Photodissociation of $(CS_2)_2^-$: $CS_2^- \cdot CS_2$ process vs. $C_2S_4^-$ process

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Photodissociation cross sections of $(CS_2)_2^-$ are measured in the photon energy of 1–5 eV. Photodissociation of $(CS_2)_2^-$ provides five fragments, S^-, S_2^-, CS_2^-, $C_2S_2^-$, and CS_3^-. Hole-burning experiments of $(CS_2)_2^-$ confirm the coexistence of the ion-molecule complex ($CS_2^- \cdot CS_2$) and the molecular anion ($C_2S_4^-$). We apply *ab initio* MO calculations (MP2/aug-cc-pVDZ) to $(CS_2)_2^-$, and obtain seven stable isomers. From the MO correlation analysis and energetics, 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 positive charge is delocalized over two molecules with the charge resonance (CR) interaction. (e. g. $(C_6H_6)_2^+$, $(CO_2)_2^+$)

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 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.

• Carbon disulfide dimer anion, $(CS_2)_2^-$, is one of 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.

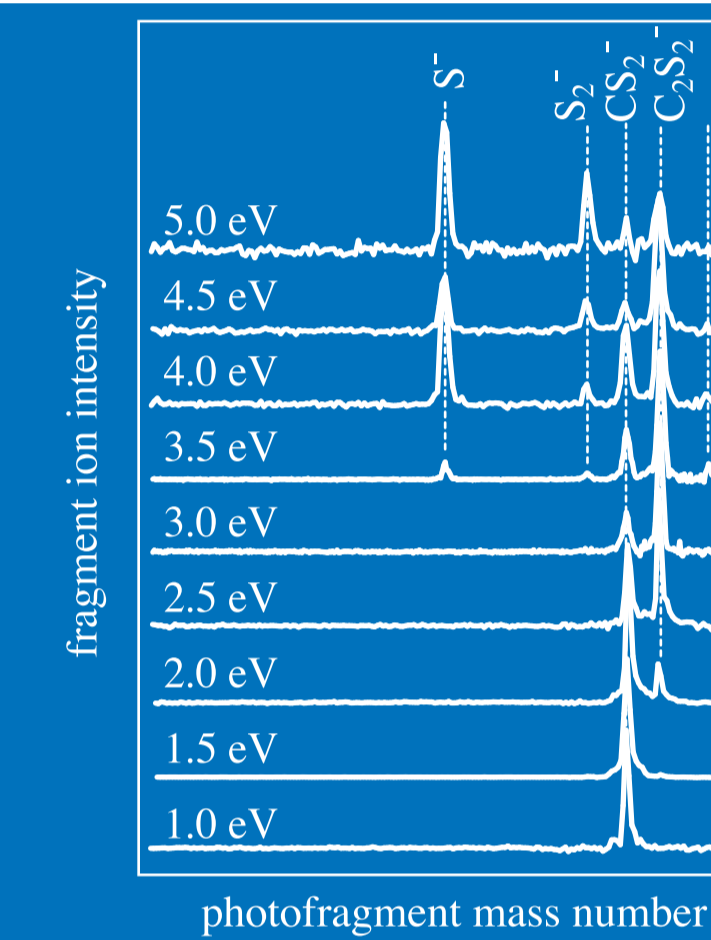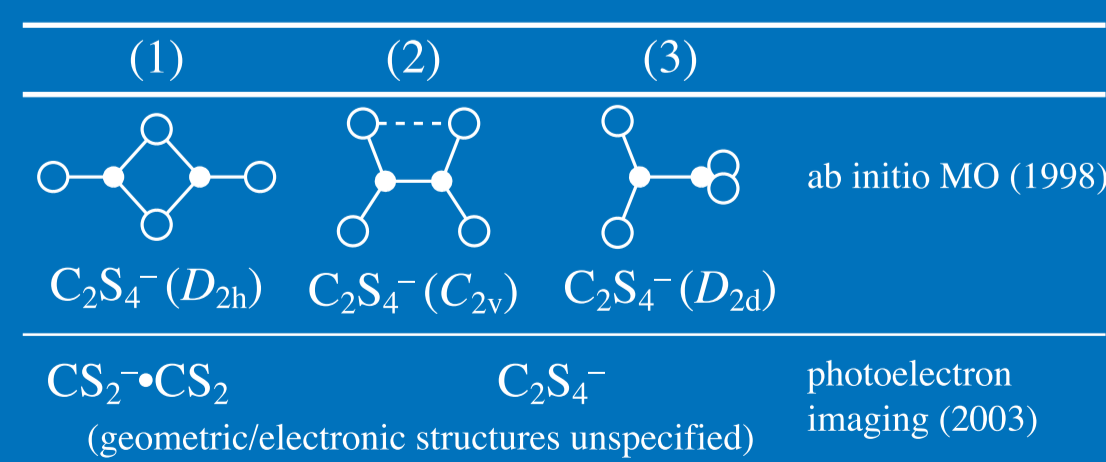## ☐ $(CS_2)_2^-$: Previous Study

◆ Tsukuda et al. (1997).
• Photoelectron spectra of $(CS_2)_n^-$ with $n = 1$–6.
• The $n = 2$ spectrum has additional bands at ~3 eV ((2) and (3) in FIG. 1).
• These bands were assigned to the molecular anion, $C_2S_4^-$, in which the negative charge is delocalized over two molecules.

◆ Sanov and co-workers (1998, 2003).
• They reassigned the photoelectron bands of $(CS_2)_2^-$.

