

Understanding the dynamics of photochemical reaction is of great importance in many areas such as chemistry, physics, and biology. Ultrafast photoelectron spectroscopy enables direct traces of electron binding energies of the chemical species and electronic states, which provides deeper insights into nonadiabatic dynamics in the photoreaction. However, it is difficult to experimentally observe and interpret the whole dynamics because both high photon energy and temporal resolution are required to detect all chemical species and electronic states involved in the ultrafast photoreaction. To this end, we have developed home-made light sources and performed time-resolved photoelectron spectroscopy (TRPES) in liquid and gas phase with a high temporal resolution of <50 fs.

◆ Internal conversion and solvation dynamics of the hydrated electron

The hydrated electron (e^-_{aq}), an electron trapped in the band gap of liquid water, is the most fundamental chemical species in radiation chemistry and biology; however, the nonadiabatic dynamics even in the first electronic excited states is elusive and remain under intense debate despite of its simplicity. The difficulty of interpretation is due to the indistinguishability between nucleic solvation dynamics and electronic internal conversion. **Our experimental results of time- and angle-resolved photoemission spectroscopy revealed that the photoemission from the first electronic excited state of e^-_{aq} is anisotropic while from the ground state is isotropic, which enabled the unambiguous identification.** [1] We concluded the nonadiabatic transition to the ground state occurs in 50-60 fs, and also confirmed spectral energy shifts owing to solvent response. This reaction time of the nonadiabatic transition is faster than the values expected by previous computational simulations, suggesting that the calculation of the ultrafast nonadiabatic process needs to be reexamined. Furthermore, measurements with different solvents revealed that the ultrafast librational response of a solvation shell to electronic excitation affects the efficiency of internal conversion. [2]

◆ Ultrafast ring-opening reaction of 1,3-cyclohexadiene

The photoisomerization reaction from 1,3-cyclohexadiene (CHD) to 1,3,5-hexatriene (HT) is a well-known example of electrocyclic ring-opening reaction following the Woodward-Hoffmann rule. It is noted that the photoexcited $S_1(\pi,\pi^*)$ state of CHD is not electronically correlated with the ground state of HT and the reaction must proceed via nonadiabatic transitions; however the reaction pathway has yet to be unambiguously identified in the previous experiments. Therefore, we employed TRPES using extreme UV (EUV) probe pulses of 21.7 eV generated by high-order harmonic generation (HHG) method and investigated nonadiabatic photoreaction from the Franck – Condon (FC) region in the excited state until the final states of the reaction products. [3,4] **We have clearly observed the nonadiabatic reaction pathway via the doubly excited state of CHD using ultrafast EUV photoelectron spectroscopy.** [4] The results indicate that the reaction occurs in ca. 70 fs and creates product vibrational coherence. Extensive computational simulations using the extended multistate complete active space second-order perturbation theory (XMS-CASPT2) method support the interpretation of experimental results and provide further insights into the electronic dynamics.

These studies provided unambiguously detailed pictures of nonadiabatic dynamics, but now I am developing sub-10 fs UV and EUV light sources to perform TRPES with even higher temporal resolution.

References

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