

Isomer-Specific Photodissociation of $(\text{CS}_2)_2^-$

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Photodissociation cross sections of $(\text{CS}_2)_2^-$ are measured in the photon energy of 1–5 eV. The $(\text{CS}_2)_2^-$ anion provides five photofragments, S^- , S_2^- , CS_2^- , C_2S_2^- , and CS_3^- . Investigation of correlation between the $(\text{CS}_2)_2^-$ isomers and the photoproducts confirms **the coexistence of the ion-molecule complex ($\text{CS}_2 \cdot \text{CS}_2$) and the molecular anion (C_2S_4^-)** for $(\text{CS}_2)_2^-$. We apply ab initio MO calculations (MP2/aug-cc-pVDZ) to $(\text{CS}_2)_2^-$, and obtain seven stable isomers. Taking the energetics and the state correlation involved in the photodissociation of $(\text{CS}_2)_2^-$ into account, we conclude that **the C_2S_4^- anion has a C_{2v} structure with the $^2\text{B}_1$ 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. benzene dimer cation, $(\text{C}_6\text{H}_6)_2^+$)

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, $(\text{CS}_2)_2^-$** , is one of rare anion species in which the negative charge is delocalized intermolecularly. However, the electronic/geometric structures and photochemical process of $(\text{CS}_2)_2^-$ are still controversial issues even though a lot of researches have been done for this dimer anion.

$(\text{CS}_2)_2^-$: Previous Study

◆ Tsukuda et al. (1997).

- Photoelectron spectra of $(\text{CS}_2)_n^-$ 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 $(\text{CS}_2)_2^-$.