(1)	(2)	(3)	
$C_2S_4^-$ (D_{2h})	$C_2S_4^-$ (C_{2v})	$C_2S_4^-$ (D_{2d})	ab initio MO (1998)
$CS_2^- \cdot CS_2$	$C_2S_4^-$		photoelectron imaging (2003)
(geometric/electronic structures unspecified)			

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

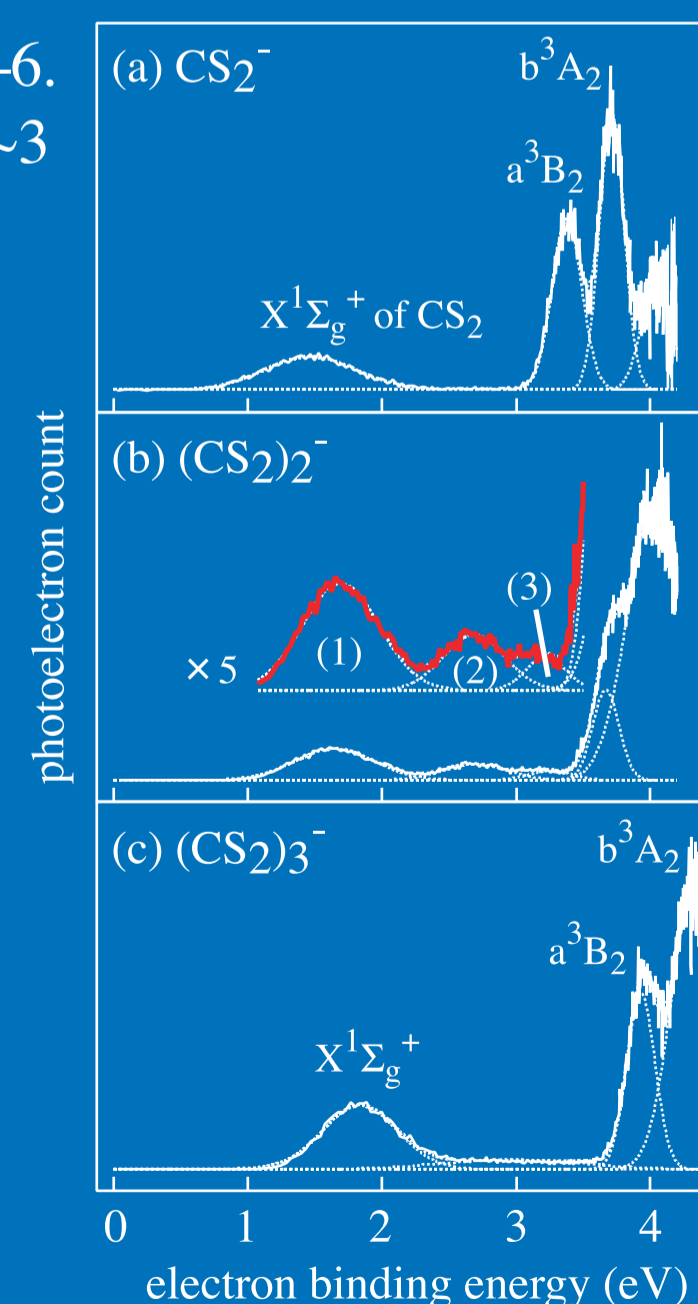FIG. 1. Photoelectron spectra of $(CS_2)_n^-$ with $n = 1$–3.

☐ Aim of This Study

• To examine whether the ion-molecule complex ($CS_2^- \cdot CS_2$) and the molecular anion ($C_2S_4^-$) really coexist for $(CS_2)_2^-$.
• To specify the electronic/geometric structures and reveal the photochemical (photodissociation) process.

☐ Methods

• Photodissociation spectroscopy
    for obtaining photofragment yield spectra (PYS) of $(CS_2)_2^-$.
• Hole-burning experiments
    for investigating correlation between $(CS_2)_2^-$ isomers, absorption/photoelectron bands, and photofragment species
• Ab initio MO calculations
    stable structures, correlation of MOs of the $(CS_2)_2^-$ isomers and photofragment species
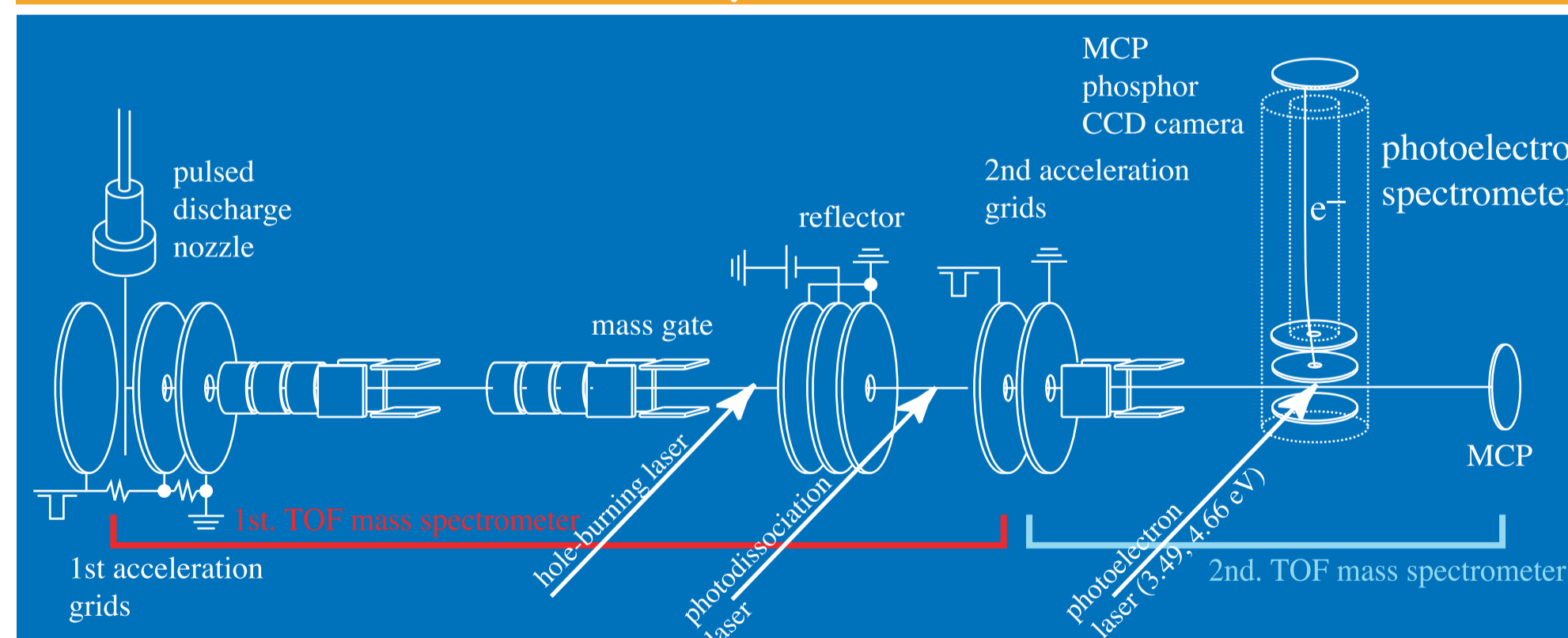
☐ Experiment

