Isomer-Specific Photodissociation of $(CS_2)_2^-$

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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^- , $C_2S_2^-$, and CS_3^- . 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 $(C_2S_4^-)$ 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 $C_2S_4^-$ anion has a C_{2v} structure with the 2B_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. benzene dimer cation, $(C_6H_6)_2^+$)

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 diffuse 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 photochemical process of $(CS_2)_2^-$ are still controversial issues even though a lot of researches have been done for this dimer anion.

\Box (CS₂)₂: Previous Study

(a) CS2⁻

(b) $(CS_2)_2^-$

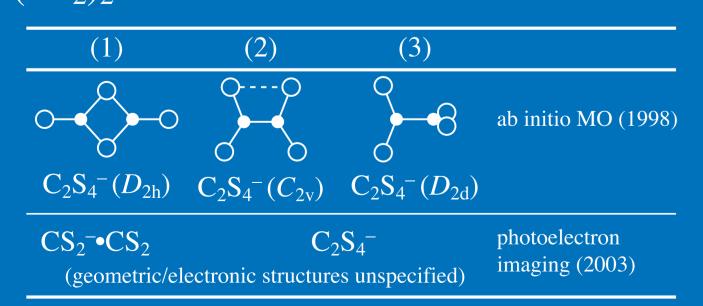
 $(c) (CS_2)_3$

electron binding energy (eV)

FIG. 1. Photoelectron spectra

of $(CS_2)_n^-$ with n = 1-3.

- ◆ Tsukuda 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, C₂S₄⁻, in which the negative charge is delocalized over two molecules.
- ◆ Sanov and co-workers (1998, 2003).
- They reassigned the photoelectron bands of $(CS_2)_2^-$.



- ◆ Maeyama et al. (1998).
 - Photodissociation spectroscopy (hv = 1-2.8 eV).
- They ascribed all the photodissociation processes of $(CS_2)_2^-$ to $C_2S_4^-$.

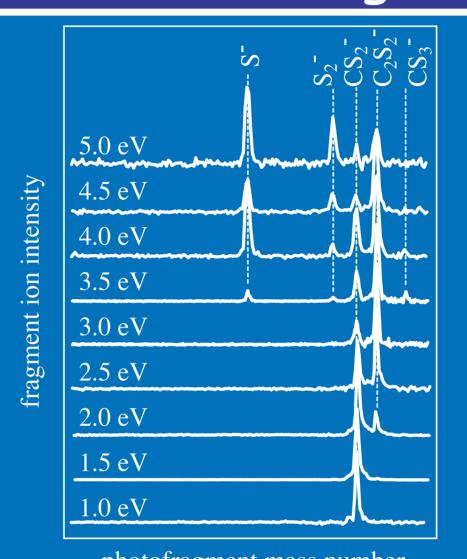
☐ Aim of This Study

- To examine whether the ion-molecule complex $(CS_2^-•CS_2)$ and the molecular anion $(C_2S_4^-)$ really coexist 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 $(CS_2)_2^-$ isomers, the absorption/photoelectron bands, and photofragment species
- Ab initio MO calculations stable structures, correlation of MOs of the $(CS_2)_2^-$ isomers and photofragment species

\square Photofragment species of $(CS_2)_2$



- photofragment mass number
- FIG. 3. Photofragment mass spectra of $(CS_2)_2^-$.

- Five photofragment anions (S⁻, S_2^- , CS_2^- , $C_2S_2^-$, and CS_3^-) are observed in the region of 1–5 eV.
- Photofragment yield spectra (PYS) of $(CS_2)_2^-$ are obtained for each of photofragments by plotting the photodissociation cross section as a function of the photon energy.

