Title of Project： Ultrafast non-adiabatic dynamics in chemical reactions

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【Purpose and Background of the Research】

Chemists have unravelled atomistic details of invisible chemical reaction mechanisms using imagination and logical thinking based on carefully designed control experiments. It is a longstanding dream of chemists and students to watch chemical reactions directly and understand their mechanisms. A chemical reaction is often regarded as a barrier-crossing process that proceeds via the transition state at the saddle-point of a potential energy surface (PES). This picture, however, is valid only for a reaction taking place on a single PES. Most chemical reactions, particularly photochemical reactions, proceed through a rapid change of electronic state due to non-adiabatic transitions (NATs) between PESs. NAT is the principal source for the diversity and efficiency of chemical reactions and is central in the studies of chemical reaction dynamics. Ultrafast photoelectron spectroscopy enables us to follow evolution of the electronic state of the reactant in the course of a chemical reaction.

Aqueous chemistry is one of the most challenging research areas in chemical reaction dynamics, owing to the high complexity caused by the ultrafast response, hydrogen bonding, and active participation of water molecules in electron and proton transfer. We will investigate chemical reaction dynamics in aqueous solutions with ultrafast extreme ultraviolet (XUV) photoelectron spectroscopy of liquids with a time resolution of 10 fs. Ultrashort XUV pulses with photon energies higher than 20 eV enable photoionization of any chemical species from any electronic state and achieve the complete observation of the electronic dynamics along the entire reaction pathway.

【Research Methods】

We will observe the real-time evolution of the electronic state and nuclear wave packet motions of excited molecules in the gas and solution phases using ultrafast XUV photoelectron spectroscopy with a time resolution of 10 fs. A microfluidic device is employed to introduce volatile liquids into a photoelectron spectrometer under a high vacuum, and the electron kinetic energy distributions are measured using a magnetic bottle time-of-flight method. As for solution samples, we also carry out ultrafast infrared absorption spectroscopy to obtain complementary information on the molecular structures and intermolecular vibrational relaxation associated with chemical reactions. Various reactions such as the ring-opening, cis-trans photoisomerization, redox, electron transfer etc. are studied. Furthermore, dynamics of non-classical chemical species such as solvated electrons are studied in detail. We collaborate with theoretical/computational research groups to compare our experimental results with advanced quantum chemical calculations and molecular dynamics simulations to extract a detailed picture of the reaction mechanisms.

【Expected Research Achievements and Scientific Significance】

Most of the energy on earth is obtained from sun light. The conversion of solar energy into electrical or chemical energy without dissipating it as heat is of great importance both in nature and in generation of renewable energy for our sustainable society. For such conversion, fast and efficient photochemical reactions are necessary. Photochemical reactions start from an excited electronic state reached by optical absorption and pass through an energy region where various electronic states exist in proximity. Therefore, almost without exception, they involve non-adiabatic transitions between electronic states. It is very important to understand how solvents influence these chemical reactions at the levels of electronic and nuclear motions. Such understanding is not only important as basic science, but also for practical purposes, such as solar energy conversion using charge separation and redox reactions, and material creation by photocatalysis. In this special project, we aim to promote research that will not only enable us to construct a scientific theory of chemical reactions, but also provide far-reaching implications for a wide range of problems.

【Publications Relevant to the Project】

· Toshinori Suzuki, “Spiers Memorial Lecture: Introduction to Ultrafast Spectroscopy and Imaging of Photochemical Reactions”, Faraday Discussions of The Royal Society, **228**, 11 – 38 (2021).
· Shutaro Karashima, Alexander Humeniuk, …, Roland Mitric, and Toshinori Suzuki, “Ultrafast Ring-Opening Reaction of 1,3-Cyclohexadiene: Identification of Non-Adiabatic Pathway via Doubly Excited State”, The Journal of American Chemical Society, **143**, 8034 – 8045 (2021).
· Junichi Nishitani, Yo-ichi Yamamoto, …, and Toshinori Suzuki, “Binding Energy of Solvated Electrons and Retrieval of True UV Photoelectron Spectra of Liquids”, Science Advances, **5**, eaaq6896 (2019).

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