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

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$(CS_2)_2^-$

- 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.

$(CS_2)_2^-$

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

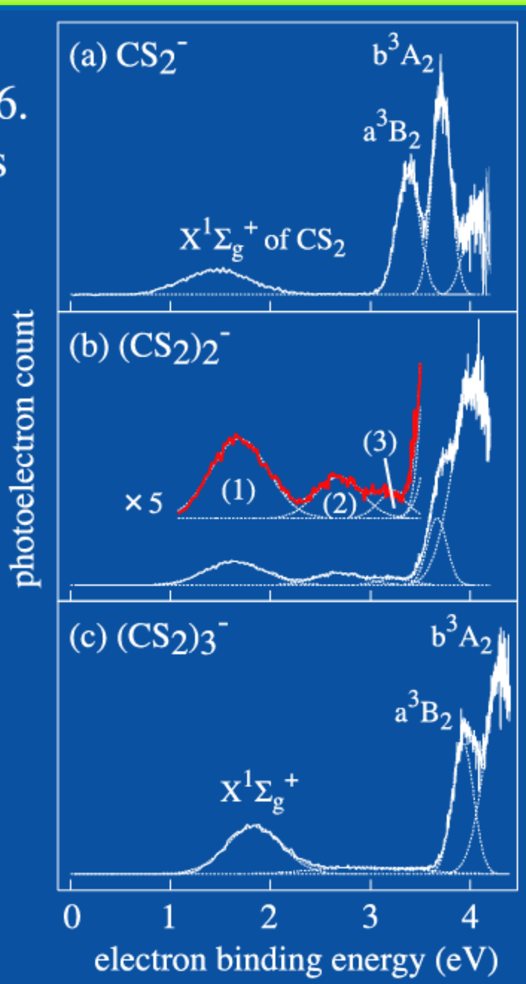


FIG. 1. Photoelectron spectra of $(CS_2)_n^-$ with $n = 1$–3.

- Maeyama et al. (1998).
  - Photodissociation spectroscopy (hν = 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.

- 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

Experiment

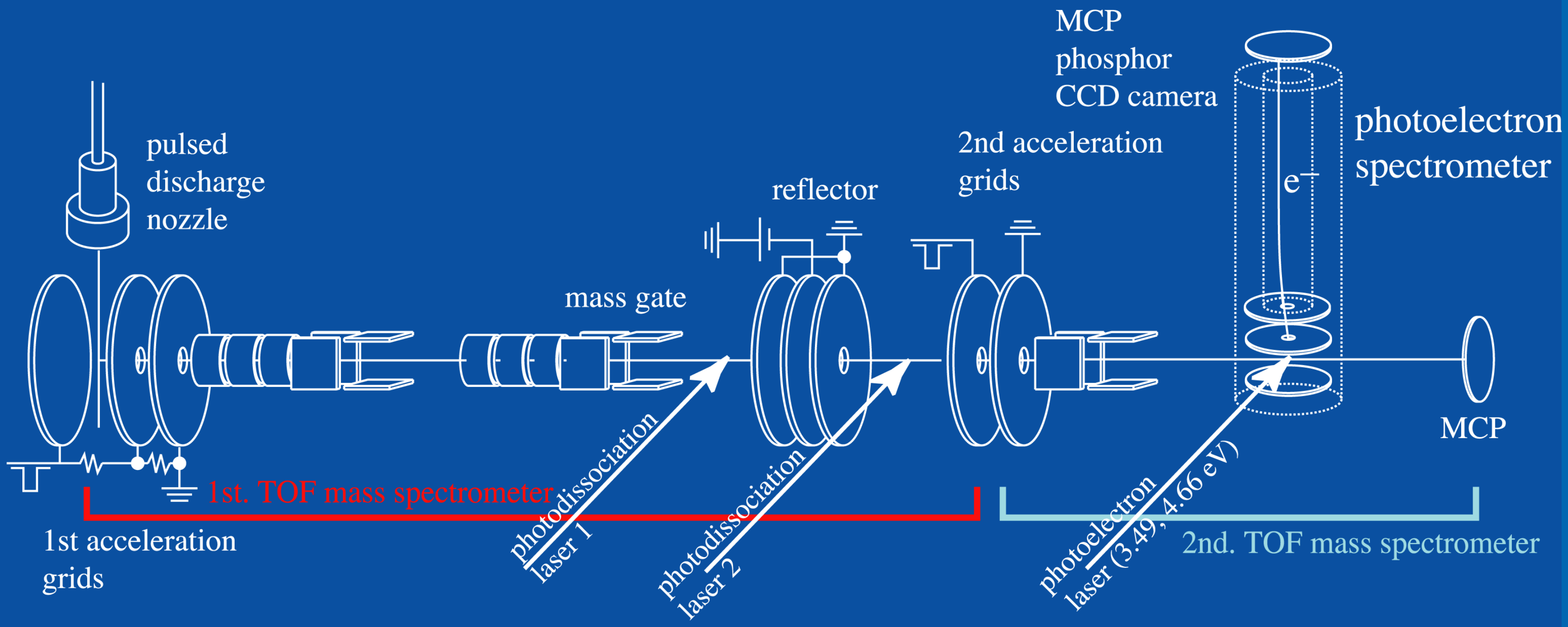


FIG. 2. Tandem time-of-flight (TOF) mass spectrometer used in this study.