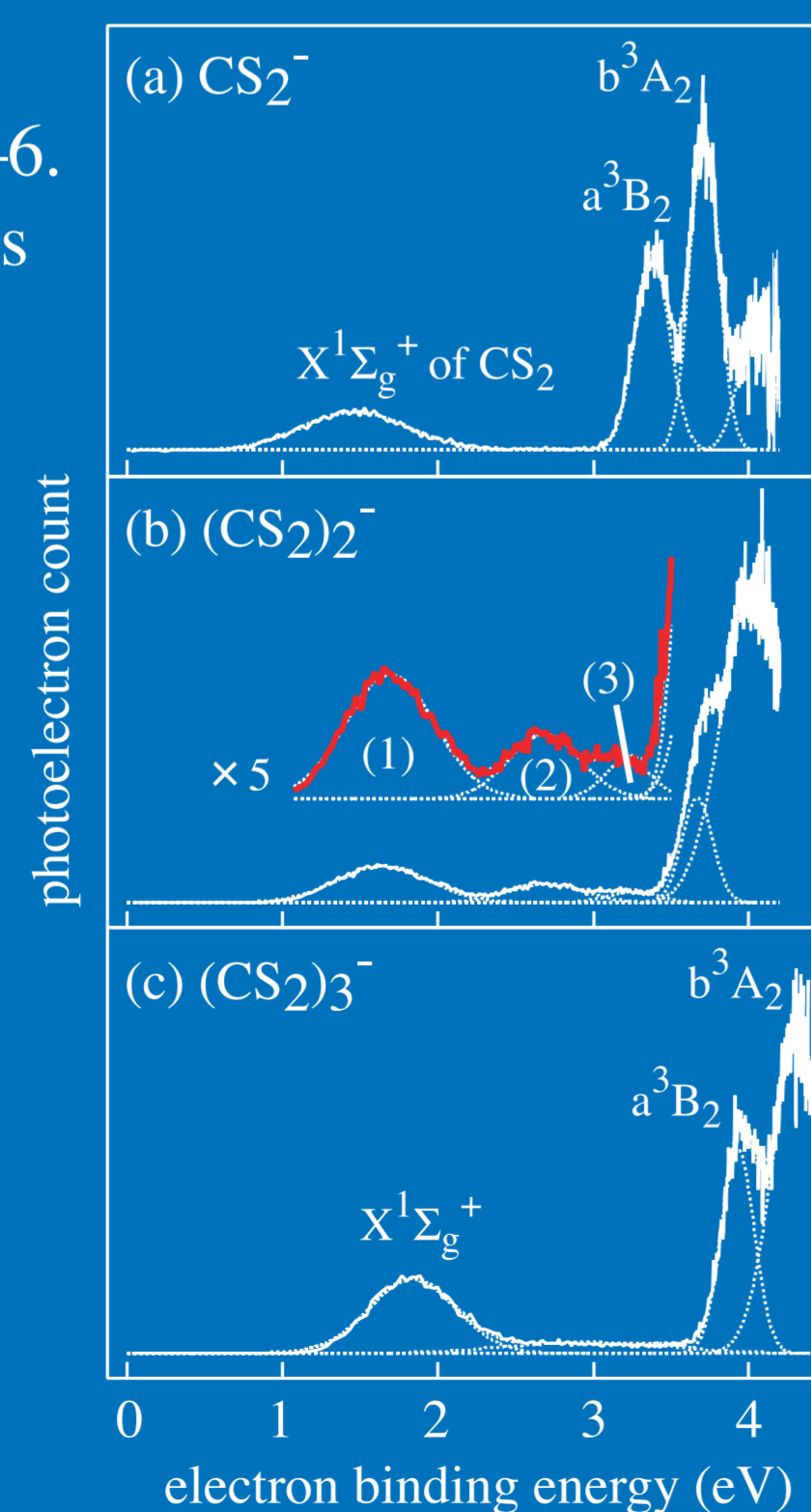
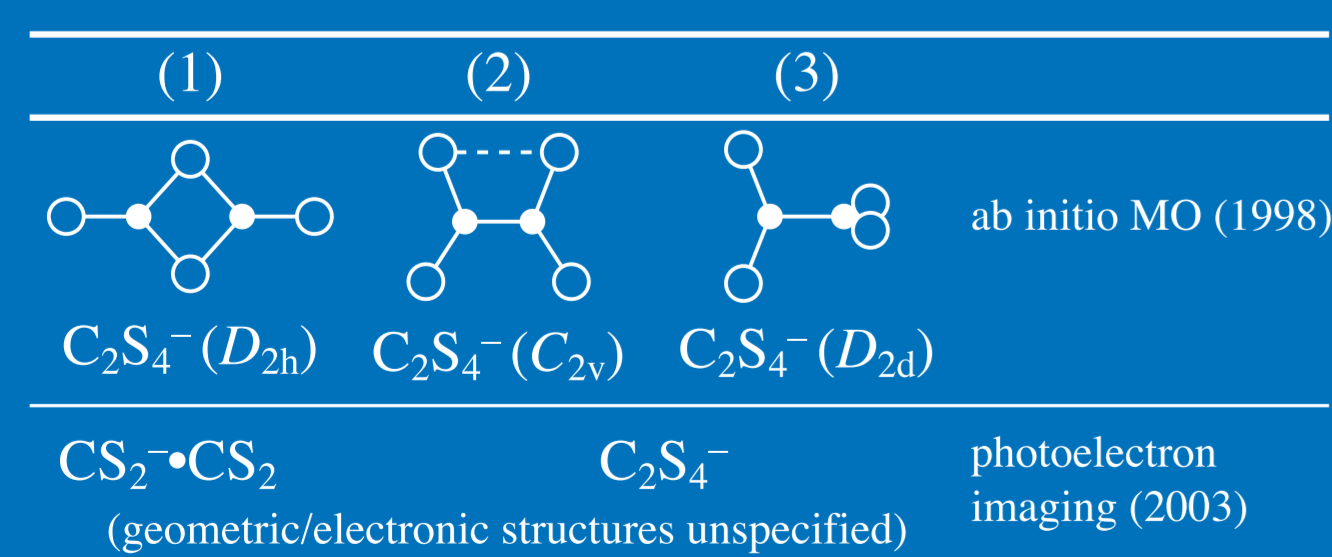


FIG. 1. Photoelectron spectra of $(\text{CS}_2)_n^-$ with $n = 1-3$.

