

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

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The structure and photodynamics of carbon disulfide dimer anion,  $(\text{CS}_2)_2^-$ , have been the subject of extensive investigations both theoretically and experimentally [1, 2]; however, discussion is still controversial regarding the isomeric forms responsible for the photodetachment and photodissociation processes. The main issues are as follows: (1) the electronic structure of  $\text{C}_2\text{S}_4^-$  molecular anion existing in the beam of  $(\text{CS}_2)_2^-$ ; (2) the relevant photodissociation process of  $\text{C}_2\text{S}_4^-$ . To shed light on these issues, we have investigated photodissociation processes of  $(\text{CS}_2)_2^-$  by photofragment mass spectrometry combined with photoelectron spectroscopy. We have first measured photofragment yield (PFY) spectrum of  $(\text{CS}_2)_2^-$  and determined product branching in a wide spectral range from 1240 to 248 nm (1.0–5.0 eV). The PFY spectrum displays three prominent peaks at 1.53, 3.33, and 4.25 eV, presenting a sharp contrast to the observation that the PFY spectrum for  $\text{CS}_2^-\cdot(\text{CS}_2)(\text{H}_2\text{O})$  species consists of only two peaks at 1.72 and 4.46 eV. On the basis of this finding, we ascribe the 1.53 and 4.25 eV bands to the monomer ion core structure,  $\text{CS}_2^-\cdot(\text{CS}_2)$ , and the 3.33 eV band to the molecular anion,  $\text{C}_2\text{S}_4^-$ . It is also revealed that the major product anion is  $\text{CS}_2^-$  in the 1.53 eV band region whereas  $\text{C}_2\text{S}_2^-$  is the dominant photoproduct in the 3.33 eV band region. By applying photoelectron spectroscopy to the photoproducts from  $(\text{CS}_2)_2^-$ , the fragment  $\text{C}_2\text{S}_2^-$  ion is further identified as a linear  $\text{SCCS}^-$  formed in its electronic ground state ( $^2\Pi_u$ ). Although our MP2/6-31+G\* calculations provides six possible isomeric forms for  $\text{C}_2\text{S}_4^-$  as previously reported by other groups [2], the orbital correlation diagram tells us that  $\text{SCCS}^-$  ( $^2\Pi_u$ ) is produced only from  $\text{C}_2\text{S}_4^-$  having  $^2\text{B}_1$  electronic structure. The answers to the issues are that (1) the isomeric form existing in the  $(\text{CS}_2)_2^-$  beam is  $\text{C}_2\text{S}_4^-$  ( $^2\text{B}_1$ ) with  $\text{C}_{2v}$  symmetry, and that (2) the photodissociation proceeds as  $\text{C}_2\text{S}_4^-$  ( $^2\text{B}_1$ ) +  $h\nu \rightarrow \text{SCCS}^-$  ( $^2\Pi_u$ ) +  $\text{S}_2(\text{X})$ .

[1] Tsukuda et al., Chem. Phys. Lett. 279 (1997) 179; Mabbs et al., Chem. Phys. Lett. 381 (2003) 479.

[2] Sanov et al., J. Phys. Chem. A 102 (1998) 2509, and references therein.