

# Structures of Cluster Ions of Triatomic Molecules Studied by Infrared Photodissociation Spectroscopy

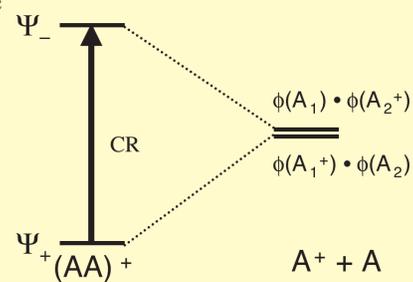
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## INTRODUCTION

### Charge resonance interaction

Some of homo-molecular cluster ions are stabilized by the charge resonance (CR) interaction.

The positive charge is delocalized over the constituent molecules. Strong CR bands are found in the near IR-VIS region.



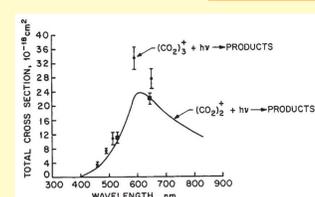
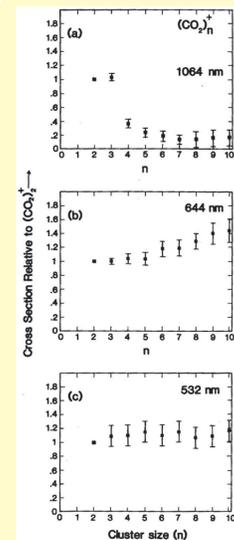
### Previous works

- Photodissociation (PD) cross section for the CR transition of  $(CO_2)_n^+$  [1]
- Binding energy of  $(CO_2)_n^+$  [2]
- **Dimer ion core structure** in  $(CO_2)_n^+$

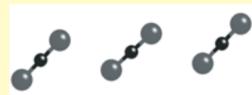
- Broad features of the CR bands [1]
- **No structural information**

- DFT calcs. predict charge-delocalized structure for  $(CO_2)_{3,4}^+$  [3]

- IR spectroscopy of  $(CO_2)_2^+$  in matrices [3,4]
- *Ab initio* MO calcs. of  $(CO_2)_2^+$  [5]
- **Planar  $C_{2h}$  structure for  $(CO_2)_2^+$  ?**



PD cross section of  $(CO_2)_{2,3}^+$  [1c]



DFT calc. of  $(CO_2)_{3,4}^+$  [3]

[1] (a) Johnson et al., CPL **112**, 285 (1984). (b) Smith and Lee, JCP **69**, 5393 (1978). (c) Bowers et al., JPC **88**, 5204 (1984). [2] (a) Hiraoka et al., CPL **146**, 535 (1988). (b) Linn and Ng, JCP **75**, 4921 (1981). (c) Meot-Ner and Field, JCP **66**, 4527 (1977). (d) Märk et al., JCP **77**, 2408 (1982). (e) Headley et al., J. Chem. Soc., Faraday Trans. **1** **78**, 933 (1982). (f) Bowers et al., Int. J. Mass Spectrom. Ion Processes **54**, 263 (1983). (g) Cameron et al., J. Chem. Soc., Faraday Trans. **90**, 935 (1994). [3] Shkrob, JPCA **106**, 11871 (2002). [4] (a) Zhou and Andrews, JCP **110**, 6820 (1999). (b) Thompson and Jacox, JCP **111**, 4487 (1999). [5] (a) Illies et al., JPC **91**, 3489 (1987). (b) McKee, CPL **165**, 265 (1990).

### This study

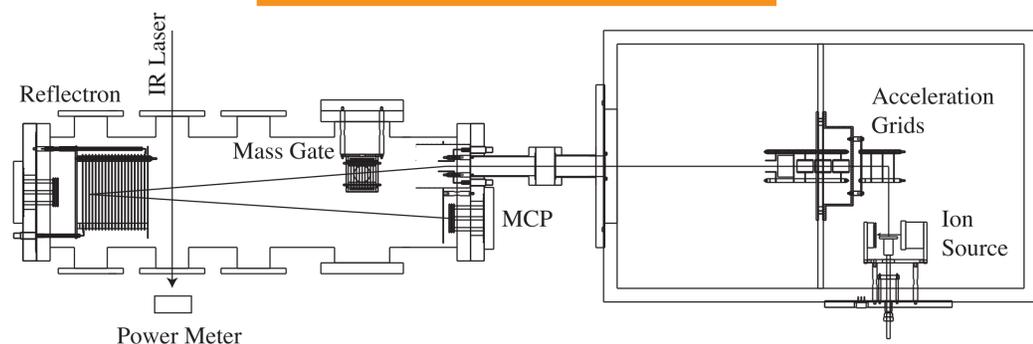
IR photodissociation (IRPD) spectroscopy of  $(CS_2)_n^+$  and  $(CO_2)_n^+$  in the 1000–4000  $cm^{-1}$  region