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

• Photodissociation experiments
    $(CS_2)_2^-$ 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
    $(CS_2)_2^-$ is photodissociated by a hole-burning laser. Fragment ions are removed by a reflector. Remaining $(CS_2)_2^-$ is probed by the photodissociation laser or a photoelectron laser.

☐ Photofragment species of $(CS_2)_2^-$

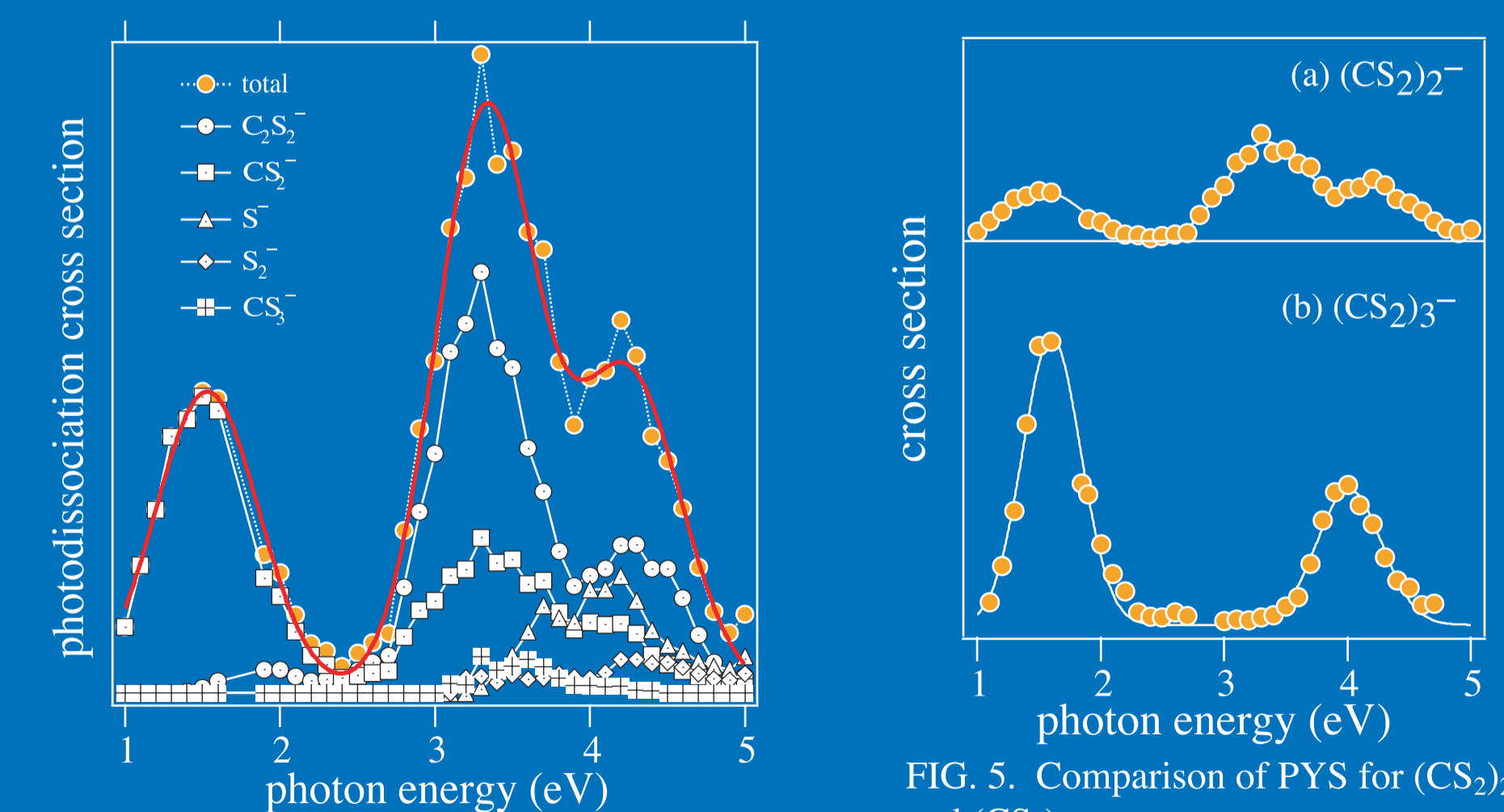FIG. 3. Photofragment mass spectra of $(CS_2)_2^-$.