- 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.

Photofragment Species

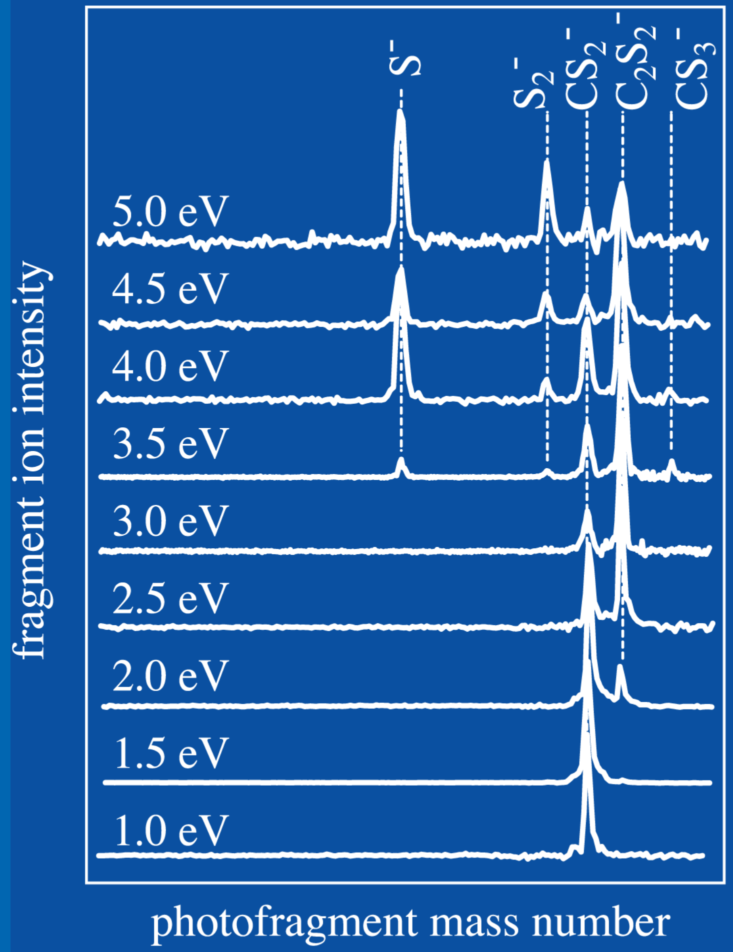


FIG. 3. Photofragment mass spectra of $(CS_2)_2^-$.

- 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.

Photofragment Yield Spectra

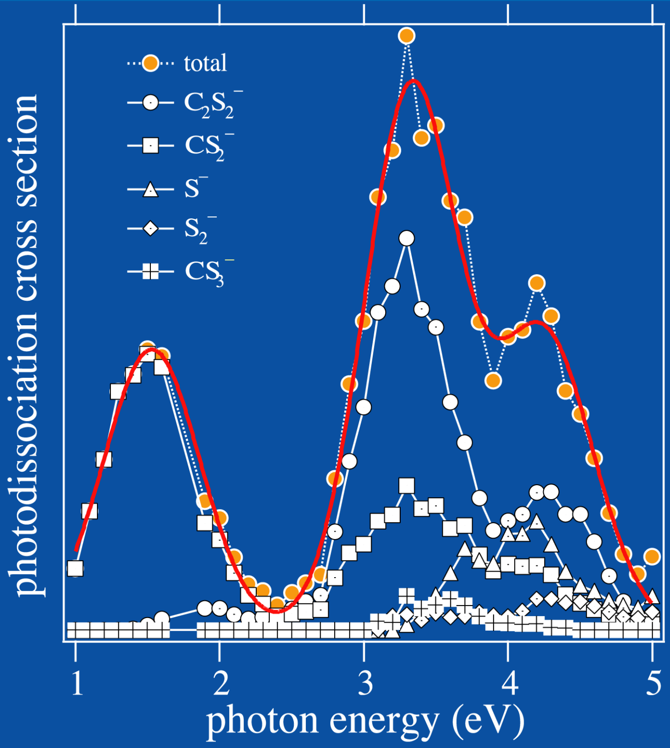


FIG. 4. Photofragment yield spectra (PYS) of $(CS_2)_2^-$.

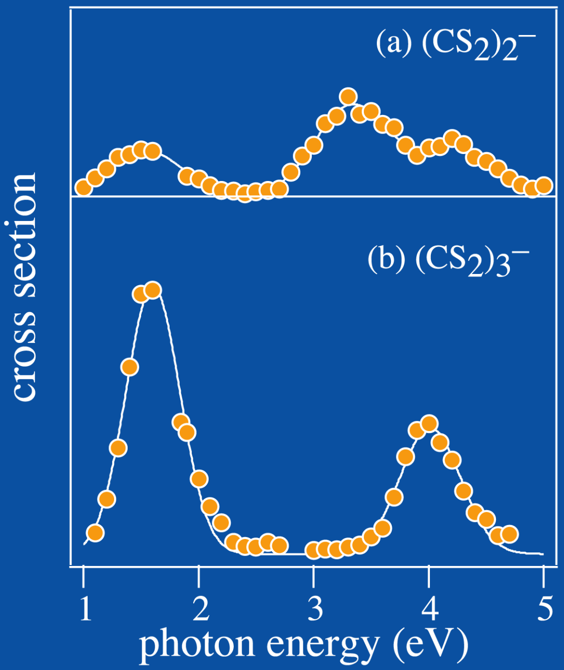


FIG. 5. Comparison of PYS for $(CS_2)_2^-$ and $(CS_2)_3^-$.