Quantum chemical calculations

Structure of the ion core in  $(CS_2)_n^+$  and  $(CO_2)_n^+$

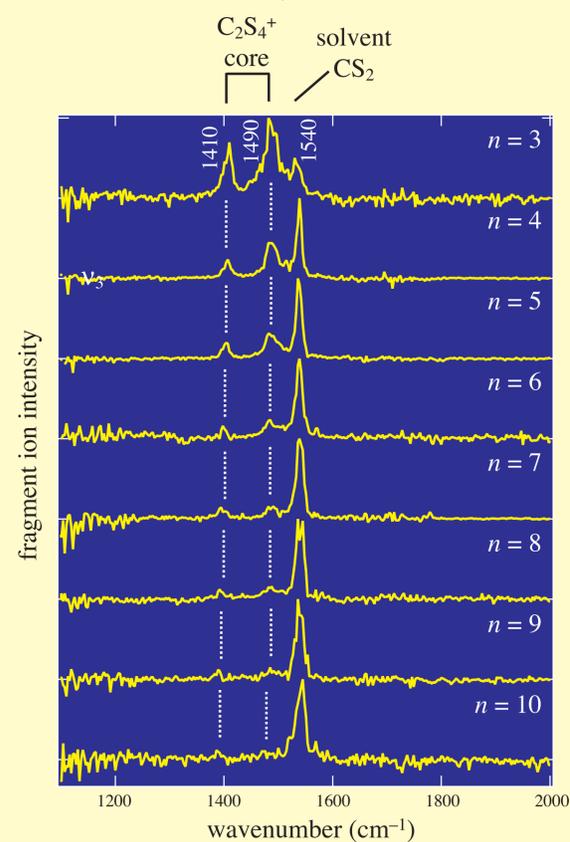
Structural evolution around the ion core as a function of cluster size

## EXPERIMENTAL



## $(CS_2)_n^+$

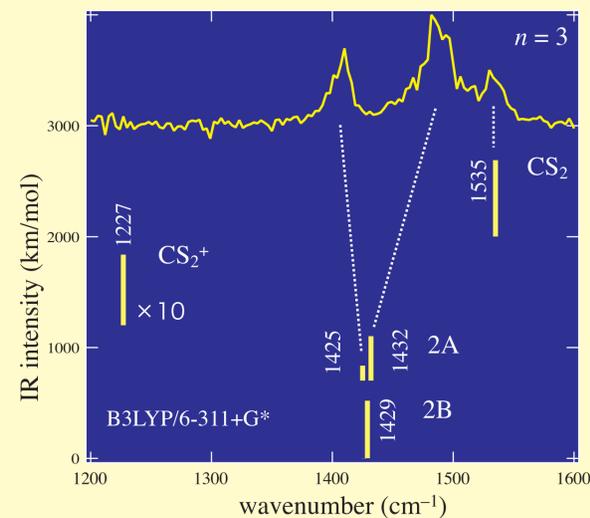
### IRPD spectra



No change is found in the band position and relative intensity of  $C_2S_4^+$  for  $n = 3-10$ .

cf. Vib. Frequency of  $CS_2$

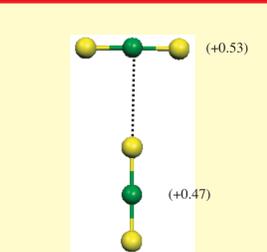
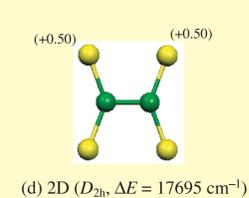
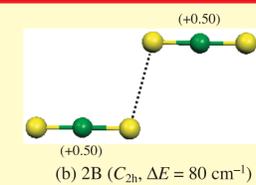
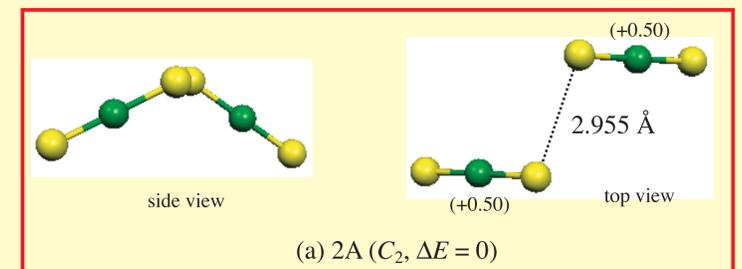
Mode	Frequency ( $cm^{-1}$ )
$v_3$	1535