• Five photofragment anions (S^-, S_2^-, CS_2^-, $C_2S_2^-$, and CS_3^-) are observed in the region of 1–5 eV.

• A photofragment yield spectrum (PYS) of $(CS_2)_2^-$ is obtained by plotting photodissociation cross sections as a function of photon energy.

☐ Photofragment yield spectra of $(CS_2)_2^-$

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

FIG. 5. Comparison of PYS for $(CS_2)_2^-$ and $(CS_2)_3^-$.

• Main photofragments are CS_2^- and $C_2S_2^-$.

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 ($CS_2^- \cdot CS_2$).

(Photoelectron spectra in FIG. 1 show that $(CS_2)_3^-$ has only the ion-molecule form, $CS_2^- \cdot (CS_2)_2$.)

☐ Identification of Photofragment $C_2S_2^-$

- $SCCS^-$ formed in the discharge has a linear structure with the electronic ground ($^2\Pi_u$) state (Endo et al., 2003).
- Photoelectron spectra of photofragment $C_2S_2^-$ are quite similar to that of the $SCCS^-$ ion.

Photofragment $C_2S_2^-$ ion has a linear structure with the $^2\Pi_u$ electronic state.

FIG. 6. (a) Photoelectron spectra of $SCCS^-$ formed in a 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.
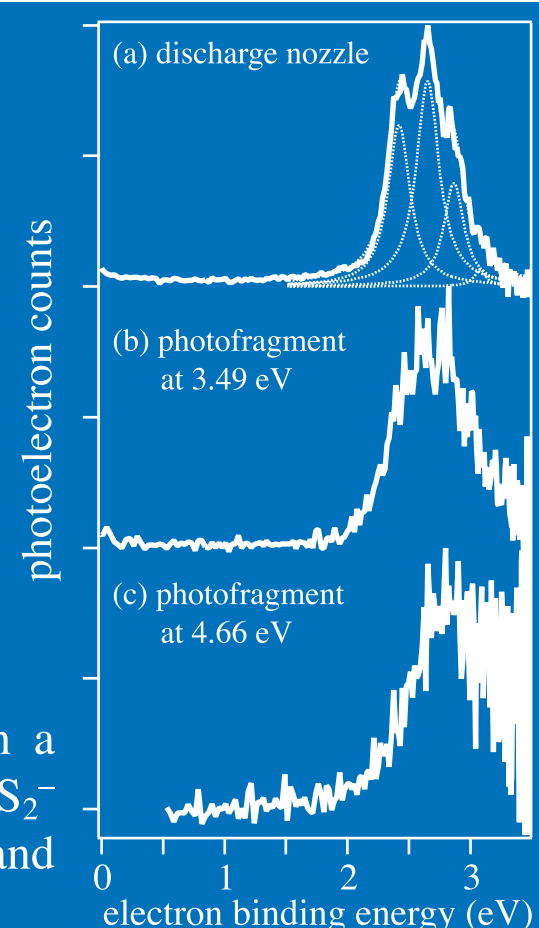
☐ Hole-Burning Experiment 1

- Only the photoelectron band of the ion-molecule complex ($CS_2^-\bullet CS_2$) is reduced under the irradiation of the hole-burning laser at 1.17 eV.

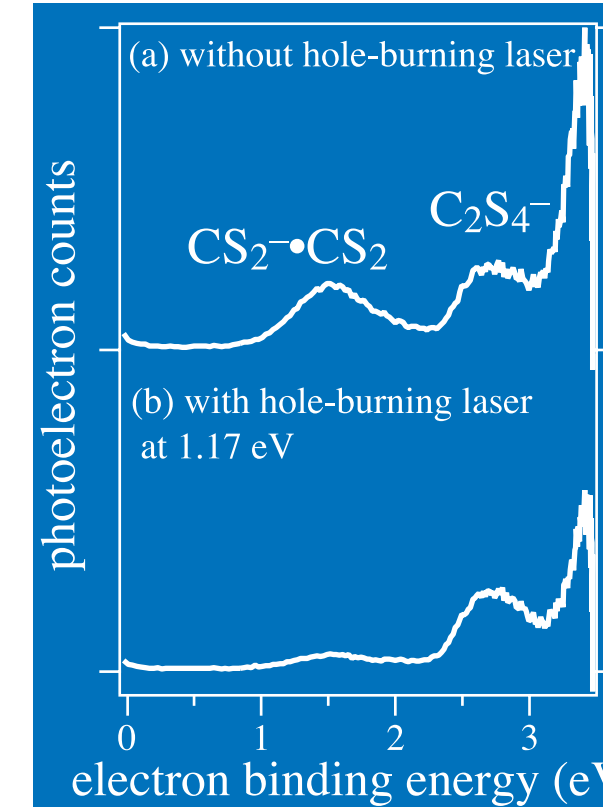*Photodissociation band around 1.5 eV (see FIG. 4) can be assigned to the $CS_2^-\bullet CS_2$ isomer.*

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

☐ Hole-Burning Experiment 2

- S^- and CS_3^- are reduced largely by the hole-burning laser at 1.17 eV.
- The laser can hardly decrease S_2^- and $SCCS^-$.
- ~50 % of CS_2^- is eliminated.