- Main photofragments are CS_2^- and $C_2S_2^-$.
- PYS of $(CS_2)_2^-$ shows three maxima at 1.5, 3.3, and 4.3 eV, whereas PYS of $(CS_2)_3^-$ has only two maxima. ($(CS_2)_3^-$ has only the ion-molecule form, CS_2^-•$(CS_2)_2$).

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 should be the molecular anion, $C_2S_4^-$.

Identification of Photofragment $C_2S_2^-$

- The $SCCS^-$ ion formed in the discharge has a linear structure with the $^2\Pi_u$ 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 $^2\Pi_u$ electronic state.

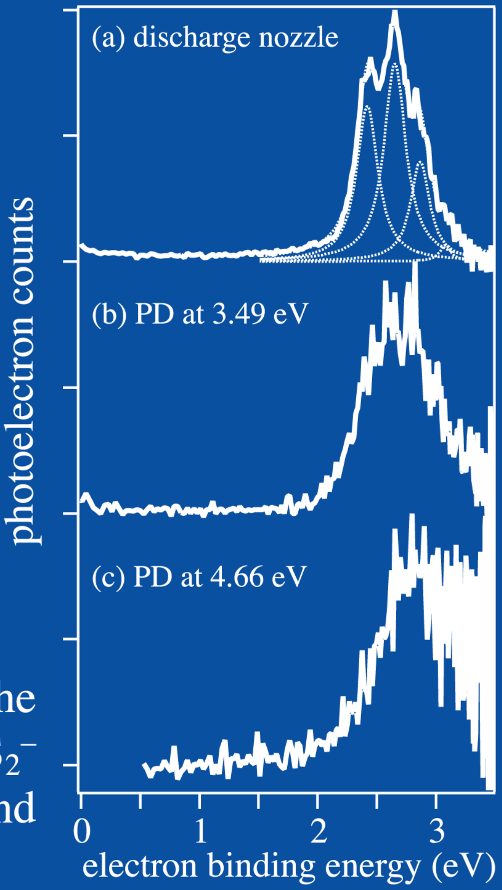
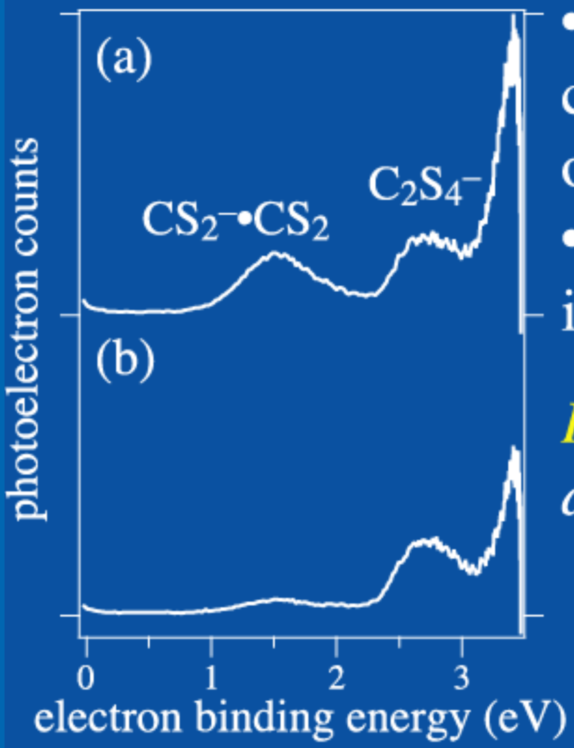


FIG. 6. (a) Photoelectron spectra of $SCCS^-$ formed in the discharge nozzle. (b, c) Photoelectron spectra of $C_2S_2^-$ produced by the photodissociation of $(CS_2)_2^-$ at 3.49 and 4.66 eV.