□ Experiment

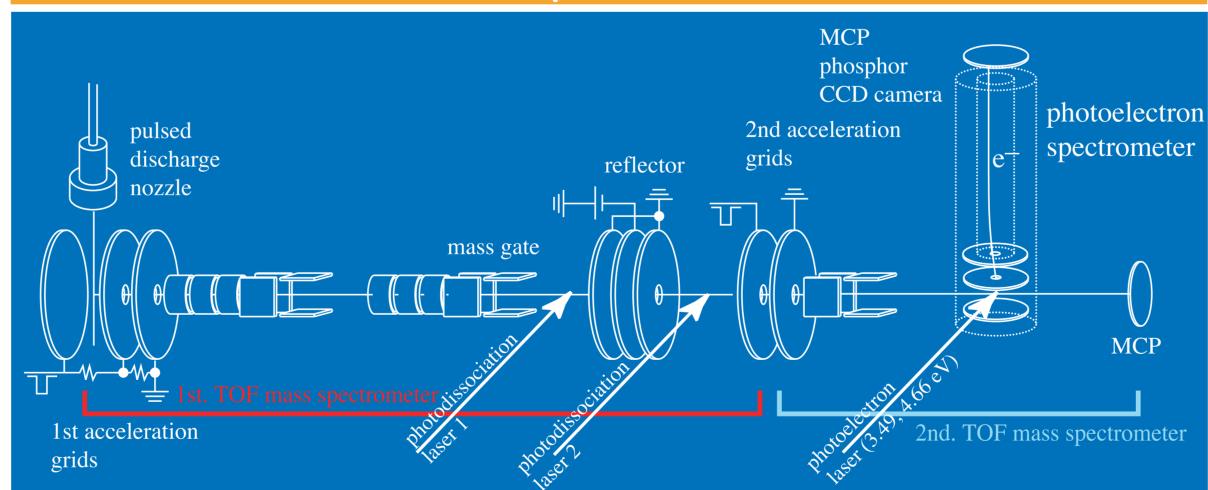
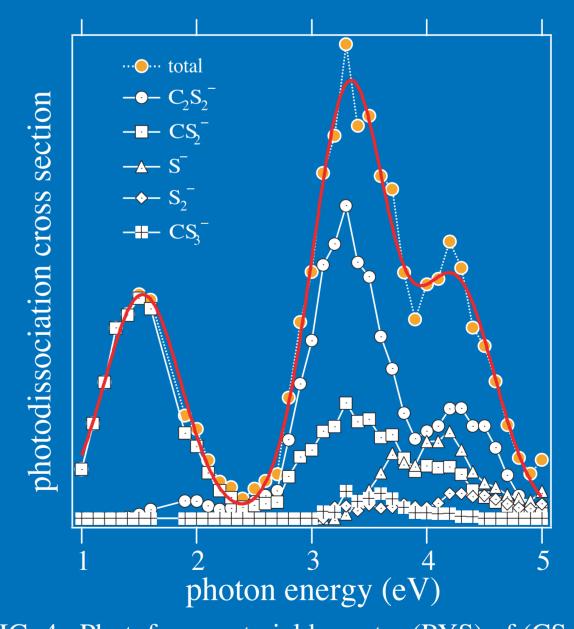


FIG. 2. Tandem time-of-flight (TOF) mass spectrometer used in this study.

- Photodissociation spectroscopy
- $(CS_2)_2^-$ is produced and isolated by the 1st. mass spectrometer, irradiated by the photodissociation laser 2, and mass-analyzed by the 2nd. mass spectrometer.
- Double-laser experiment $(CS_2)_2^-$ is photodissociated by the photodissociation laser 1, and probed by the photodissociation laser 2 or the photoelectron laser.

\square Photofragment yield spectra of $(CS_2)_2$



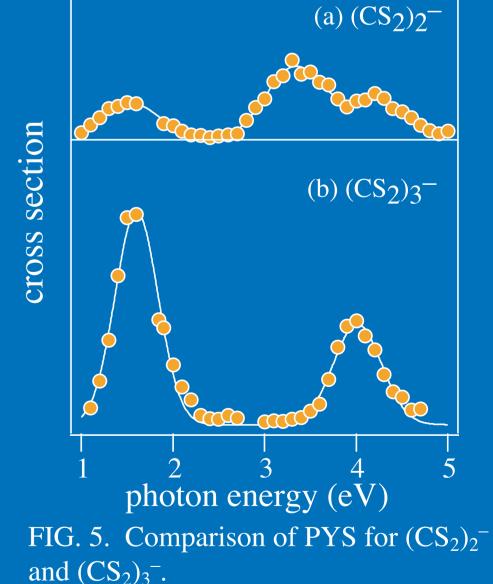


FIG. 4. Photofragment yield spectra (PYS) of $(CS_2)_2^-$.

