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Two-photon photoemission spectroscopy of CCl_4 on Ag(111): probing hot electron-driven chemistry

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Dissociation of chlorofluorocarbons (CFCs) by low energy electrons on polar stratospheric cloud (PSC) particles has been recently proposed as a key step to stratospheric ozone depletion. By two-photon photoemission (2PPE) spectroscopy, we investigated photochemistry of CCl_4 on Ag(111) to model the electron-driven reaction of CFCs on PSC. We identified a modified image potential state with an effective mass of 1.6 m_e at 3.42 eV above the Fermi level. From polarization dependence of the 2PPE signal, detailed excitation mechanisms were revealed. The lifetime of the image potential state was much shorter on the CCl_4-covered Ag(111) surface than on the clean one, implying that the electron in the image potential state is scavenged effectively by CCl_4, probably through dissociative attachment to it. Effective photodissociation cross sections were determined over 1.62 ~ 5.69 eV and compared to a simple hot electron transfer model. Also, various thermal reaction products were identified and a thermal dissociation model was proposed.