Ultrafast photoelectron spectroscopy of photoisomerization reaction of ethylene

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Ethylene (ethene: C\textsubscript{2}H\textsubscript{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. (Figure 1) 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\textsubscript{2}H\textsubscript{3}).

\begin{figure}[ht]
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\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{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.}
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