Radiation induced reactions in liquids in the picosecond time range and in supercritical conditions

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At Nuclear Engineering Research Laboratory, the University of Tokyo, the construction of the ultrafast pulse radiolysis system based on the pump and probe method has been completed. Electron pulses with duration of a few picoseconds are generated from an 18 MeV S-band linear accelerator by using a combination of a laser photocathode rf-gun and a chicane-type magnetic compressor. The precision of synchronization between the pump and the probe has attained within 1.6 ps (rms). By converting the fundamental laser pulse into white light continuum, it allows to measure in the wavelength range from 400 to 1100 nm. With a sample cell having an optical path of 1 mm, a time resolution of 5 ps has been achieved.

The yield of the hydrated electron in the picosecond time range has been re-evaluated with above system, and a value of 4.1 ± 0.2 per 100 eV of absorbed energy at 20 ps was derived. This is consistent with recent experimental results and Monte Carlo calculations. Extended measurements of the solvated electrons in different alcohols are under study and solvation processes would be compared.

In parallel, the radiation chemistry study of high temperatures and supercritical water is in progress. We have observed a variety of radicals at elevated temperatures and measured the temperature dependence of the absorption band. The rate constants of the several reactions have been determined.

To estimate the radiolytic yields of water decomposition products from room temperature to 400 ºC by pulse radiolysis method, methyl viologen (1,1'-dimethyl-4,4' -bipyridinium dichloride) is used as a scavenger. $\{G(e_{aq}^-) + G(OH) + G(H)\}$ has been studied using a 0.5 mM MV^{2+} solution in presence of 10 mM NaCOOH up to 200 ºC and in presence of 0.2 M ethanol up to 400 ºC. The results show that the $\{G(e_{aq}^-) + G(OH) + G(H)\}$ increases with temperature up to 350 °C at 25 MPa, while it depends also on pressure in supercritical conditions. The $G(e_{aq}^-)$ was estimated using MV^{2+} solutions in presence of 0.2 M *tert*-butanol. The results agree well with the reported data up to around 300 °C at 25 MPa, however, in supercritical conditions, a very significant pressure or density effect was observed.

The behaviors of solvated electrons in different alcohols are also studied as a function of temperatures above their critical temperatures. Red shift of the absorption of the solvated electrons and pressure dependence of the decay rate were also found.