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 calc. predict charge-delocalized structure for (CO$_2$)$_n^+$ [3]
- IR spectroscopy of (CO$_2$)$_n^+$ in matrices [3,4]
- Ab initio MO calc. of (CO$_2$)$_n^+$ [5] → Planar C$_{2v}$ Structure for (CO$_2$)$_n$?

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

![Experimental setup diagram]

The IRPD spectrum can be reproduced by the IR spectrum of CS$_2$ monomer and isomer 2A. → Dimer ion core structure

Optimized structures of CS$_2$+$^+

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

Summary 1: (CS$_2$)$_n^+$

Dimer ion core structure.
The CS$_2^+$ ion core has C$_2$ symmetry. The structure of CS$_2$+$^+$ kept intact with increasing the cluster size.
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 $\text{C}_{2\text{h}}$ and lower ones.

**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 $\text{C}_{2\text{h}}$ symmetry, different from $\text{C}_2\text{S}_2^+$ (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.

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 CASSCI 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

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

<table>
<thead>
<tr>
<th>Symmetric CO stretch</th>
<th>Anti-symmetric CO stretch</th>
<th>In-phase combination</th>
<th>Out-of-phase combination</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_1$ (1324 cm$^{-1}$, 0 km/mol)</td>
<td>$\nu_2$ (2090 cm$^{-1}$, 0 km/mol)</td>
<td>$\nu_1 + \nu_2$ (1328 cm$^{-1}$, 78 km/mol)</td>
<td>$\nu_1 - \nu_2$ (2143 cm$^{-1}$, 311 km/mol)</td>
</tr>
</tbody>
</table>

B3LYP/6-311+G*