Since the photon energy of 1.17 eV corresponds to the transition of the $CS_2^-\bullet CS_2$ ion,
S^- and CS_3^- are attributed to $CS_2^-\bullet CS_2$
S_2^- and $SCCS^-$ are to $C_2S_4^-$
*CS_2^- is to both of $CS_2^-\bullet CS_2$ and $C_2S_4^-$.*

FIG. 8. (a, b) Photofragment mass spectra of $(CS_2)_2^-$ at 3.49 eV with and without the hole-burning laser (1.17 eV). (c, d) Photofragment mass spectra of $(CS_2)_2^-$ at 4.66 eV with and without the hole-burning laser (1.17 eV).
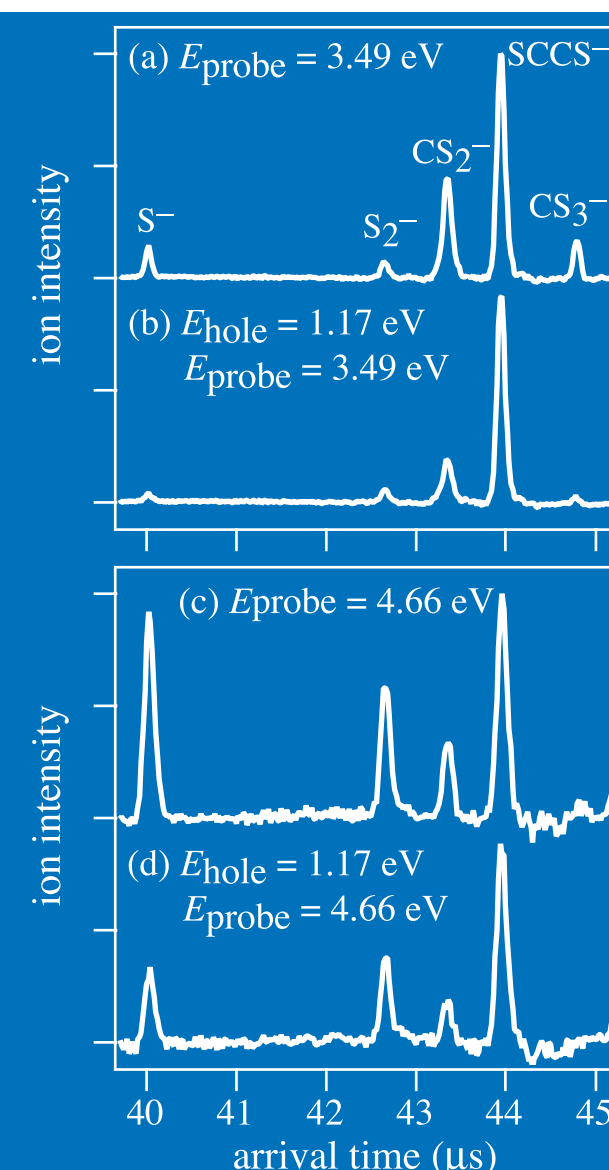
- Considering the depletion of the photofragments shown in FIG. 8 quantitatively, we divide the photodissociation cross sections of $(CS_2)_2^-$ into components of $CS_2^-\bullet CS_2$ and $C_2S_4^-$.

The spectrum of $CS_2^-\bullet CS_2$ has maxima at 1.5 and 3.5 eV; $C_2S_4^-$ has three bands at 1.9, 3.3, and 4.3 eV.

FIG. 9. Photofragment yield spectra of (a) $CS_2^-\bullet CS_2$ and (b) $C_2S_4^-$.
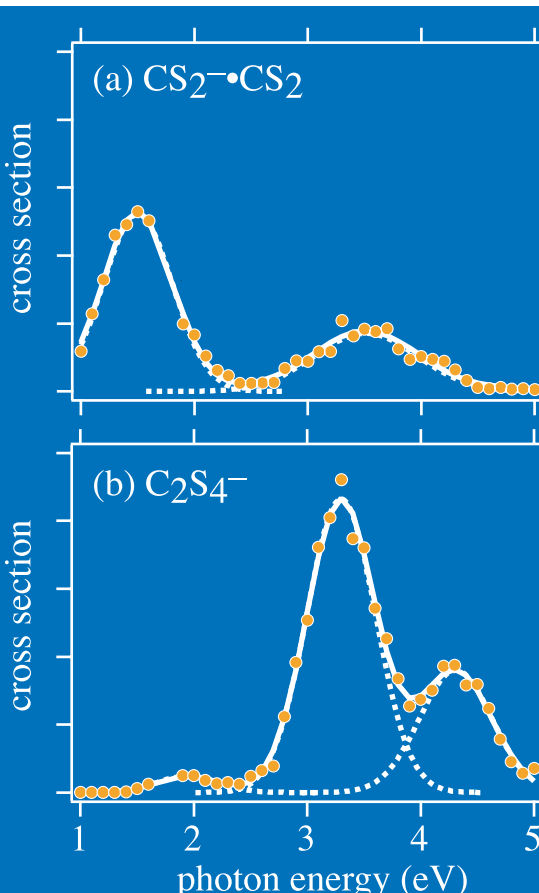
☐ Ab Initio MO Calculations

