 140.