• Main photofrogments are CS_{-} and $C_{-}S_{-}$

• Main photofragments are CS_2^- and $C_2S_2^-$. (Photoelectron spectra in FIG. 1 shows that $CS_2)_3^-$ has only the ion-molecule form, $CS_2^{-\bullet}(CS_2)_2$.)

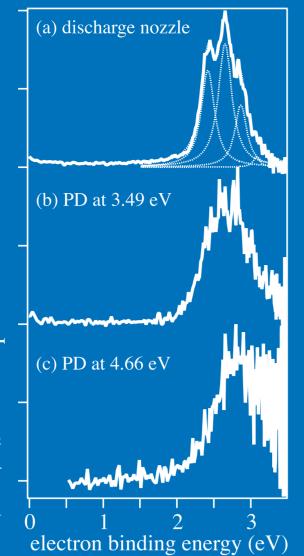
Difference in PYS between $(CS_2)_2^-$ and $(CS_2)_3^-$ suggests that $(CS_2)_2^-$ has an isomer other than the ion-molecule form $(CS_2^- CS_2)$; it must be the molecular anion, $C_2S_4^-$.

\square Identification of Photofragment $C_2S_2^-$

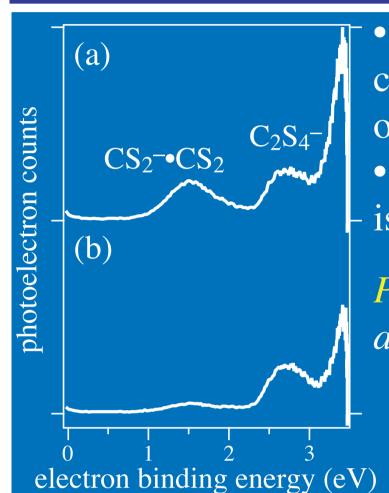
- The SCCS⁻ ion formed in the discharge has a linear structure with the ${}^2\Pi_{\rm u}$ electronic state (Endo et al., 2003).
- Photoelectron spectra of $C_2S_2^-$ produced by the photodissociation of $(CS_2)_2$ are quite similar to that of the SCCS⁻ ion.

Photofragment $C_2S_2^-$ ion has a linear structure with the $^2\Pi_{\rm u}$ electronic state.

> FIG. 6. (a) Photoelectron spectra of SCCS⁻ formed in the discharge nozzle. (b, c) Photoelectron spectra of $C_2S_2^$ produced by the photodissociation of $(CS_2)_2^-$ at 3.49 and 4.66 eV.



☐ Double Laser Experiment 1

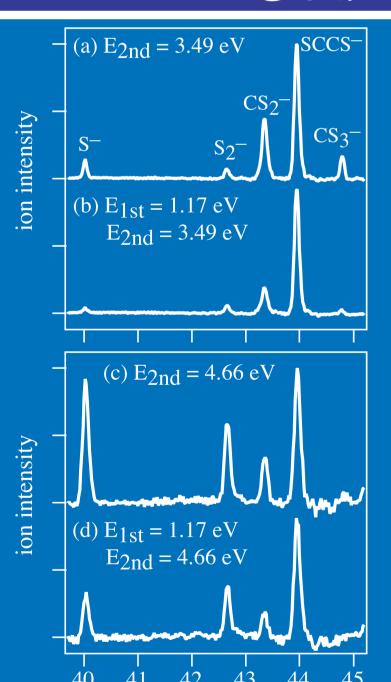


- Only the photoelectron band of the ion-molecule complex (CS₂-CS₂) is reduced under the irradiation of the 1.17 eV light.
- The 1.17 eV light dissociates only the CS₂-CS₂ isomer.

Photodissociation band around 1.5 eV can be assigned to the $CS_2^{-\bullet}CS_2$ isomer.

FIG. 7. (a) Photoelectron spectrum of $(CS_2)_2^-$. (b) Photoelectron spectrum of $(CS_2)_2$ measured after the irradiation of the photodissociation laser 1 at 1.17 eV.

□ Double Laser Experiment 2



arrival time (µs)

- S^- and CS_3^- are reduced largely by the 1st. photodissociation laser (1.17 eV).
- The laser can hardly decreases S_2^- and SCCS $^-$.
- Around half of CS₂⁻ is eliminated by the 1.17 eV light.