- The $CS_2^-\bullet CS_2$ 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 $C_2S_4^-$ isomer.
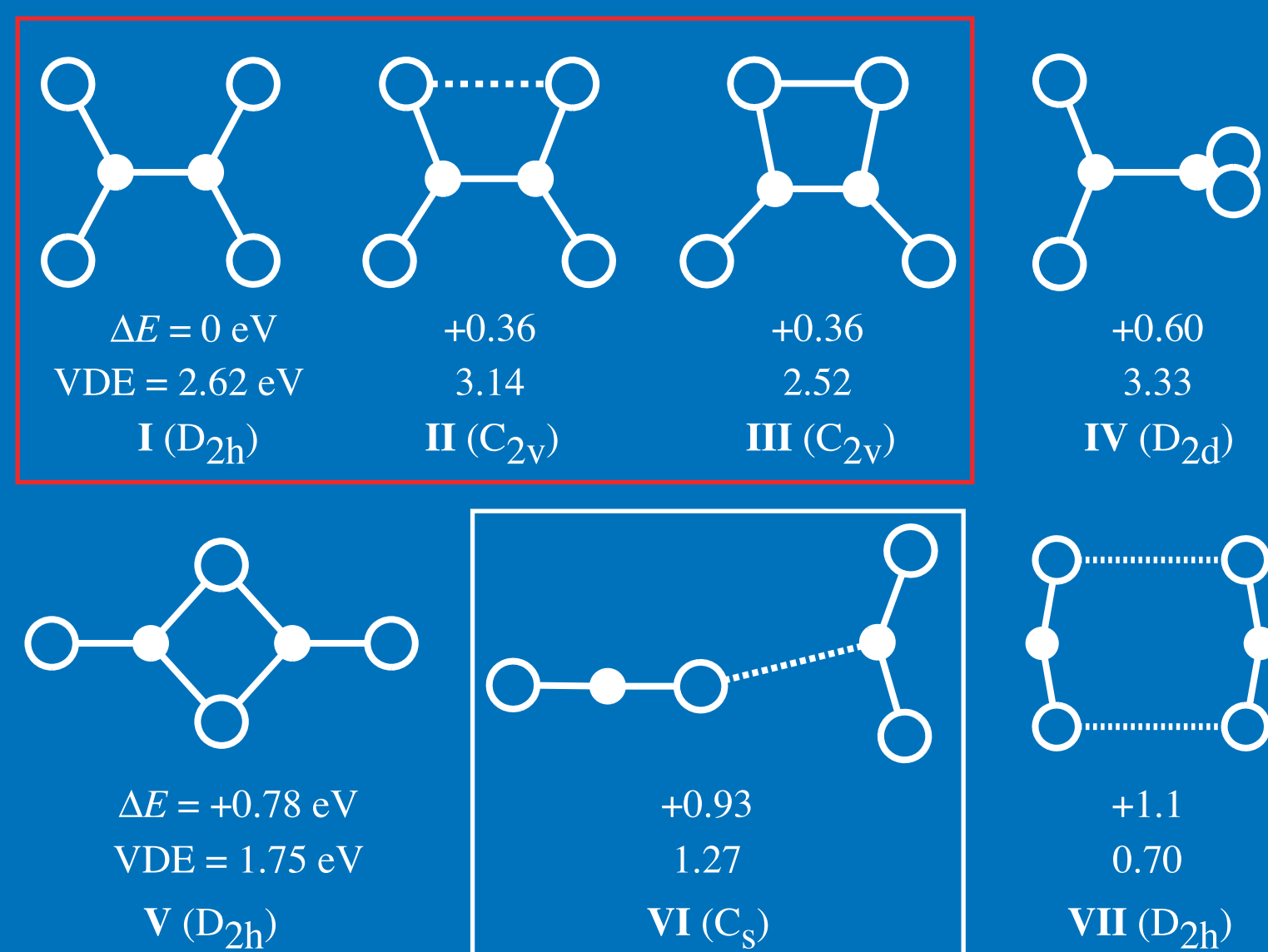 (As seen in FIG. 7a, the observed VDE of $C_2S_4^-$ is around 2.8 eV.)

$\Delta E = 0$ eV	+0.36	+0.36	+0.60
VDE = 2.62 eV	3.14	2.52	3.33
I (D_{2h})	**II** (C_{2v})	**III** (C_{2v})	**IV** (D_{2d})
$\Delta E = +0.78$ eV	+0.93	+1.1	
VDE = 1.75 eV	1.27	0.70	
V (D_{2h})	**VI** (C_s)	**VII** (D_{2h})	

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

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

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

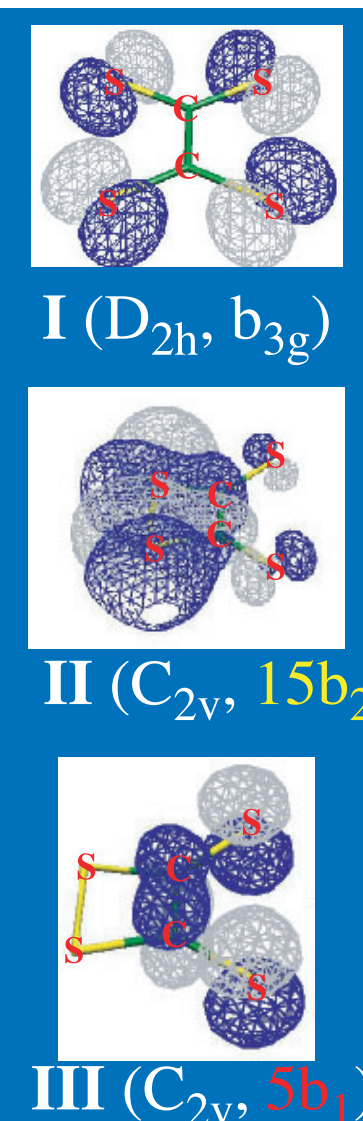**II** (C_{2v}, $15b_2$)

III (C_{2v}, $5b_1$)

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 b_2 and b_1, respectively.

