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

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The structure and photodynamics of $(CS_2)_2^-$ isomers, CS_2^-•CS_2 and $C_2S_4^-$, 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 $C_2S_4^-$ 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 $C_2S_2^-$ is produced only from $C_2S_4^-$ in the region > 2.5 eV. The fragment $C_2S_2^-$ 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}A', C_s) and $C_2S_4^-$ ($^2B_1$, C_{2v}), and that (ii) the $(CS_2)_2^-$ photodissociation proceeds primarily as CS_2^-•$CS_2(^2A') + h\nu \rightarrow CS_2^-(X^2A_1) + CS_2(X^1\Sigma_g^+)$ or $C_2S_4^-(^2B_1) + h\nu \rightarrow SCCS^-(^2\Pi_u) + S_2(X)$.

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