Isomer-Specific Photodissociation of (CS$_2$)$_2^{-}$
(Univ. of Tokyo) Y. Matsuyama, R. Nakanishi, Y. Inokuchi, and T. Nagata

Photodissociation cross sections of (CS$_2$)$_2^{-}$ are measured in the photon energy of 1–5 eV. The (CS$_2$)$_2^{-}$ anion provides five photofragments, S$^-$, S$_2$$^-$, CS$_2$$^-$, C$_2$S$_4$$^-$, and CS$_4$$^-$.

Investigation of correlation between the (CS$_2$)$_2^{-}$ isomers and the photoproducts confirms the coexistence of the ion-molecule complex (CS$_2$-CS$_2$) and the molecular anion (C$_2$S$_4$) for (CS$_2$)$_2^{-}$.

We apply ab initio MO calculations (MP2/aug-cc-pVDZ) to (CS$_2$)$_2^{-}$, and obtain seven stable isomers. Taking the energetics and the state correlation involved in the photodissociation of (CS$_2$)$_2^{-}$ into account, we conclude that the C$_2$S$_4$$^-$ anion has a C$_{2v}$ structure with the B$_1$ electronic ground state.

### Charge Distribution in Cluster Ions

- For cations, it is frequently seen that the positive charge is delocalized over two molecules with the charge resonance (CR) interaction. (c.f. benzenoid dimer, C$_6$H$_{12}$$^{+}$)
The origin of the CR interaction is the overlap of a singly-occupied MO (SOMO) of a cation and a HOMO of a neutral molecule.
- For anions, the negative charge is usually localized in one molecule, because diffusely nature of LUMO more than HOMO prevents occurrence of effective MO overlap and the CR interaction.
- Carbon disulfide dimer anion (CS$_2$)$_2$$^-$ is one of rare anion species in which the negative charge is delocalized intermolecularly. However, the electronic/geometric structures and chemical process of (CS$_2$)$_2$$^-$ are still controversial issues even though a lot of researches have been done for this dimer anion.

### Aim of This Study

- To examine whether the ion-molecule complex (CS$_2$-CS$_2$) and the molecular anion (C$_2$S$_4$) really exist for (CS$_2$)$_2^{-}$.
- To specify the electronic/geometric structures of the isomers and reveal the photochemical (photodissociation) process.

### Methods

- Photodissociation spectroscopy for obtaining photofragment yield spectra (PYS) of (CS$_2$)$_2^{-}$:
  - Equivalent to absorption spectra
  - Double-laser experiments
  - For investigating correlation between the (CS$_2$)$_2$ anion, the absorption/photoelectron bands, and photofragment species
  - Ab initio MO calculations
  - Stable structures, correlation of MOs of the (CS$_2$)$_2$ anion and photofragment species

### Previous Study

- Tsukada et al. (1997):
  - Photoelectron spectra of (CS$_2$)$_n^{-}$ with n = 1–6.
  - Only the n = 2 spectrum has additional bands around 3 eV (2) and (3) in FIG. 1.
  - These bands were assigned to the molecular anion, C$_2$S$_4$$^-$, in which the negative charge is delocalized over two molecules.
  - They reassigned the photoelectron bands of (CS$_2$)$_n$$^-$.
- Maeyama et al. (1998):
  - Photodissociation spectroscopy (h$_\nu$ = 1–2.8 eV).
  - They ascribed all the photodissociation processes of (CS$_2$)$_n$$^-$ to C$_2$S$_4$$^-$.  

### (CS$_2$)$_2$$^-$: Previous Study

\[ \text{FIG. 1. Photoelectron spectra of (CS$_2$)$_2$$^-$ with n = 1+}. \]

### Experiment

- Photodissociation spectroscopy:
  - Producing (CS$_2$)$_2$ anion by photodissociation laser 2, and mass-analyzed by the 2nd. mass spectrometer.
- Double-laser experiment:
  - Photodissociation laser 2 (CS$_2$)$_2$ is photodissociated by the photodissociation laser 1, and probed by the photodissociation laser 2 or the photoelectron laser.

### Photofragment yield spectra of (CS$_2$)$_2$$^-$

- Main photofragments are CS$_2$$^-$ and C$_2$S$_4$$^-$. (Photoelectron spectra in FIG. 1 shows that CS$_2$$^-$ has only the ion-molecule form, CS$_2$-CS$_2$.)

### Difference in PYS between (CS$_2$)$_2$$^-$ and (CS$_2$)$_2$$^-$ suggests that (CS$_2$)$_2$$^-$ has an isomer other than the ion-molecule form (CS$_2$-CS$_2$); it must be the molecular anion, C$_2$S$_4$$^-$.  

\[ \text{FIG. 3. Photofragment mass spectra of (CS$_2$)$_2$$^-$}. \]

\[ \text{FIG. 4. Photodissociation yield spectra (PYS) of (CS$_2$)$_2$$^-$}. \]

\[ \text{FIG. 5. Comparison of PYS for (CS$_2$)$_2$$^-$ and (CS$_2$)$_2$$^-$}. \]
Identification of Photofragment $C_2S_2^-$

The $SCS^-$ ion formed in the discharge has a linear structure with the $\Pi_v^0$ electronic state (Enido et al. 2003).