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

(Isomers **I** and **II** correlate with the electronically excited $SCCS^-$ ($A^2\Pi_g$).)

$3\pi_g$

$15b_2$

$5b_1$

$3\pi_u$

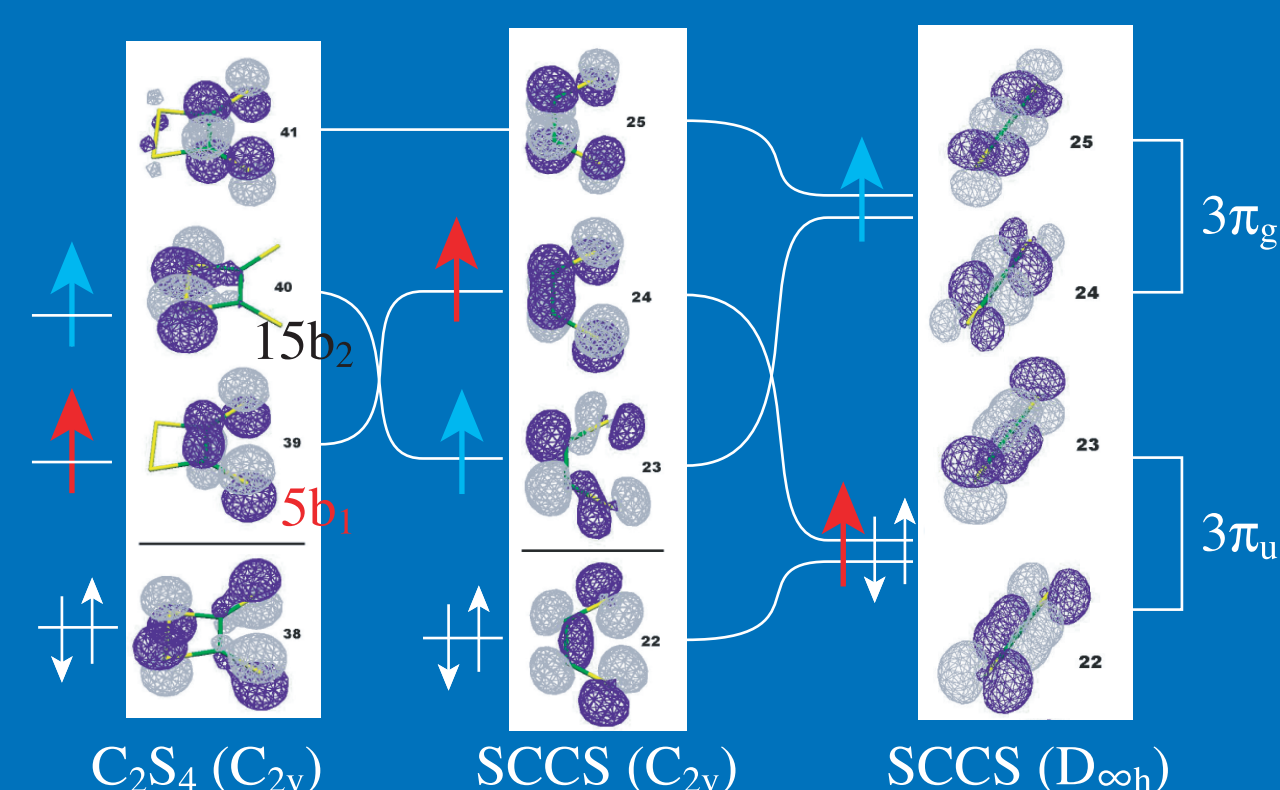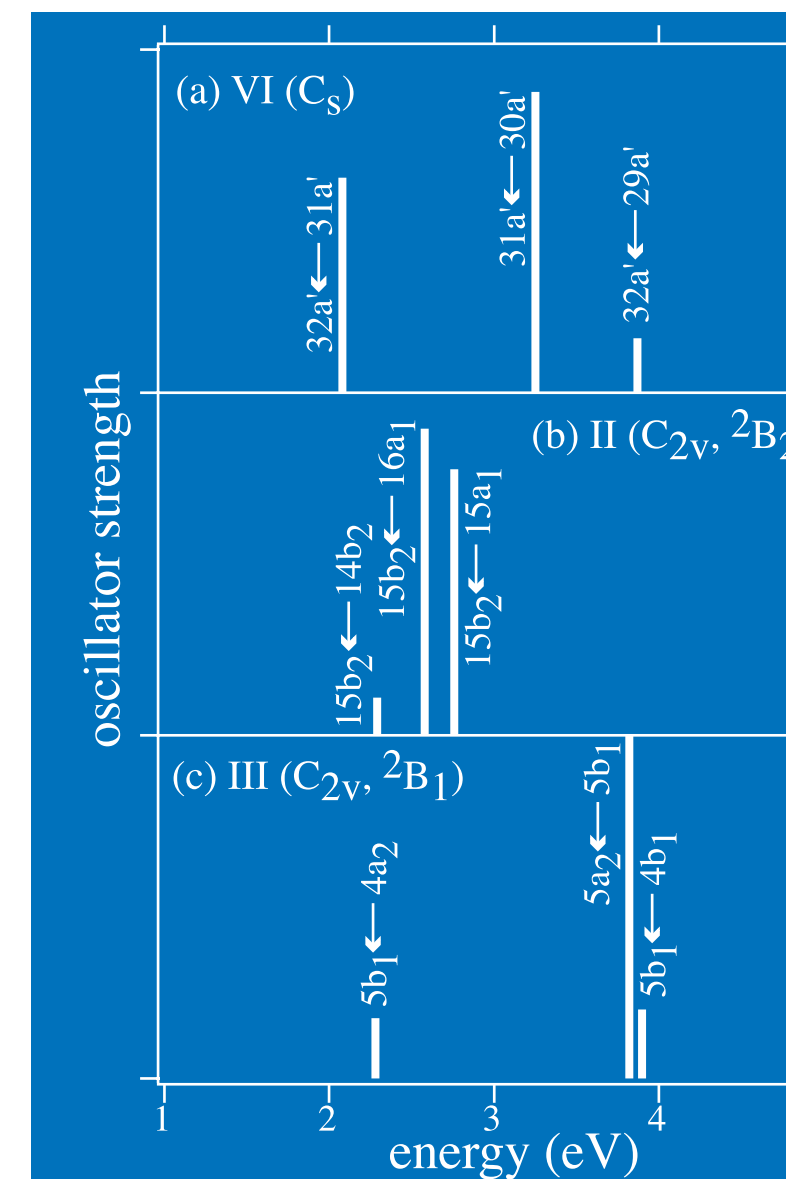C_2S_4 (C_{2v}) $SCCS$ (C_{2v}) $SCCS$ ($D_{\infty h}$)