Double Laser Experiment 1

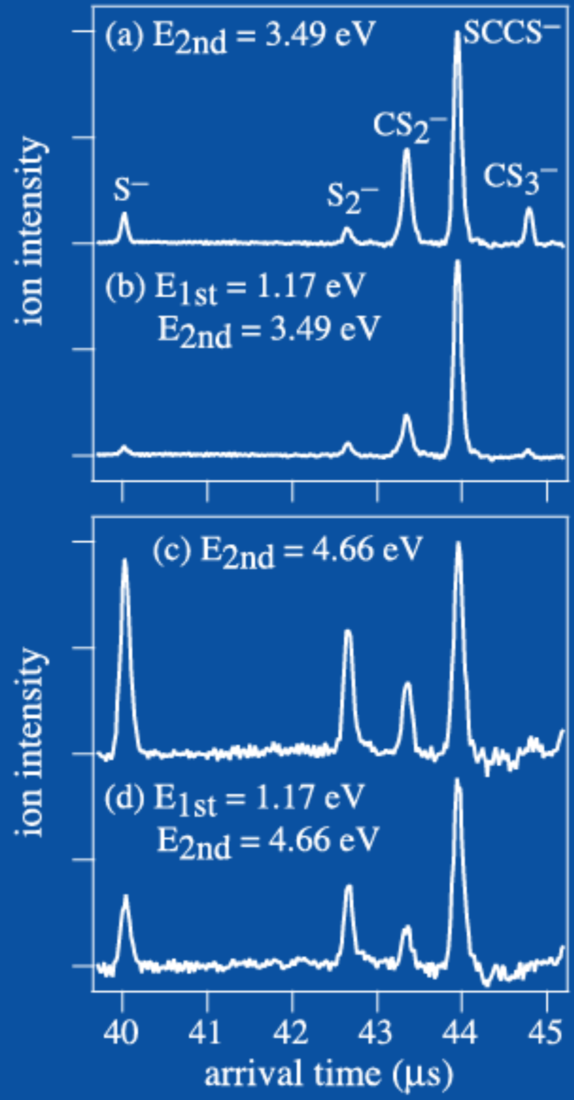


- Only the photoelectron band of the ion-molecule complex ($CS_2^-•CS_2$) is reduced under the irradiation of the 1.17 eV light.
- The 1.17 eV light dissociates only the $CS_2^-•CS_2$ isomer.

Photodissociation band around 1.5 eV can be assigned to the $CS_2^-•CS_2$ 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



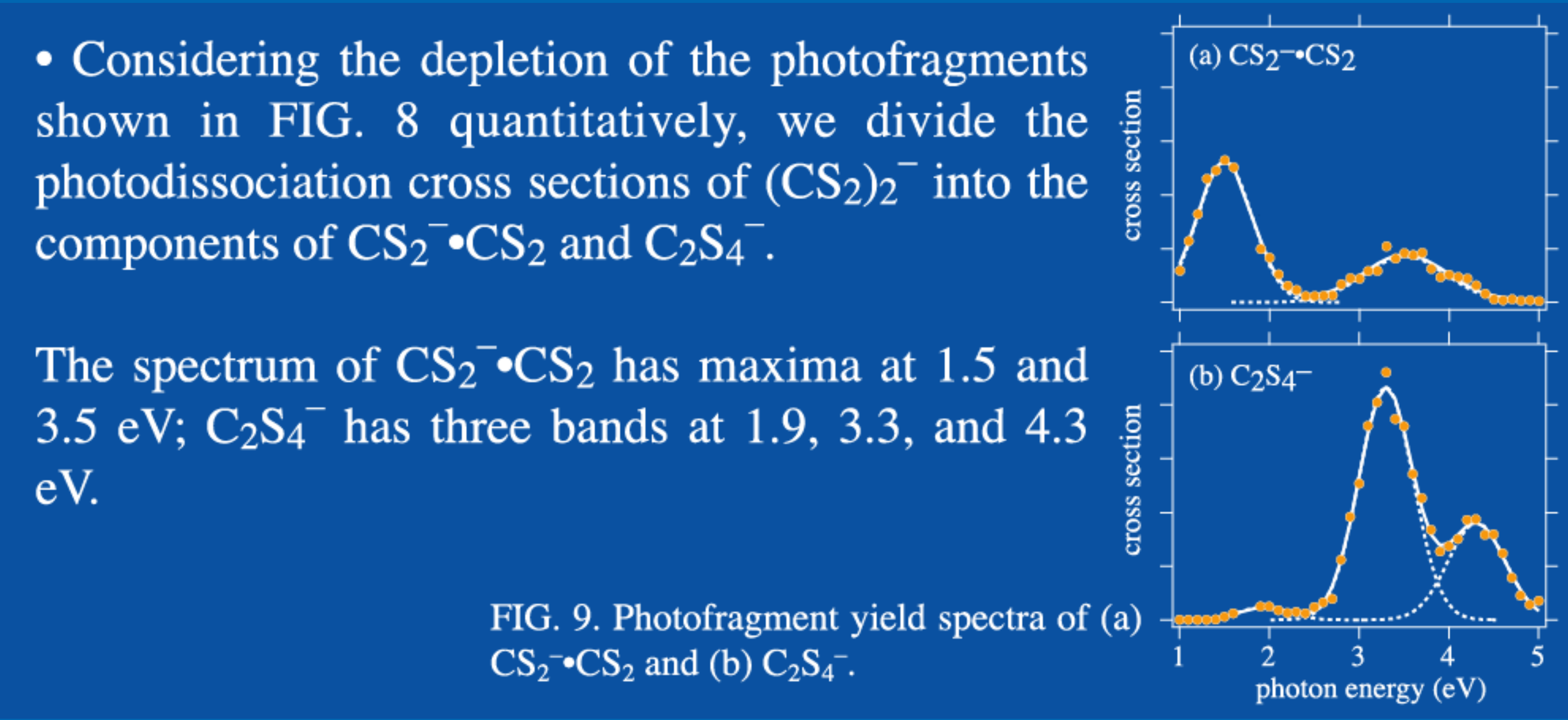
- S^- and CS_3^- are reduced largely by the 1st. photodissociation laser (1.17 eV).
- The laser can hardly decreases S_2^- and $SCCS^-$.
- Around half of CS_2^- is eliminated by the 1.17 eV light.

