Photodissociation of (CS$_2$)$_2^-$: CS$_2$•CS$_2$ process vs. C$_2$S$_4^-$ process

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The structure and photodynamics of (CS$_2$)$_2^-$ isomers, CS$_2$•CS$_2$ and C$_2$S$_4^-$, have been the subject of extensive investigations both theoretically and experimentally; however, discussion is still controversial regarding the isomeric forms responsible for the observed photodetachment and photodissociation processes. We have studied photodissociation process of (CS$_2$)$_2^-$ by photofragment mass spectrometry combined with a photodepletion method. The photofragment yield (PFY) spectrum of (CS$_2$)$_2^-$ displays three prominent bands at 1.53, 3.33, and 4.25 eV. The photodepletion-photodissociation measurements, where one of the (CS$_2$)$_2^-$ isomers is selectively photodepleted prior to photodissociation, have revealed that (1) the 1.53 eV band arises from CS$_2$•CS$_2$, and that (2) both C$_2$S$_4^-$ and CS$_2$•CS$_2$ contribute to the 3.33 and 4.25 eV bands. It is also revealed that CS$_2^-$ and S$^-$ fragments are formed primarily from CS$_2$•CS$_2$ in the energy range of 1.0–5.0 eV whereas C$_2$S$_2^-$ is produced only from C$_2$S$_4^-$ in the region $>$ 2.5 eV. The fragment C$_2$S$_2^-$ is further identified by photoelectron spectroscopy as a linear SCCS$^-$ formed in its electronic ground state ($^2\Pi_u$). With the aid of the orbital correlation diagram based on MP2/6-31+G* calculations, we conclude that (i) the isomeric forms existing in our (CS$_2$)$_2^-$ beam are CS$_2$•CS$_2$ ($^2\Pi$, $^1\Sigma_g^+$) and C$_2$S$_4^-$ ($^2\Pi_1$, $^3\Sigma_g^+$), and that (ii) the (CS$_2$)$_2^-$ photodissociation proceeds primarily as CS$_2$•CS$_2$($^2\Pi$) + hν $\rightarrow$ CS$_2$(X$^2\Sigma_g^+$) + CS$_2$(X$^1\Sigma_g^+$) or C$_2$S$_4$(X$^3\Pi_1$) + hν $\rightarrow$ SCCS$^-$($^2\Pi_u$) + S$_2$(X).

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