◆ Maeyama et al. (1998).

- Photodissociation spectroscopy ($h\nu = 1-2.8$ eV).
- They ascribed all the photodissociation processes of $(\text{CS}_2)_2^-$ to C_2S_4^- .

Aim of This Study

- To examine whether the ion-molecule complex ($\text{CS}_2 \cdot \text{CS}_2$) and the molecular anion (C_2S_4^-) really coexist for $(\text{CS}_2)_2^-$.
- 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 $(\text{CS}_2)_2^-$: equivalent to absorption spectra
- Double-laser experiments for investigating correlation between the $(\text{CS}_2)_2^-$ isomers, the absorption/photoelectron bands, and photofragment species
- Ab initio MO calculations stable structures, correlation of MOs of the $(\text{CS}_2)_2^-$ isomers and photofragment species

Experiment

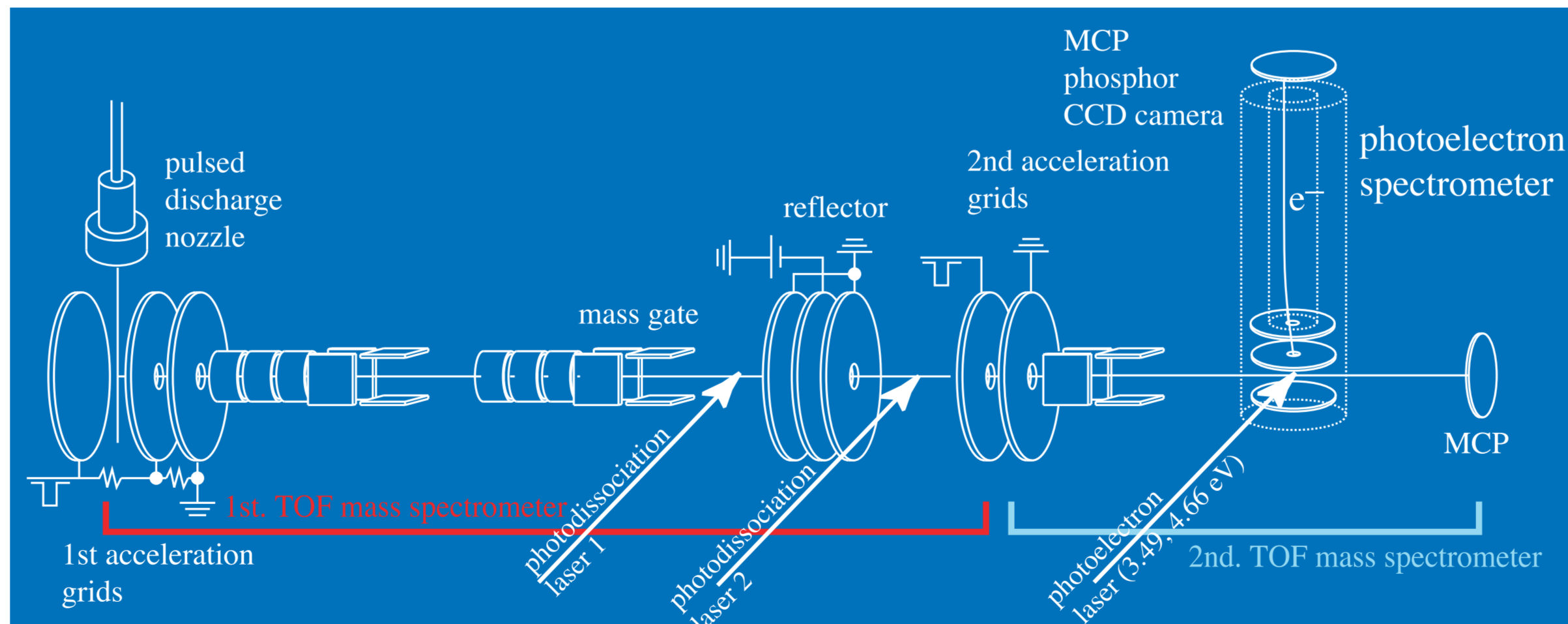


FIG. 2. Tandem time-of-flight (TOF) mass spectrometer used in this study.