Since the photon energy of 1.17 eV corresponds to the electronic transition of the CS₂⁻•CS₂ ion,

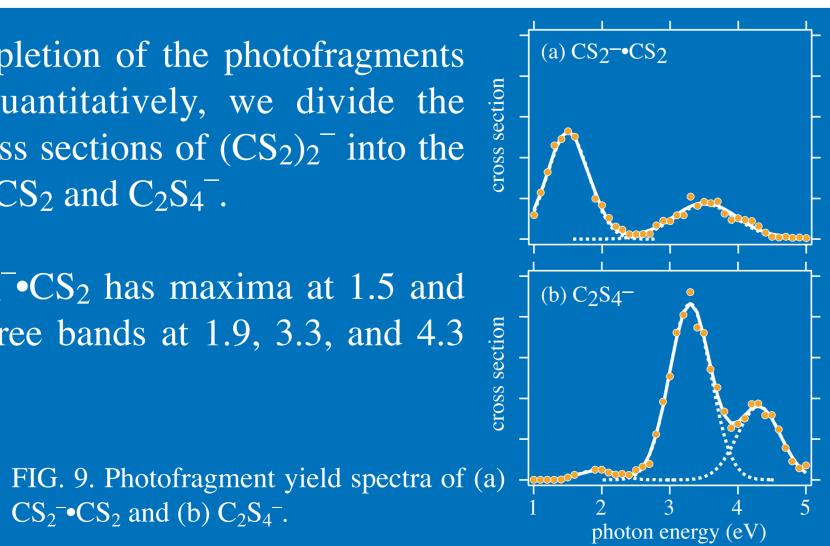
(S and CS₃ are originated from CS₂ •CS₂ S_2^- and SCCS are from $C_2S_4^ CS_2^-$ comes from both of CS_2^- • CS_2 and $C_2S_4^-$.

FIG. 8. (a, b) Photofragment mass spectra of $(CS_2)_2^-$ at 3.49 eV with and without the 1st. photodissociation laser (1.17 eV). (c, d) Photofragment mass spectra of $(CS_2)_2$ at 4.66 eV with and without the 1st. photodissociation laser (1.17 eV).

• Considering the depletion of the photofragments shown in FIG. 8 quantitatively, we divide the photodissociation cross sections of $(CS_2)_2^-$ into the components of $CS_2^- \cdot CS_2$ and $C_2S_4^-$.

The spectrum of CS₂-CS₂ has maxima at 1.5 and 3.5 eV; $C_2S_4^-$ has three bands at 1.9, 3.3, and 4.3 eV.

 $CS_2^{-}CS_2$ and (b) $C_2S_4^{-}$.



Ab Initio MO Calculations

- The CS₂ •CS₂ 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 $C_2S_4^-$ isomer.

(As seen in FIG. 7a, the observed VDE of C₂S₄ is around 2.8 eV.)

