IR Photodissociation (IRPD) Spectroscopy of Ion-Molecule Complexes as Chemical Intermediates
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Summary
- Dimer ion core structure.
- The semi-covalent bond formed in dimer ion core.

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
- Semi-Covalent Bonds
  - Electronic and geometric characteristics
  - not well understood
  - Involved in chemical reactions whose mechanism unclear?
  - Discover new chemical reactions?

This Study
- Quantum Chemical Calculations
- Electronic and Geometric Structures

Structure of Dimer Ion Core
- IR activity of dimer ion
  - Point Group: C_n
  - n = 2
  - In-phase: inactive active (weak)
  - Out-of-phase: active active (strong)

IRPD spectra of (CO_2)_n^+
- Band position almost the same as that of CO_2
  - Solvent CO_2 molecules

IRPD spectra of (OCS)_n^+ and (CS_2)_n^+
- Anti-symmetric C=O stretching

Structure of C_nO_4^+
- Structure of dimer ion core determined by balance between two factors
- Overlap between MOs
- Dimer structure
- Repulsive force between components

Structure and Band Number for Dimer
- The number of IR bands indicates the planarity.
- C_nO_4^+ ion core
  - Intensity decreases with increasing n.
  - Band position not coincident with that of CO_2

Structure of Dimer Ion Core
- Calculation cannot reproduce correctly the PES.
- PES shallow

Q1: Why structure of C_2O_4^+ alternately changes?

Q2: Why bare C_nO_2S_n^+ has bent (C_n) structure?

Q3: Why structure different between 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:

A2: Due to broad nature of HOMO of OCS.
- Contains 2p component of C atom
- Minimizes repulsive force
- Overlap increases with decreasing the angle.

A3: Due to weaker interaction in C_nS_n^+.
- PES shallow ➔ weaker intermolecular interaction
- Calculation cannot reproduce correctly the PES.