- Photodissociation spectroscopy $(\text{CS}_2)_2^-$ 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 $(\text{CS}_2)_2^-$ is photodissociated by the photodissociation laser 1, and probed by the photodissociation laser 2 or the photoelectron laser.

Photofragment species of $(\text{CS}_2)_2^-$

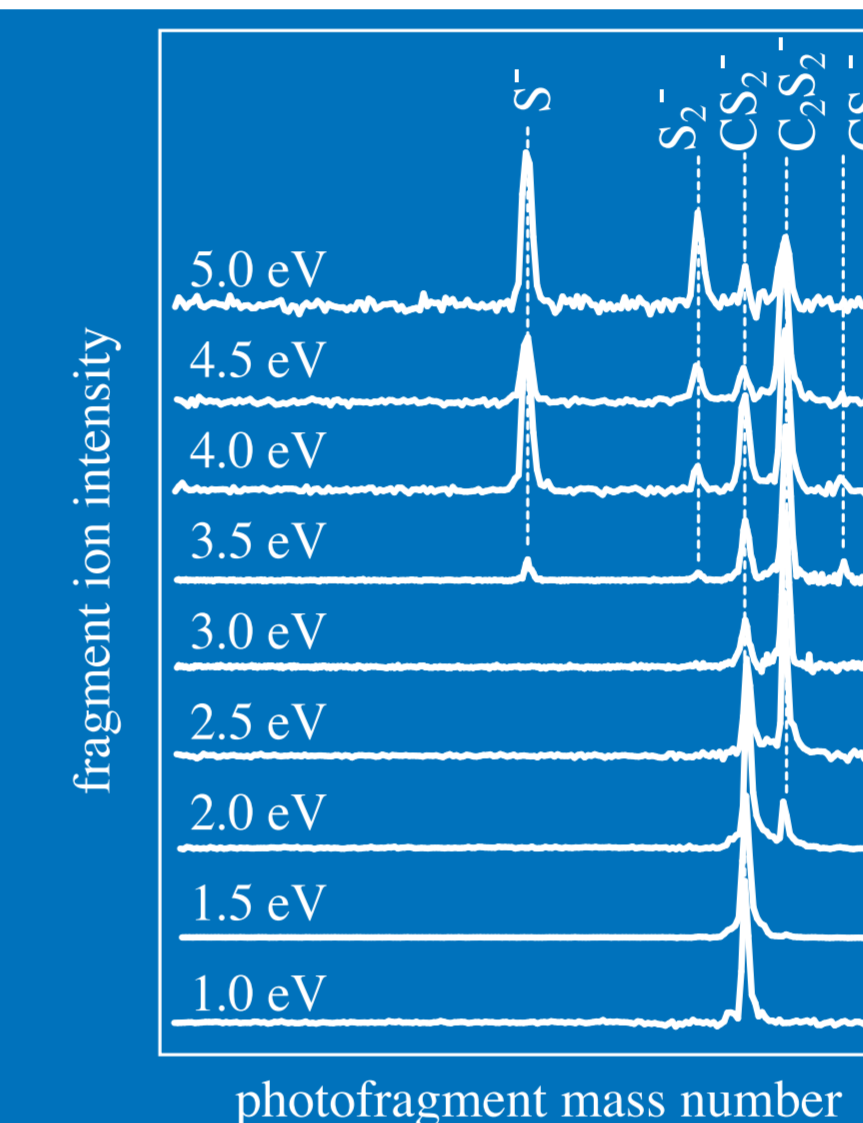


FIG. 3. Photofragment mass spectra of $(\text{CS}_2)_2^-$.

• 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 $(\text{CS}_2)_2^-$ are obtained for each of photofragments by plotting the photodissociation cross section as a function of the photon energy.