The IRPD spectrum can be reproduced by the IR spectrum of  $CS_2$  monomer and isomer 2A.

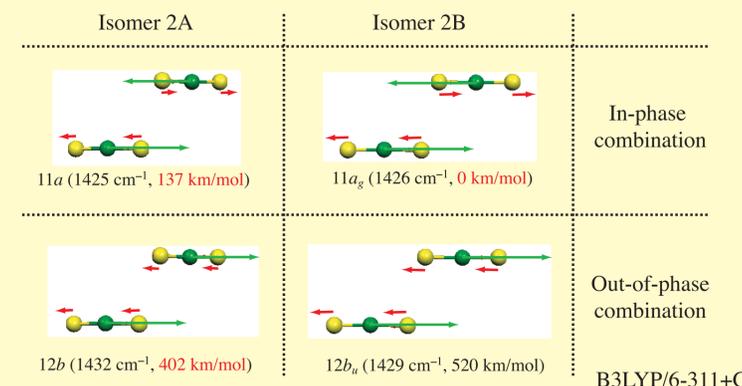
→ **Dimer ion core structure**

### Optimized structures of $C_2S_4^+$



B3LYP/6-311+G\*

### Normal modes of isomers 2A and 2B with anti-symmetric CO stretching vibrations



In-phase combination of 2B ( $C_{2h}$ ) is IR-forbidden. Isomer 2A has two bands of the anti-symmetric CS stretching vibration.

### Summary 1: $(CS_2)_n^+$

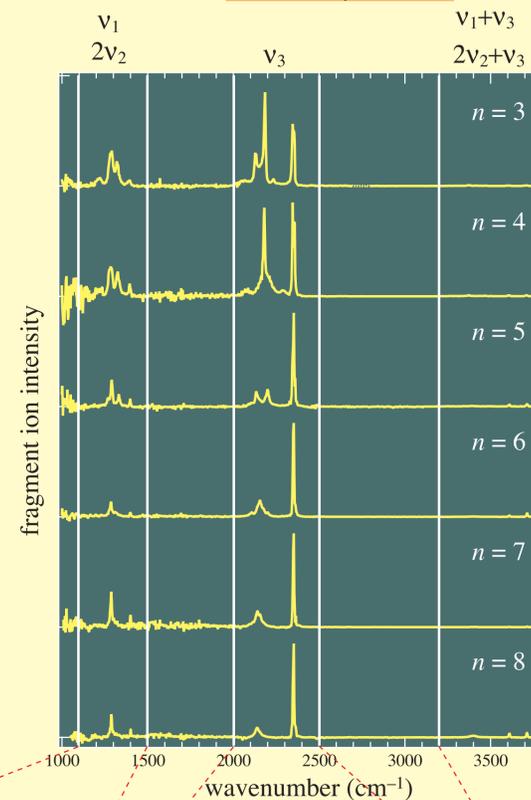
Dimer ion core structure.

The  $C_2S_4^+$  ion core has  $C_2$  symmetry.

The structure of  $C_2S_4^+$  kept intact with increasing the cluster size.