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

- 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.
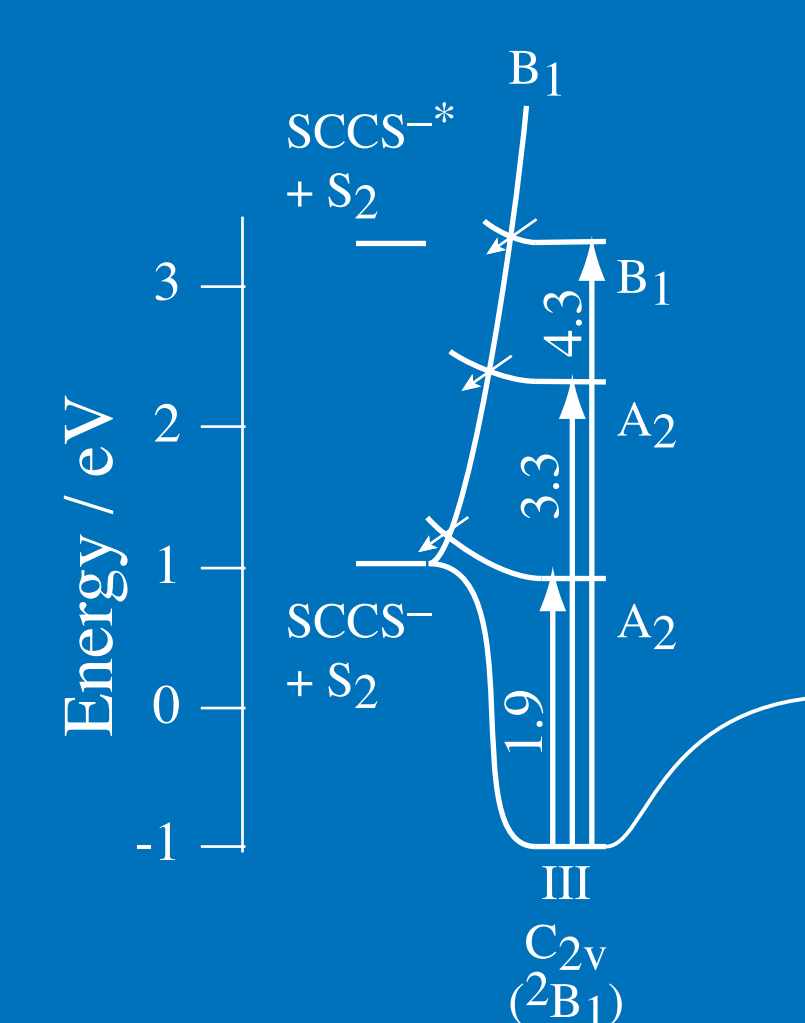
- PYS bands of $C_2S_4^-$ at 1.9, 3.3, and 4.3 eV (FIG. 9b) are assigned to the three transitions of **III** displayed in FIG. 13c.

- The electronic ground state of Isomer **II** ($^2B_2$) correlates with the excited $SCCS^-*$; there is a possibility that the ground $SCCS^-$ is produced after the radiative relaxation of $SCCS^-*$ formed by the photodissociation of Isomer **II**.

- However, since the excited state of $SCCS^-*$ is ~4.3 eV higher than the ground state of Isomer **II**, this process is not possible energetically for most of the photodissociation region.

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

☐ Conclusion

We have performed photodissociation spectroscopy of $(CS_2)_2^-$ in the 1–5 eV region. From the hole-burning experiments, coexistence of the ion-molecule complex ($CS_2^-\bullet CS_2$) and the molecular anion ($C_2S_4^-$) has been proved for $(CS_2)_2^-$. Interconversion between these isomers does not occur in several μs time window due to a certain potential barrier between them. By taking the relationship between the $(CS_2)_2^-$ isomers and photofragments into account 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 MO correlation analysis of $(CS_2)_2^-$, we have concluded that the $C_2S_4^-$ molecular anion, which is responsible for the $SCCS^-$ photoproduct, has a C_{2v} structure with the $^2B_1$ electronic ground state.