Photofragment yield spectra of $(\text{CS}_2)_2^-$

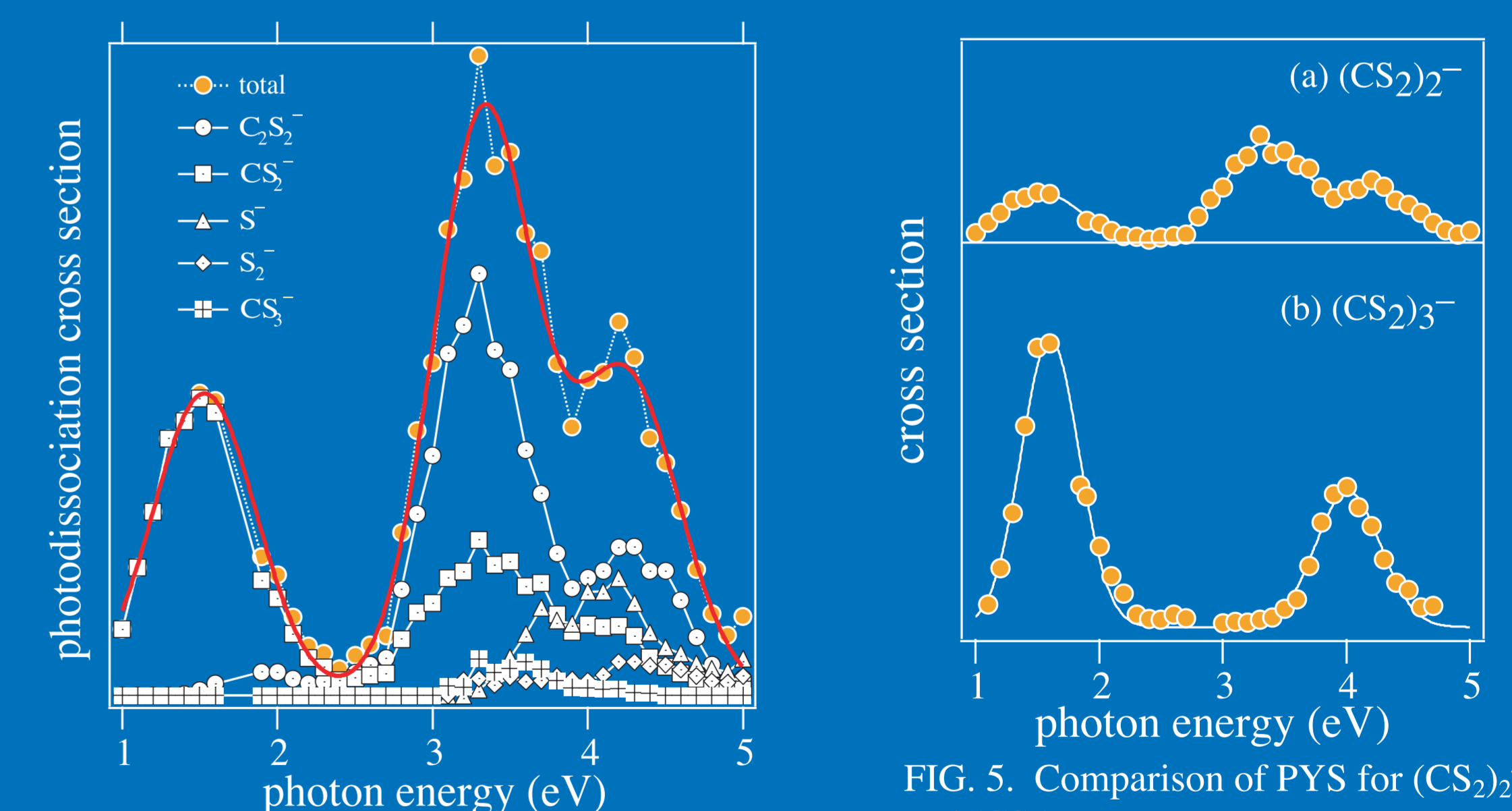


FIG. 4. Photofragment yield spectra (PYS) of $(\text{CS}_2)_2^-$.