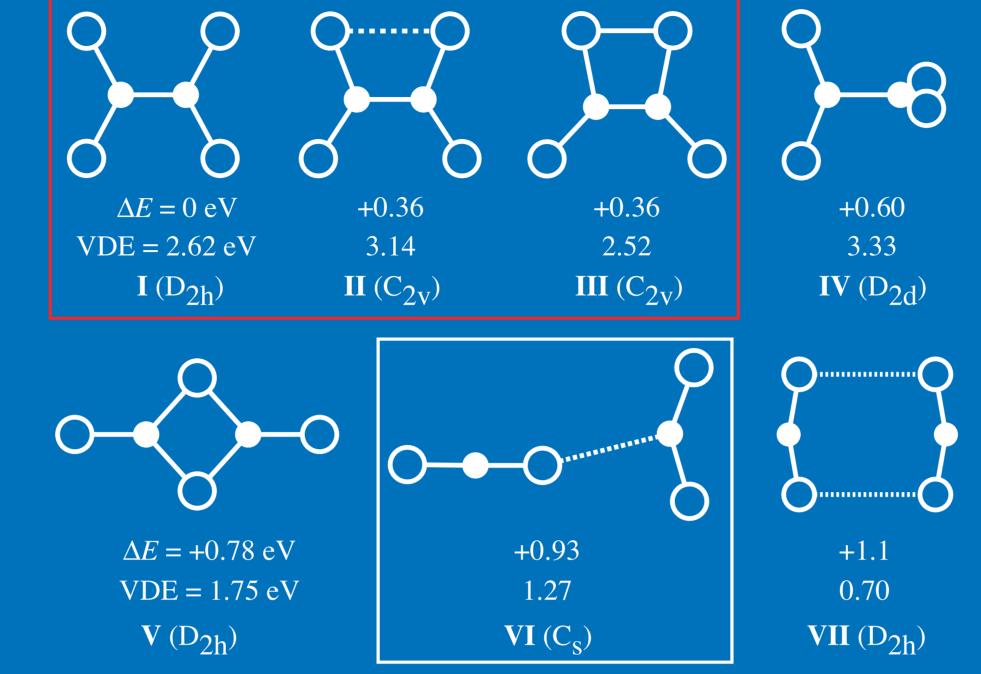
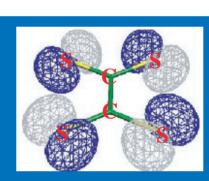
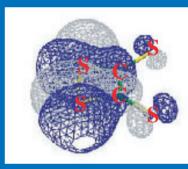


FIG. 10. Stable structures, difference in total energy (ΔE), and vertical detachment energy (VDE) determined by ab initio MO calculations at MP2/aug-cc-pVDZ level.

- SOMOs of I and II are located in-plane of the isomers, whereas that of III is out-ofplane.
- Since the photofragment SCCS anion originates from $C_2S_4^-$, examination of correlation between MOs of C₂S₄⁻ and SCCS⁻ will provide information on the probable isomer of $C_2S_4^-$.



 $I(D_{2h}, b_{3g})$



II $(C_{2v}, 15b_2)$

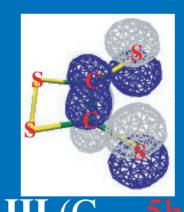


FIG. 11. Singly-occupied MO (SOMO) of Isomers I, II, and III. Although Isomers II and III have similar C_{2v} structures, the symmetry species of SOMOs are b₂ and b₁, respectively.

From the MO diagram, Isomer III (whose SOMO is $5b_1$) correlates with the photofragment SCCS $(D_{\infty h}, X^2\Pi_{n})$.

(Isomer II correlates with the electronically excited SCCS $^-$ (A $^2\Pi_{o}$).)

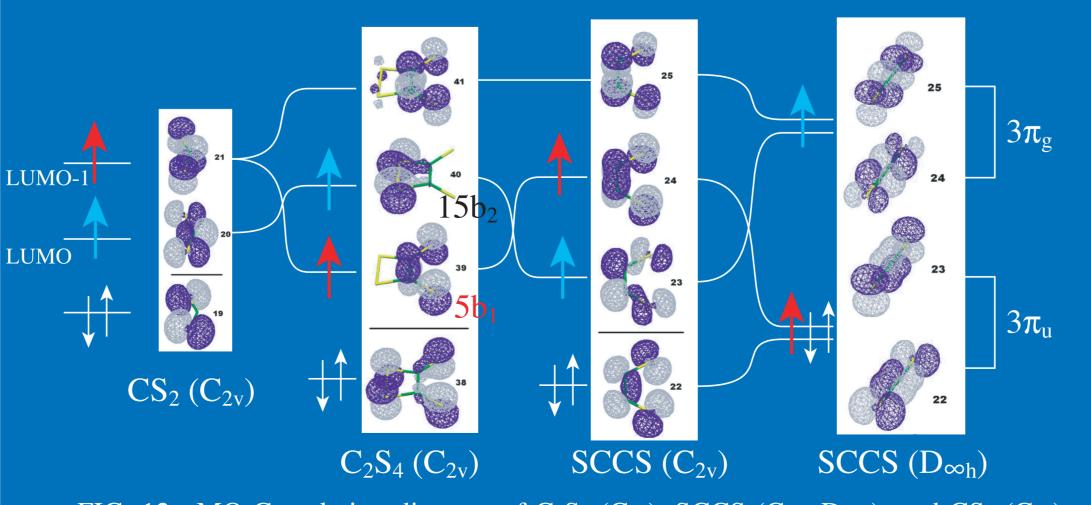
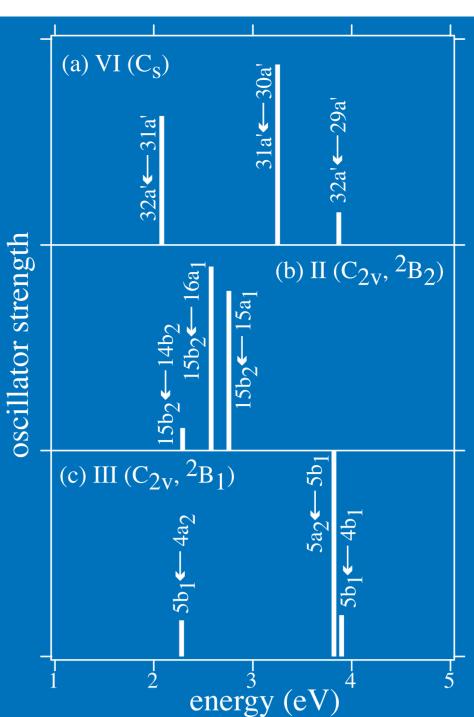