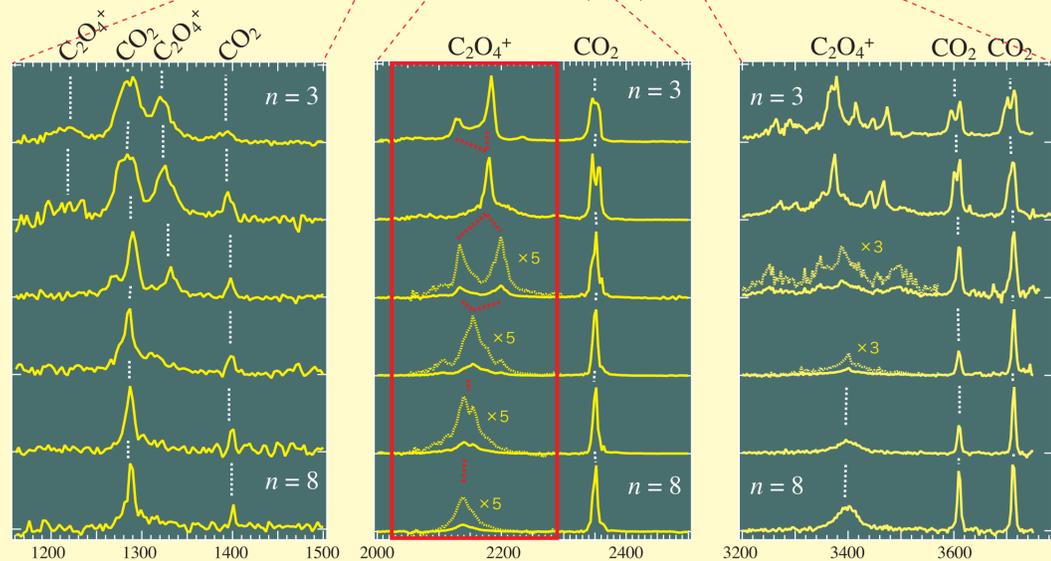


## IRPD spectra

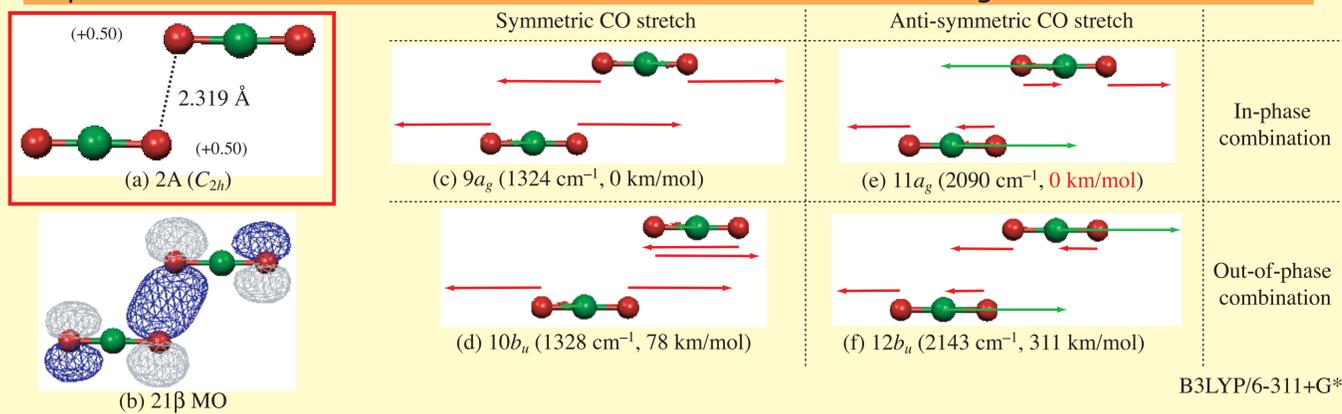


cf. Vib. Frequency of  $\text{CO}_2$

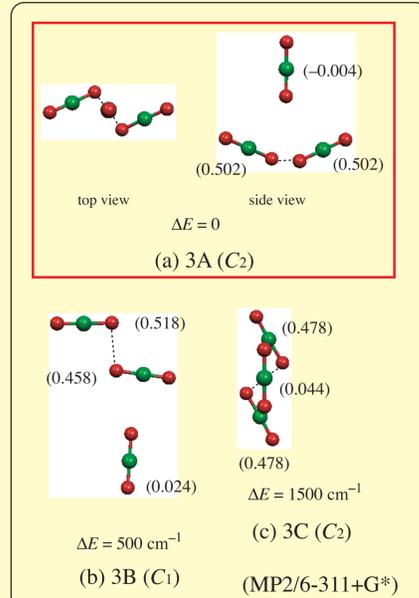
Mode	Frequency ( $\text{cm}^{-1}$ )
$\nu_1$	1290, 1400
$2\nu_2$	
$\nu_3$	2350
$\nu_1 + \nu_3$	3610, 3713
$2\nu_2 + \nu_3$	



