Photodissociation of \((\text{CS}_2)_2^-\): \(\text{CS}_2^-\cdot\text{CS}_2\) process vs. \(\text{C}_2\text{S}_4^-\) process

(Univ. of Tokyo) Y. Matsuyama, R. Nakanishi, Y. Inokuchi\(^\text{a}\), and T. Nagata*

Photodissociation cross sections of \((\text{CS}_2)_2^-\) are measured in the photon energy of 1–5 eV. Photodissociation of \((\text{CS}_2)_2^-\) provides five fragments, \(\text{S}^-\), \(\text{S}_2^-\), \(\text{CS}_2^-\), \(\text{C}_2\text{S}_2^-\), and \(\text{CS}_3^-\). Hole-burning experiments of \((\text{CS}_2)_2^-\) confirm the coexistence of the ion-molecule complex \((\text{CS}_2)^-\cdot\text{CS}_2\) and the molecular anion \((\text{C}_2\text{S}_4)^-\). We apply \textit{ab initio} MO calculations (MP2/aug-cc-pVZD) to \((\text{CS}_2)_2^-\), and obtain seven stable isomers. From the MO correlation analysis and energetics, we conclude that the \(\text{C}_2\text{S}_4^-\) anion has a \(\text{C}_2\)\(_{\text{v}}\) structure with the \(^3\text{B}_1\) electronic ground state.

\(\text{a}\) ino@cluster.c.u-tokyo.ac.jp

### Charge Distribution in Cluster Ions
- For cations, it is frequently seen that positive charge is delocalized over two molecules with the charge resonance (CR) interaction. (e.g. \((\text{C}_4\text{H}_8)_n^+\), \((\text{CO}_2)_n^+\))
  - 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 valence anions, negative charge is usually localized in one molecule, because diffuse nature of LUMO more than HOMO prevents occurrence of effective MO overlap and the CR interaction.
- \textit{Carbon disulfide dimer anion, (CS\(_2\))\(_2^-\)}, is one of anion species in which the negative charge is delocalized intermolecularly. However, the electronic/geomeric structures and photochemical process of \((\text{CS}_2)_2^-\) are still controversial issues.

### Aim of This Study
- To examine whether the ion-molecule complex \((\text{CS}_2)^-\cdot\text{CS}_2\) and the molecular anion \((\text{CS}_2\text{S}_2)^-\) really coexist for \((\text{CS}_2)_2^-\).
- To specify the electronic/geometric structures and reveal the photochemical (photodissociation) process.

### Methods
- Photodissociation spectroscopy for obtaining photofragment yield spectra (PYS) of \((\text{CS}_2)_2^-\).
- Hole-burning experiments for investigating correlation between \((\text{CS}_2)_2^-\) isomers, absorption/photoelectron bands, and photofragment species.
- \textit{Ab initio} MO calculations stable structures, correlation of MOs of the \((\text{CS}_2)_2^-\) isomers and photofragment species

### \((\text{CS}_2)_2^-\): Previous Study
- Tsukada et al. (1997).
  - Photoelectron spectra of \((\text{CS}_2)_n^-\) with \(n = 1\rightarrow6\).
  - The \(n = 2\) spectrum has additional bands at \(\approx 3\) eV (2) and (3) in FIG. 1.
  - These bands were assigned to the molecular anion, \(\text{CS}_2\text{S}_2^-\), in which the negative charge is delocalized over two molecules.
  - They reassigned the photoelectron bands of \((\text{CS}_2)_2^-\).
  - \(\text{C}_2\text{S}_2\text{D}_2^+\), \(\text{C}_2\text{S}_2\text{(C)}^+\), \(\text{C}_2\text{S}_2\text{(D)}^+\).
  - \(\text{C}_2\text{S}_2\text{D}_2\text{(C}^\text{molecular structure unspecified})\)
- Inokuchi et al. (1998).
  - They performed photodissociation spectroscopy (1–2.8 eV).
  - They ascribed all the photodissociation processes of \((\text{CS}_2)_2^-\) to \(\text{CS}_2^\text{+}\).

### Experiment
- FIG. 2. Tandem time-of-flight (TOF) mass spectrometer used in this study.
- Photodissociation experiments \((\text{CS}_2)_2^-\) is isolated by the 1st. mass spectrometer and irradiated by a photodissociation laser. Resultant fragment ions are mass-analyzed by the 2nd. mass spectrometer.
- Hole-burning experiments \((\text{CS}_2)_2^-\) is photodissociated by a hole-burning laser. Fragment ions are removed by a reflector. Remaining \((\text{CS}_2)_2^-\) is probed by the photodissociation laser or a photoelectron laser.

### Photofragment species of \((\text{CS}_2)_2^-\)
- \(\text{Five photofragment anions (S}^-, \text{S}_2^-, \text{CS}_2^-, \text{C}_2\text{S}_2^-, \text{and CS}_3^-)\) are observed in the region of 1–5 eV.
- A photofragment yield spectrum (PYS) of \((\text{CS}_2)_2^-\) is obtained by plotting photodissociation cross sections as a function of photon energy.

