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Time-resolved photoelectron spectroscopy of liquid methanol

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Time-resolved photoelectron spectroscopy (TRPES) enables direct observation of electronic dynamics such as electron transfer reactions and non-adiabatic dynamics. Since photoelectron spectroscopy requires high vacuum conditions, TRPES has been used to study gaseous molecules or solids. However, we have extended TRPES to liquids in our laboratory in 2010. In this study, we performed TRPES using 134-nm vacuum ultraviolet pulse to generate solvated electrons in methanol, and observed their relaxation processes. Solvated electrons are very important in radiation chemistry and biology, and we previously studied solvated electrons in water.

We employed a high performance liquid chromatography (HPLC) pump to discharge 50 mM NaCl solution in methanol through a fused silica capillary (ϕ15 μm) into a vacuum chamber. The 134-nm pump pulse excited a liquid micro jet 1 mm downstream the capillary, and the 266-nm probe pulse induced photoemission from transient species. The photoelectrons emitted from the liquid surface were detected using a magnetic bottle time-of-flight (TOF) electron energy analyzer. The time-resolution of our experiment is about 100 fs. The experimental setup is summarized in Fig.1.

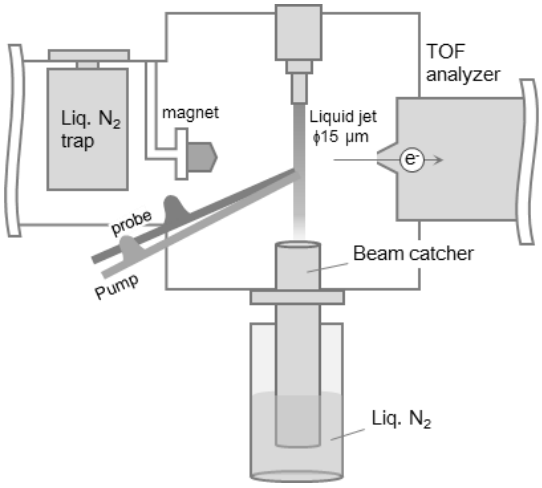

Fig.1 The experimental setup in vacuum chamber.

The observed electron kinetic energy (eKE) distribution is shown in Fig.2. The electron signal rapidly decays in about 100 fs and exhibits a plateau at later time. At long delay time, eKE becomes 0 - 3.5 eV. This eKE is in good agreement with the previously reported value of a solvated electron in methanol.

The generation process of a solvated electron, fitting analysis and other time constant will be discussed.

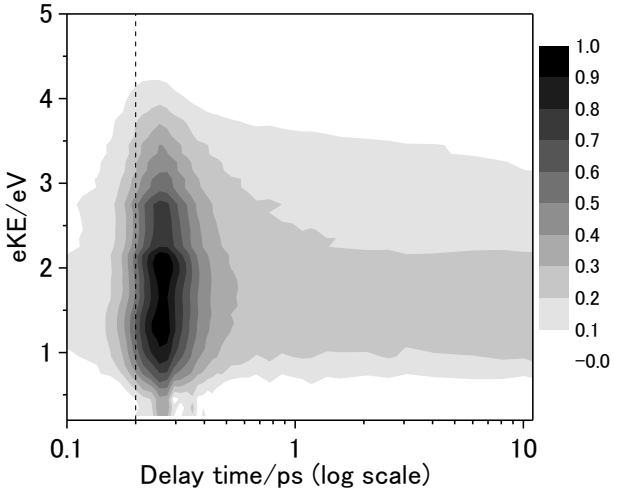

Fig.2 Time-resolved electron kinetic energy map of liquid methanol. The offset of 0.2 ps was added to true delay time to show a whole data.