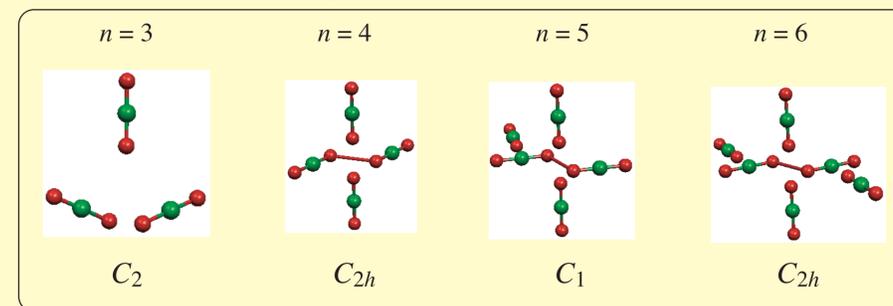
The band number of the  $\nu_3$  vibration of the  $\text{C}_2\text{O}_4^+$  ion core alternately changes between one ( $n = 4$  and  $6-8$ ) and two ( $n = 3$  and  $5$ ).

Optimized structure, MO, and normal modes with the CO stretching vibrations for  $\text{C}_2\text{O}_4^+$ Structural evolution for  $(\text{CO}_2)_n^+$ 

The alternate change of the band number of  $\text{C}_2\text{O}_4^+$  in the anti-sym. CO stretching region  
 → The symmetry of the  $\text{C}_2\text{O}_4^+$  ion core changes between  $C_{2h}$  and lower ones.

Optimized structures of  $(\text{CO}_2)_3^+$ 

## Proposed structural evolution

Summary 2:  $(\text{CO}_2)_n^+$ 

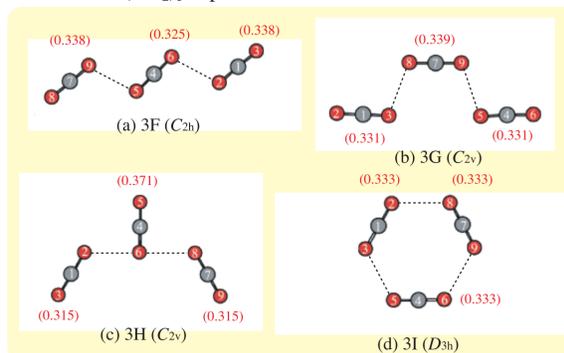
Dimer ion core structure. No monomer ion core in  $(\text{CO}_2)_n^+$ .  
 The  $\text{C}_2\text{O}_4^+$  ion has  $C_{2h}$  symmetry, different from  $\text{C}_2\text{S}_4^+$  ( $C_2$ ).  
 The structure of the  $\text{C}_2\text{O}_4^+$  ion core changes alternately with increasing the cluster size.

Difficulties in quantum chemical calculations for  $(\text{CS}_2)_n^+$  and  $(\text{CO}_2)_n^+$ 

DFT calcs. (B3LYP) do not provide isomers with the dimer ion core.

*Ab initio* MO calcs. (HF, MP2) show unphysical values for the vibrational analysis.

Isomers of  $(\text{CO}_2)_3^+$  optimized at the B3LYP/6-311+G\* level



Vibrational frequency and IR intensity of isomer 2A

B3LYP		MP2	
Freq. ( $\text{cm}^{-1}$ )	IR int. (km/mol)	Freq. ( $\text{cm}^{-1}$ )	IR int. (km/mol)
1324	0 ( $a_g$ )	1266	0 ( $a_g$ )
1328	78 ( $b_u$ )	1472	13434 ( $b_u$ )
2090	0 ( $a_g$ )	2437	0 ( $a_g$ )
2143	311 ( $b_u$ )	3879	670020 ( $b_u$ )

The MP2 calcs. overestimate force constants.

→ Symmetry breaking effects

Single-reference calcs. cannot describe the wavefunctions correctly.

The DFT calcs. do not include complete electron correlation for the CR system.

## FUTURE WORK

Multi-reference calculations such as CASSCF for  $(\text{CS}_2)_n^+$  and  $(\text{CO}_2)_n^+$   
 $(\text{OCS})_n^+$ ,  $(\text{N}_2\text{O})_n^+$ , and mixed clusters

Spectroscopy of cold cluster ions with the argon tagging