### Photofragment yield spectra of \((\text{CS}_2)_2^-\)
- Main photofragments are \(\text{CS}_2^-\) and \(\text{C}_2\text{S}_2^-\).
- Difference in PYS between \((\text{CS}_2)_2^-\) and \((\text{CS}_2)_n^-\) suggests that \((\text{CS}_2)_2^-\) has an isomer other than the ion-molecule form \((\text{CS}_2)^-\cdot\text{CS}_2\).

(Photolysis spectra in FIG. 1 show that \((\text{CS}_2)_2^-\) has only the ion-molecule form, \((\text{CS}_2)^-\cdot\text{CS}_2\).)
Identification of Photofragment \( \text{C}_2\text{S}_2^- \)

- \( \text{SCS}^- \) formed in the discharge has a linear structure with the electronic ground (\( \text{D}_{1}\)) state (Endo et al., 2005).
- Photoelectron spectra of photofragment \( \text{C}_2\text{S}_2^- \) are quite similar to that of the \( \text{SCS}^- \) ion.

Photofragment \( \text{C}_2\text{S}_2^- \) ion has a linear structure with the \( \text{D}_{1}\) electronic state.

![Figure 6](image)

Hole-Burning Experiment 1

- Only the photoelectron band of the ion-molecule complex (\( \text{C}_2\text{S}_2^- \text{CS}_2 \)) is reduced under the irradiation of the hole-burning laser at 1.17 eV.
- Photodissociation band around 1.5 eV (see FIG. 4) can be assigned to the \( \text{C}_2\text{S}_2^- \text{CS}_2 \) isomer.

![Figure 7](image)

Hole-Burning Experiment 2

- \( \text{S}^- \) and \( \text{CS}_2^- \) are reduced largely by the hole-burning laser at 1.17 eV. The laser can hardly decrease \( \text{S}^- \) and \( \text{SCS}^- \).
- \( \sim 50 \% \) of \( \text{CS}_2^- \) is eliminated.

Since the photon energy of 1.17 eV corresponds to the transition of the \( \text{C}_2\text{S}_2^- \text{CS}_2 \) ion, \( \text{S}^- \) and \( \text{CS}_2^- \) are attributed to \( \text{C}_2\text{S}_2^- \text{CS}_2 \), \( \text{S}^- \) and \( \text{CS}_2^- \) are attributed to \( \text{C}_2\text{S}_2^- \text{CS}_2 \).

![Figure 8](image)

Ab Initio MO Calculations

- The \( \text{CS}_2^- \text{CS}_2 \) isomer has a structure like VI.
- On the basis of VDEs, the isomers of I, II, and III can be selected as candidates of a \( \text{C}_2\text{S}_2^- \text{CS}_2 \) isomer.

(As seen in FIG. 7a, the observed VDE of \( \text{C}_2\text{S}_2^- \) is around 2.8 eV)

![Figure 9](image)

- \( \Delta E = 0 \) eV
- VDE = 2.62 eV
- 2.52 eV
- 3.35 eV
- 0.36
- 0.36
- 0.60
- 1.27
- 1.11
- 0.70

![Figure 10](image)

SOMOs of I and II are located in-plane of the isomers, whereas that of III is out-of-plane.
- Since the photofragment \( \text{SCS}^- \) anion originates from \( \text{C}_2\text{S}_2^- \text{CS}_2 \), examination of correlation between MOs of \( \text{C}_2\text{S}_2^- \text{CS}_2 \) and \( \text{SCS}^- \) will provide information on the probable isomer of \( \text{C}_2\text{S}_2^- \).

![Figure 11](image)

We have performed photodissociation spectroscopy of \( \text{CS}_2^- \text{CS}_2 \) in the 1-5 eV region. From the hole-burning experiments, coexistence of the ion-molecule complex \( \text{CS}_2^- \text{CS}_2 \) and the molecular anion \( \text{C}_2\text{S}_2^- \) has been proved for \( \text{CS}_2^- \text{CS}_2 \). Interconversion between these isomers does not occur in several us time window due to a certain potential barrier between them. By taking the relationship between the \( \text{CS}_2^- \text{CS}_2 \) isomers and photofragments into account quantitatively, we have obtained the photofragment yield spectra of \( \text{CS}_2^- \text{CS}_2 \) and \( \text{C}_2\text{S}_2^- \) separately. According to the energetics and the MO correlation analysis of \( \text{CS}_2^- \text{CS}_2 \), we have concluded that the \( \text{C}_2\text{S}_2^- \text{CS}_2 \) molecular anion, which is responsible for the \( \text{SCS}^- \text{CS}_2 \) photoproduction, has a \( \text{C}_2\text{S}_2^- \text{CS}_2 \) structure with the \( \text{B}_1 \) electronic ground state.

![Figure 12](image)

![Figure 13](image)

Conclusion

- Oscillator strength calculations for \( \text{CS}_2^- \text{CS}_2 \) show all the transitions have their dipole moments in-plane of the clusters; these results imply that a transition between the electronic states of II and III hardly occurs.

Photodissociation \( \text{SCS}^- \) comes only from isomer III.

![Figure 14](image)