Since the photon energy of 1.17 eV corresponds to the electronic transition of the CS_2^-•CS_2 ion,

S^- and CS_3^- are originated from CS_2^-•CS_2
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).

Photofragment Yield Spectra of $CS_2^-\cdot CS_2$ and $C_2S_4^-$



- 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 $CS_2^-\cdot CS_2$ 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) $CS_2^-\cdot CS_2$ and (b) $C_2S_4^-$.

Stable Structures of $(CS_2)_2^-$

- The CS_2^-•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 $C_2S_4^-$ isomer.

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

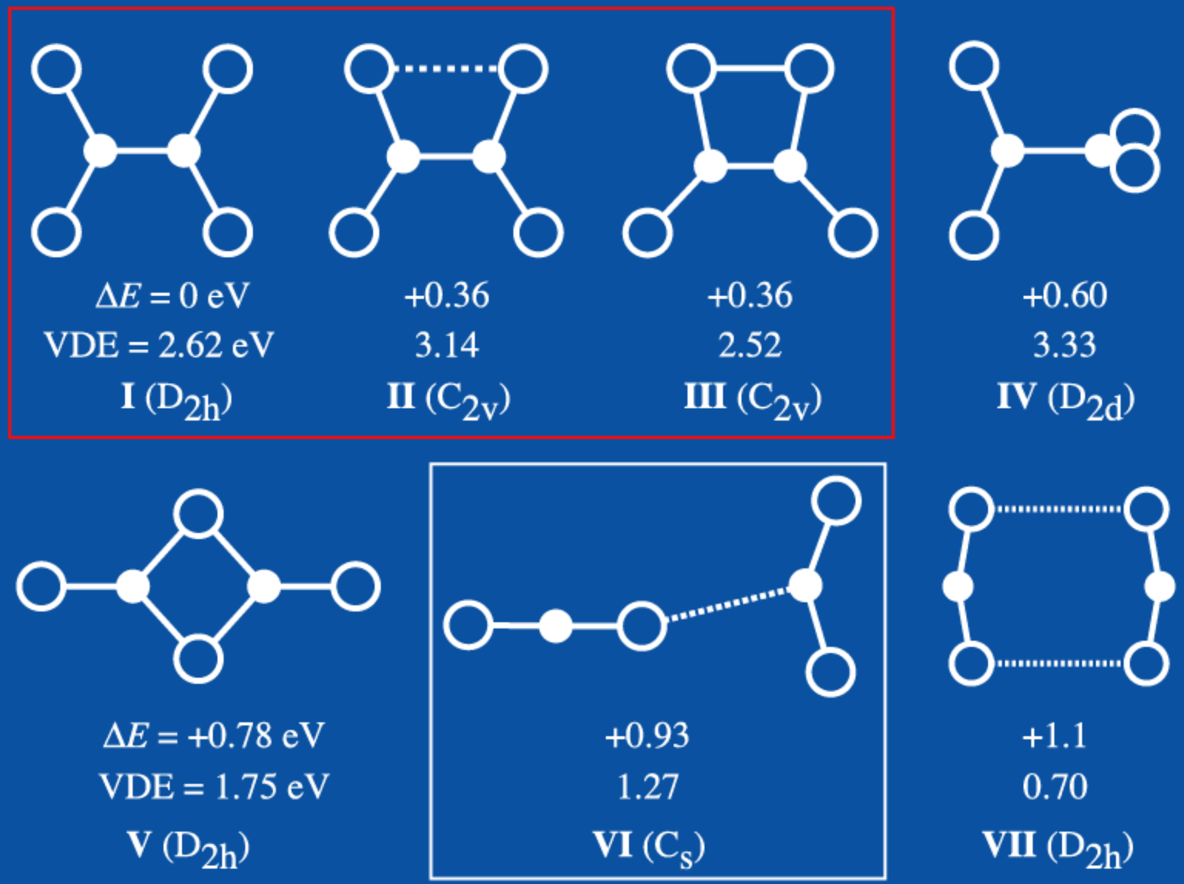
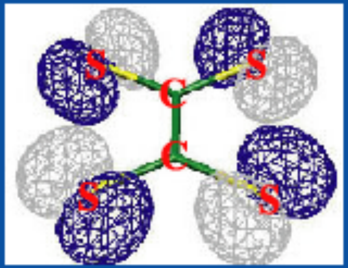


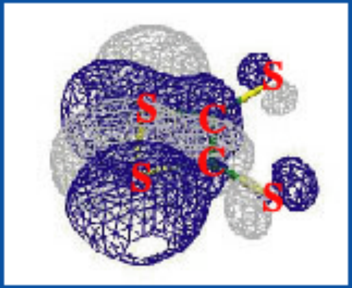
FIG. 10. Stable structures, difference in total energy (ΔE), and vertical detachment energy (VDE) determined by ab initio MO calculations at MP2/aug-cc-pVDZ level.

