Time-resolved Spectroscopic Study on Excited-state Intramolecular Proton Transfer in 1-hydroxyanthra-quinone

Dae Won Cho, Seung Hoon Kim, Sae Chae Jeoung[1]

Department of Chemistry, Seonam Universty, Namwon, Chonbuk, 590-711, Korea
[1]Laser Metrology Lab., Korean Research Institute of Standards and Science, Taejon, 305-340

The Photodynamics of excited-state intramolecular proton transfer (ESIPT) reaction of 1-hydroxyanthraquinone (1-HAQ) was investigated with time-resolved emission and femtosecond transient transmittance techniques at room temperature. The temporal profiles of spontaneous emission, a stimulated emission and the photoinduced absorption of 1-HAQ could be well described with multi-decaying time constants. The ultrafast component within *ca.* 260 fs reflects the dynamics on ESIPT. The decay component of 2 ps is assigned to an additional intramolecular vibrational relaxation induced proton translocation, whereas the component of 18 ps is to the vibrational cooling, while the long component (200 ps) can be explained in terms of the relaxation from excited-state *keto*-tautomer to its ground state. Finally, the comparative studies on photodynamics between 1-HAQ and 1-DAQ are consistent with the supposition that ESIPT process is very fast due to its negligible activation barrier, and the vibrational relaxations could not involve high energy O-H(D) stretching vibrations. Contrast to this, the relaxation of excited *keto*-tautomer has a prominent isotope effects. Also, the structural changes arise from the ESIPT of 1-HAQ were investigated by using the transient Raman spectroscopy. To assign the observed excited-state vibrational modes, we carried out the mode analysis through the *ab initio* calculation with HF/4-31G(d) and CIS/4-31G(d) methods. The frequency changes of carbonyl stretching modes provide more quantitative pictures on the reverse proton transfer as well as the ESIPT process. Especially, the solvent natures affect to the deactivation process of the excited *keto*-tautomer.