Ultrafast photoelectron spectroscopy of photoisomerization reaction of ethylene

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Ethylene (ethene: C_2H_4) is one of the most fundamental organic molecules, and its ultrafast internal conversion (IC) from the $^1\pi\pi^*$ state is the paradigm for *cis-trans* photoisomerization of olefines; however, the isomerization dynamics of isolated ethylene have not been observed entirely from the Franck-Condon region in the $^1\pi\pi^*$ state to ground-state (GS) products via conical intersections and the interpretation of the reaction remains elusive. In the present study, we performed real-time observations of the ultrafast photoreaction from the $^1\pi\pi^*$ state up to the creation of the GS products using time-resolved photoelectron spectroscopy with 160 nm pump and 57 nm (21.7 eV) probe pulses with a temporal resolution of 31 fs.

The experimental result shows the rapid spectral energy shift due to a large structural deformation in the excited state. (Figure1) The nuclear wave packet created by a 160-nm pump pulse accesses the C=C twisted geometry within 10 fs, and the population transfer from the excited to the ground state occurs in 20 – 30 fs. The photoelectron signal of vibrationally highly excited GS molecules appears in in less than 45 fs, and they decayed with two time constants of 0.87 and > 5 ps. The photoelectron spectra of GS products measured at 2 and 7 ps exhibits a hump at 9 eV, which we assigned to the signal of a vinyl radical (C_2H_3).

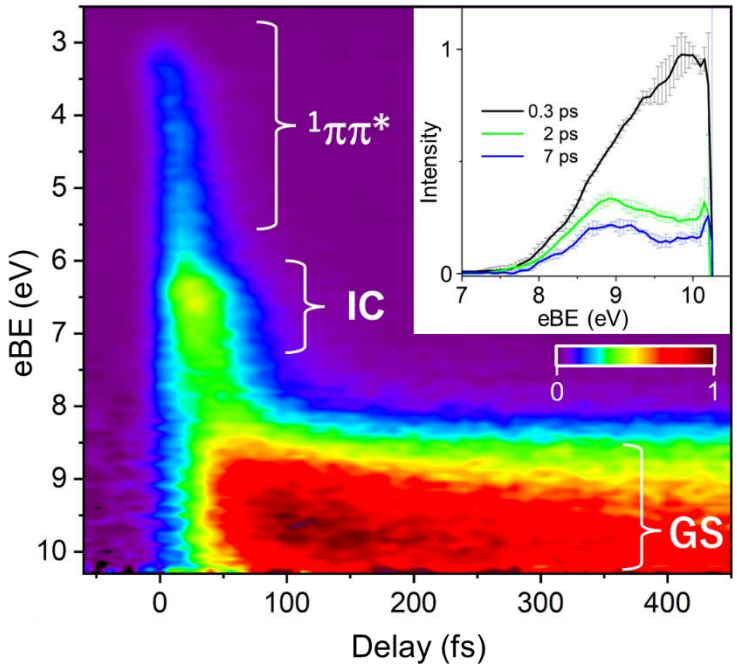

Figure 1. Two-dimensional map of photoelectron spectra measured for jet-cooled ethylene using 160 nm pump and 21.7 eV probe pulses. The inset shows photoelectron spectra measured at 0.3, 2 and 7 ps. The electron binding energy (eBE) is given by the difference between the probe photon energy (21.7 eV) and the observed electron kinetic energy.