Singly-Occupied MO

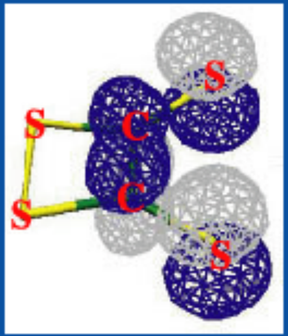
- SOMOs of **I** and **II** are located in-plane of the isomers, whereas that of **III** is out-of-plane.
- Since the photofragment $SCCS^-$ anion originates from $C_2S_4^-$, examination of correlation between MOs of $C_2S_4^-$ and $SCCS^-$ will provide information on the probable isomer of $C_2S_4^-$.



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.

Correlation of MOs

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

(Isomer II correlates with the electronically excited SCCS$^-$ ($A^2\Pi_g$).)

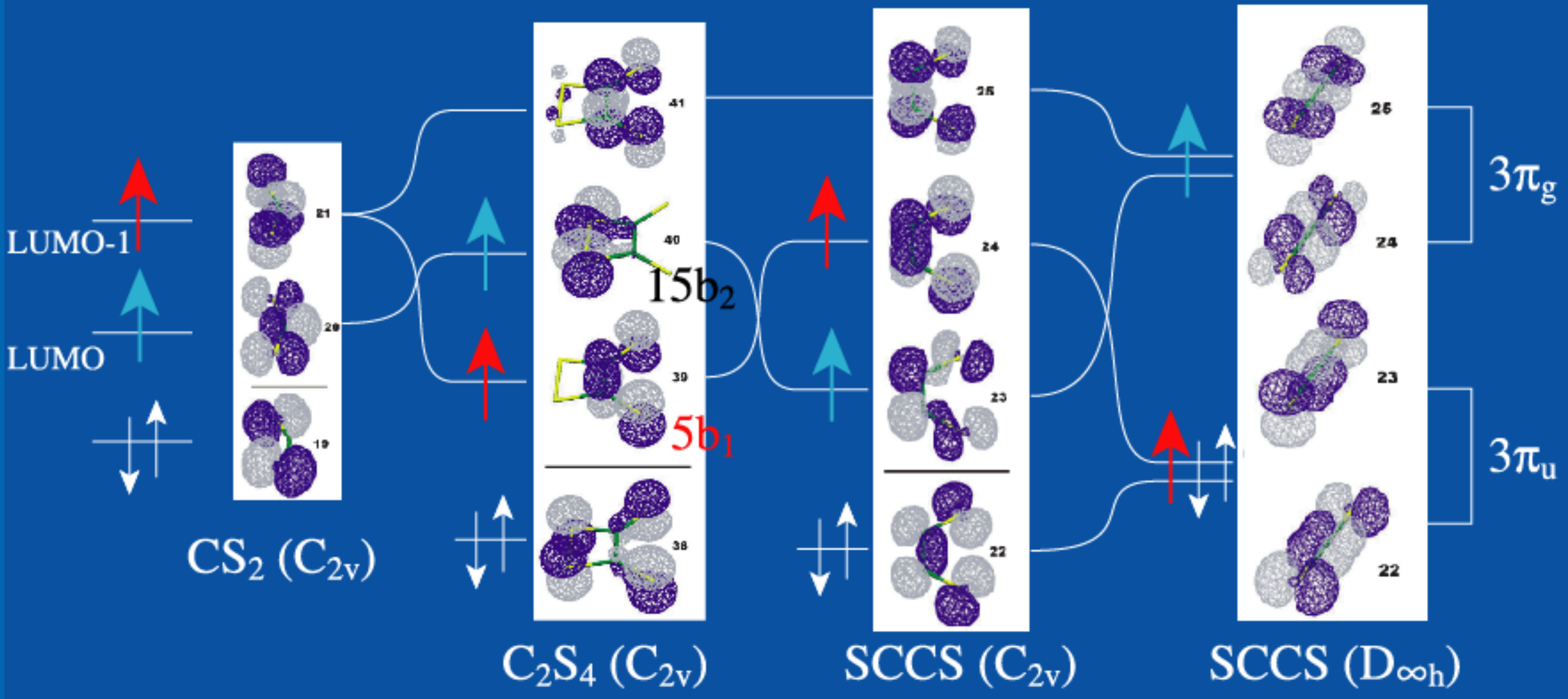
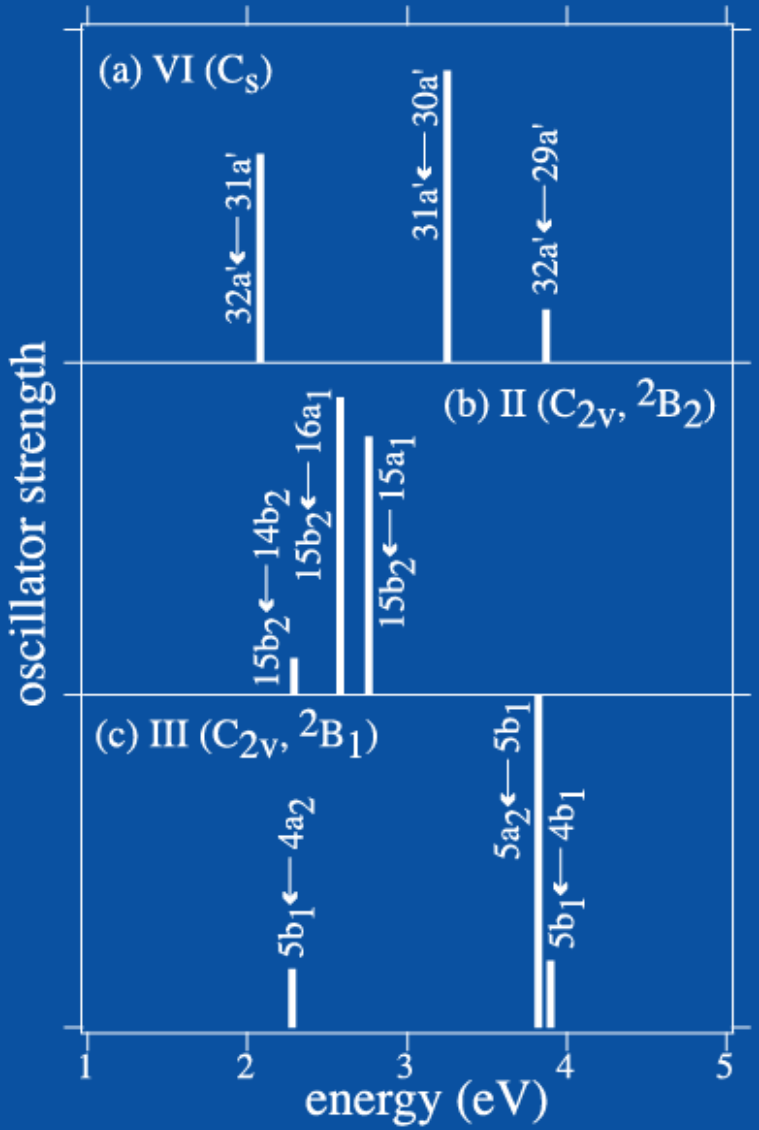