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

(Photoelectron spectra in FIG. 1 shows that $\text{CS}_2)_3^-$ has only the ion-molecule form, $\text{CS}_2 \cdot (\text{CS}_2)_2$.)

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

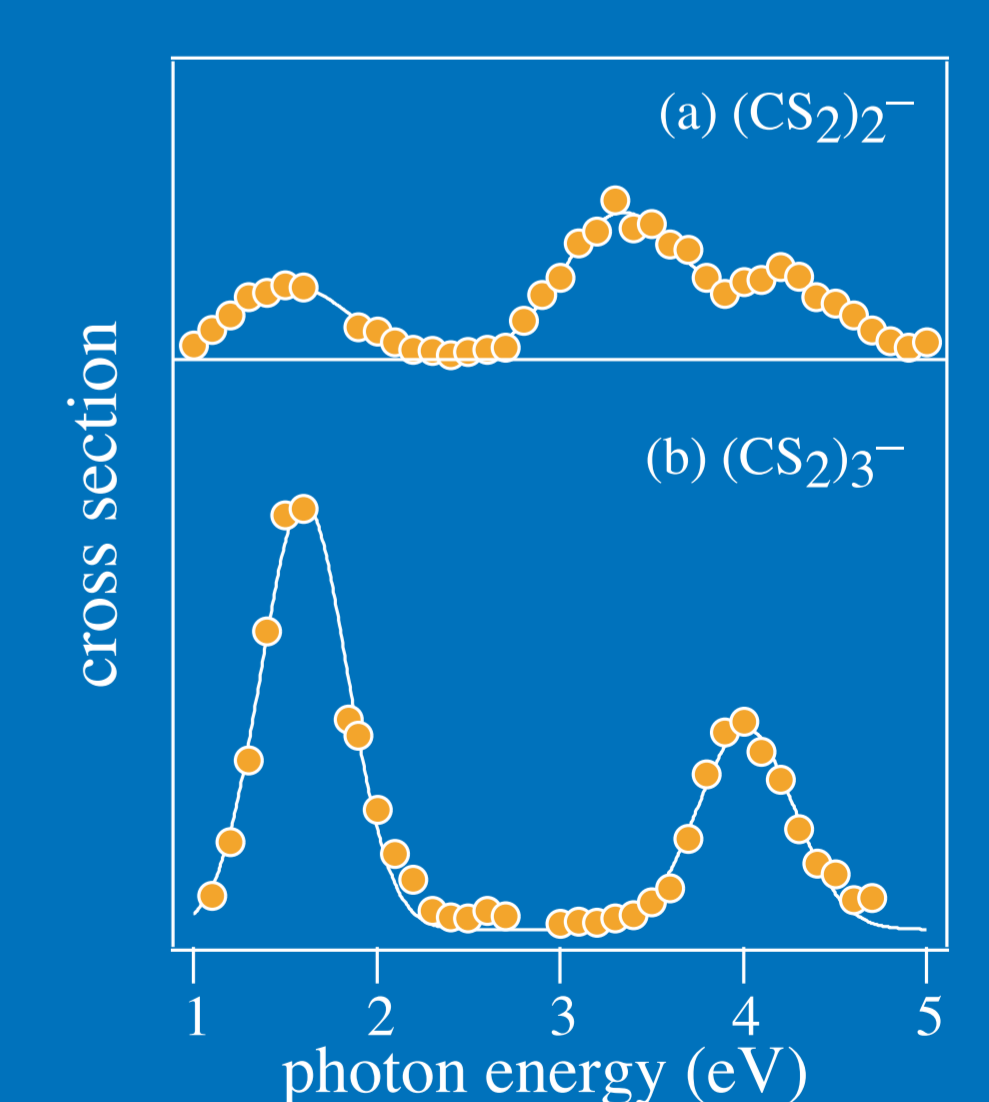


FIG. 5. Comparison of PYS for $(\text{CS}_2)_2^-$ and $(\text{CS}_2)_3^-$.