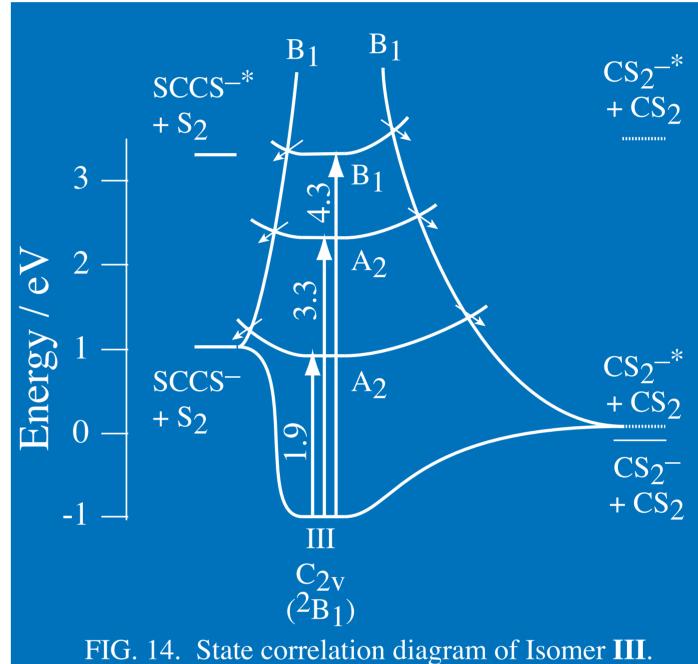
FIG. 12. MO Correlation diagram of C_2S_4 (C_{2v}), SCCS (C_{2v} , $D_{\infty h}$), and CS_2 (C_{2v}).



• Oscillator strength calculations for $(CS_2)_2$ show that 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.

Photofragment SCCS comes only from Isomer III.

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



- PYS bands of $C_2S_4^-$ 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 A₂ state (3.3 eV) corresponds to the CR transition.
- MOs for which the CR CS₂^{-*} interaction occurs are not LUMO $+ CS_2$ but the upper LUMO-1 of CS_2 , as seen on the left side of FIG. 12.

☐ Conclusion

We have performed the photodissociation spectroscopy of $(CS_2)_2$ in the 1–5 eV region. From the photodissociation-photoelectron and the photodissociation-photodissociation experiments, the coexistence of the ion-molecule complex $(CS_2^- \cdot CS_2)$ and the molecular anion $(C_2S_4^-)$ has been proved for $(CS_2)_2$. 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 $(CS_2)_2^{-1}$ isomers and the fragment anions quantitatively, we have obtained the photofragment yield spectra of $CS_2^{-\bullet}CS_2$ and $C_2S_4^{-}$ separately. According to the energetics and the state correlation analysis of $(CS_2)_2^-$, we have concluded that the $C_2S_4^-$ molecular anion, which is responsible for the production of SCCS⁻, has a C_{2v} structure with the 2B_1 electronic ground state.