FIG. 12. MO Correlation diagram of C_2S_4 (C_{2v}), SCCS (C_{2v}, $D_{\infty h}$), and CS_2 (C_{2v}).

Oscillator Strength Calculations



- 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.

Potentials of Isomer III and Fragments

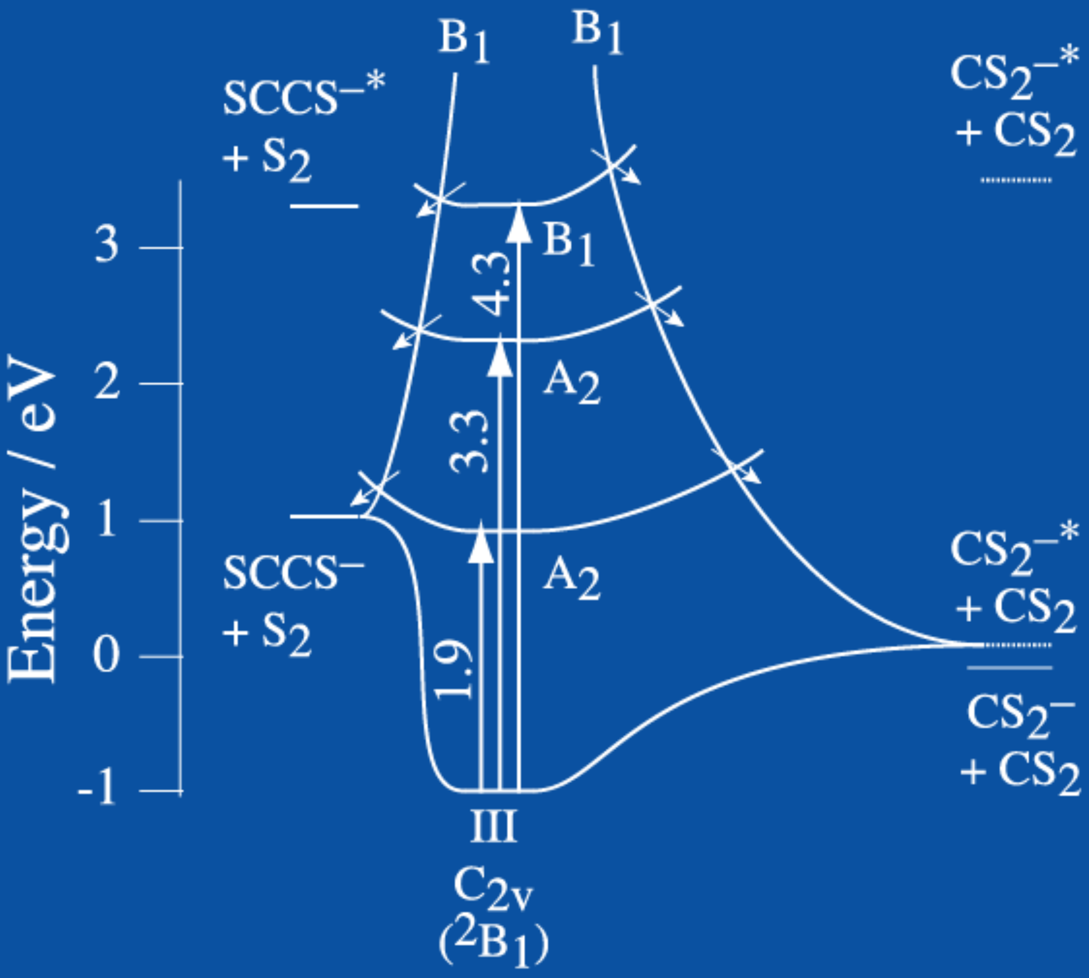
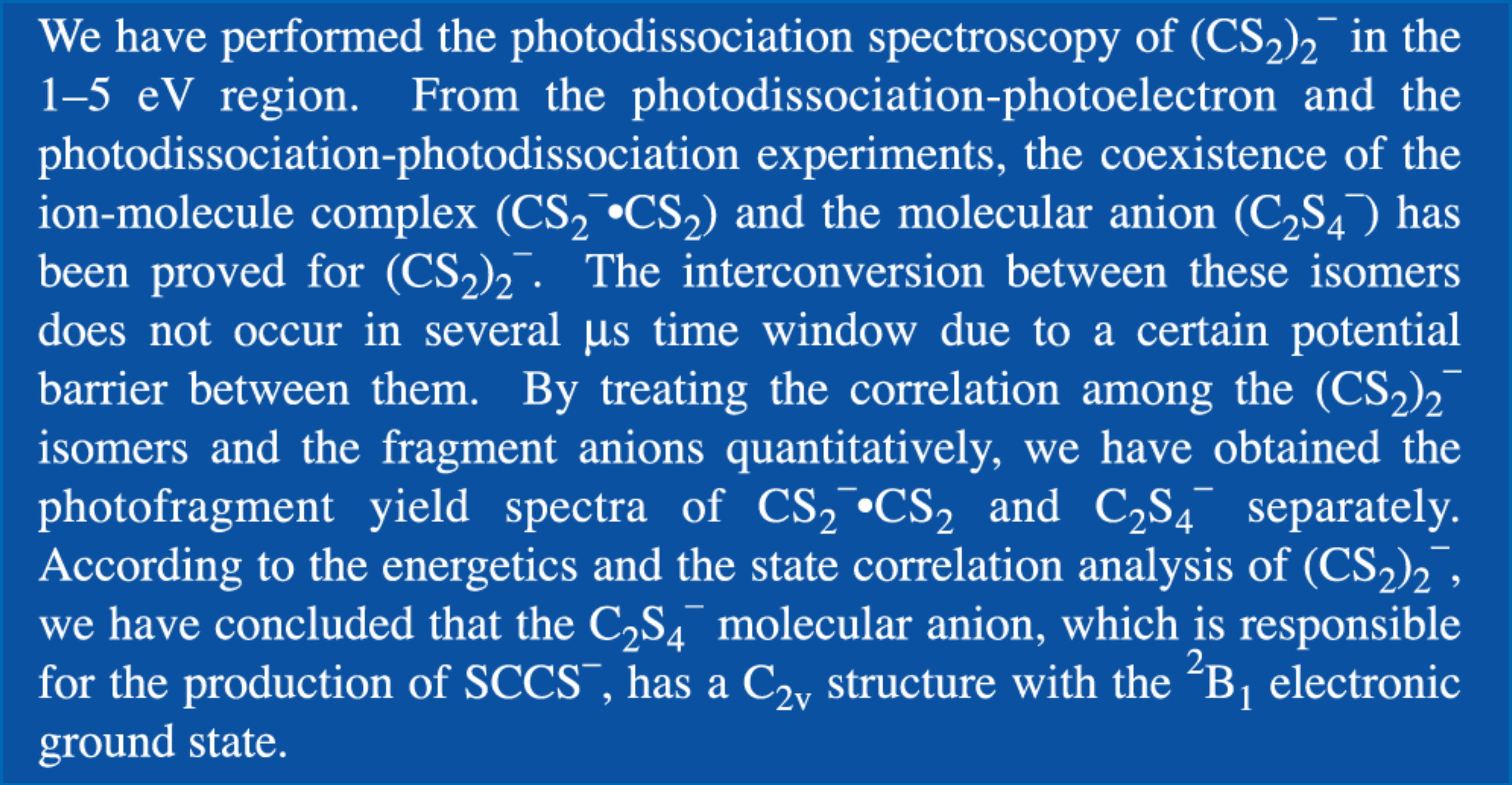


FIG. 14. State correlation diagram of Isomer **III**.

- 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 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-1 of CS_2, as seen on the left side of FIG. 12.

Conclusion (3)



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 ($CS_2^- \bullet CS_2$) 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 $(CS_2)_2^-$ 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.

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