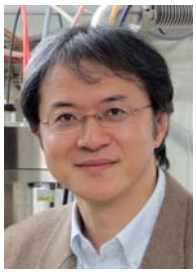
【Grant-in-Aid for Scientific Research (S)】

Science and Engineering (Chemistry)



Title of Project : Ultrafast Photoelectron Spectroscopy of Solution Chemistry

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Research Project Number : 15H05753 Researcher Number : 10192618
Research Area : Fundamental Chemistry
Keyword : Solution Chemistry, Non-Adiabatic Transition, Photoelectron Spectroscopy

【Purpose and Background of the Research】

Development of molecular quantum mechanics and statistical mechanics over the last century have provided us with deeper understanding of the structures, reactions and properties of materials. However, liquids have tremendous complexities due to their disorders and thermal fluctuations, which make them remain the frontier in chemistry. Water is the liquid of the greatest importance in nature and, at the same time, of the greatest complexity due to a strong hydrogen-bonding network. A solute hydrated in liquid water experiences strong electrostatic interactions with water molecules, which alter the photochemical reaction pathway. Moreover, liquid water acts not only as a solvent but also as a reactant for electron and proton transfer reactions.

The present research project aims at real-time observation of chemical dynamics in aqueous solution by introducinga novel experimental method of time-resolved photoemission spectroscopy (TRPES) of liquids. TRPES of liquid was realized in 2010 after our research on this subject over a decade. Since then, we have developed TRPES of liquids further and realized angle-resolved TRPES in 2014. In this project, we produce ultrashort pulses in the vacuum UV region to observe simultaneously a number of electronic states, including the triplet states and the ground electronic state, of a solute to elucidate the entire photo-induced dynamics including intersystem crossing, internal conversion, and associated isomerization reactions in solution.

【Research Methods】

A pressurized aqueous solution is discharged into a photoelectron spectrometer from a capillary nozzle 20 μm in inner diameter. The solution is photoexcited with a femtosecond UV/VIS pulse at 1mm downstream the nozzle to induce photochemical reaction of a solute. A time-delayed femtosecond vacuum UV pulse induces photoemission from a solute during the course of a chemical reaction. The photoelectron is sampled into a time-of-flight electron energy analyzer, and the electron energy distribution is mapped out as a function of the pump-probe time delay. By studying the reactions in H_2O and D_2O, the dynamical roles of librational and vibrational motions of water will be elucidated. We generate the vacuum UV radiation using filamentation four-wave mixing we developed in our laboratory. The fundamental output and the second harmonic of a Ti:sapphire laser are gently focused into a rare gas to induce non-degenerate four-wave mixing and produce UV and vacuum UV pulses with sub-20 fs pulse duration.

【Expected Research Achievements and Scientific Significance】

The entire photochemical reaction dynamics in aqueous solution, from the Franck-Condon state to products, are observed in real-time and the reaction mechanisms are elucidated. Fundamental understanding of reactions will be of significant value for elucidating energy conversion processes in solar cells and photocatalysis.

【Publications Relevant to the Project】

・ “Time- and angle-resolved photoemission spectroscopy of hydrated electrons near a liquid water surface”, Y. Yamamoto, Y. Suzuki, G. Tomasello, T. Horio, S. Karashima, R. Mitrić, and T. Suzuki, *Phys. Rev. Lett.*, **112**, 187603 (2014).
・ ”Direct measurement of vertical binding energy of hydrated electron", Ying Tang, Huan Shen, Kentaro Sekiguchi, Naoya Kurahashi, Yoshi-Ichi Suzuki, and Toshinori Suzuki, *Phys. Chem. Chem. Phys.*, **12**, 3653-3655 (2010)

【Term of Project】 FY2015-2019

【Budget Allocation】 146,500 Thousand Yen

【Homepage Address and Other Contact Information】

http:// kuchem.kyoto-u.ac.jp/bukka/