Photoelectron spectra of $CS^-$ produced by the photodissociation of $(CS)_2^-$ at 3.49 and 4.66 eV show a linear structure with the $\Pi_v^0$ electronic state.

**FIG. 6.** (a) Photoelectron spectra of $SCS^-$ formed in the discharge needle. (b) Photoelectron spectra of $CS^-$ produced by the photodissociation of $(CS)_2^-$ at 3.49 and 4.66 eV.

Ab Initio MO Calculations

The $(CS)_2^-$ isomer has a structure like VI.

On the basis of VDEs, the isomers of I, II, and III can be selected as candidates of the $(CS)_2^-$ isomer.

As seen in FIG. 7, the observed VDE of $(CS)_2^-$ is around 2.6 eV.

**FIG. 7.** (a) Photoelectron spectrum of $(CS)_2^-$ measured after the photodissociation of $(CS)_2^-$ at 1.17 eV.

Double Laser Experiment 1

Only the photoelectron band of the ion molecule complex $(CS^--CS_2)$ is reduced under the irradiation of the 1.17 eV light.

The 1.17 eV light dissociates only the $CS^--CS_2$ isomer.

**FIG. 8.** (a) Mass spectrum of $(CS)_2^-$ measured after the photodissociation of $(CS)_2^-$ at 1.17 eV.

Double Laser Experiment 2

$S^-$ and $CS^-$ are reduced largely by the 1st photodissociation laser (1.17 eV).

The laser can hardly decrease $S^-$ and $SCS^-$.

Around half of $CS^-$ is eliminated by the 1.17 eV light.

**FIG. 9.** Photoelectron spectra of (a) CS and (b) $CS^-$.

Since the photon energy of 1.17 eV corresponds to the electronic transition of the $CS^--CS_2$ ion, $S^-$ and $CS^-$ are originated from $CS^--CS_2$.

$S_2$ and $SCS^-$ are from $CS_2^-$.

$CS_2^-$ comes from both of $CS^--CS_2$ and $CS_2^-$.

**FIG. 10.** Stable structures, difference in total energy (AM), and vertical detachment energy (VDEs) determined by ab initio MO calculations at MP2(full)/6-31G(d,p) level.

Double Laser Experiment 3

$S^-$ and $CS^-$ are reduced largely by the 1st photodissociation laser (1.17 eV).

The laser can hardly decrease $S^-$ and $SCS^-$.

Around half of $CS^-$ is eliminated by the 1.17 eV light.

**FIG. 11.** Single occupied MO (SOMO) of Isomers I, II, and III. Although Isomers II and III have similar $S_2$ structures, the symmetry species of SOMOs are $b_3$ and $b_2$, respectively.

Some MOs of I and II are located in-plane of the isomers, whereas that of III is out-of-plane.

Since the photofragment $SCS^-$ anion originates from $CS_2^-$, examination of correlation between MOs of $CS^-$ and $SCS^-$ will provide information on the probable isomer of $CS_2^-$.

**FIG. 12.** MO Correlation diagram of $CS_2^- (D_{2h})$, $SCS^-$, and $CS_2^-$.

From the MO diagram, Isomer III (whose SOMO is $S_b$) correlates with the photofragment $SCS^-$ ($D_{2h}$, X\(\overline{2}L\)).

(Isomer II correlates with the electronically excited $SCS^-$ ($A^1\overline{1}L_1$)).

**FIG. 13.** Oscillator strength of Isomers VI, II, and III obtained by MRCI calculations.

**FIG. 14.** State correlation diagram of Isomer III.

- PY3 bands of $SCS^-$ at 1.9, 3.3, and 4.3 eV (FIG. 9b) are assigned to the three transitions displayed in FIG. 13c.
- The transition to the second $A^2$ state (3.3 eV) corresponds to the CR transition.
- MOs for which the CR interaction occurs are not LUMO but the upper LUMO of $CS_2^-$ as seen on the left side of FIG. 12.

Conclusion

We have performed the photodissociation spectroscopy of $(CS)_2^-$ in the 1-5 eV region. From the photodissociation-photoelectron and the photodissociation-photoelectron experiments, the coexistence of the ion molecule complex $(CS^-CS_2)$ and the molecular anion $(CS_2^-)$ has been proved for $(CS)_2^-$.

The interconversion between these isomers does not occur in several μs time window due to a certain potential barrier between them. By treating the correlation among the $(CS_2^-)$ isomers and the fragment anions quantitatively, we have obtained the photofragment yield spectra of $(CS^-CS_2)$ and $(CS_2^-)$ separately.

According to the energetics and the state correlation analysis of $(CS)_2^-$, we have concluded that the $CS_2^-$ molecular anion, which is responsible for the production of $SCS^-$, has a $S_2$ structure with the $E_b$ electronic ground state.