

Photoinduced Proton Transfer of N-Methyl-Hydroxyquinolinium to Small Water Clusters

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The excited-state proton transfer (ESPT) to water was studied in the presence of a series of strong photoacids, N-methyl-n-hydroxyquinolinium ions, with a hydroxyl group at 3 (NM3HQ⁺), 5 (NM5HQ⁺), 6 (NM6HQ⁺), 7 (NM7HQ⁺) and 8 (NM8HQ⁺) positions, in an aprotic solvent of acetonitrile.

We measured excited-state lifetimes of the prototropic species of NMnHQ⁺ using picosecond-resolved fluorescence spectroscopy and analyzed their chemical kinetics to reveal the ESPT mechanism. The results show that water, as a base, forms small clusters during the ESPT process, the sizes of which have are: three for NM7HQ⁺, two for NM3HQ⁺ and NM6HQ⁺, and one for NM5HQ⁺ and NM8HQ⁺.

From the Förster analysis modified from its original version [1], acid dissociation constants in excited state (pK^{a*}) of the photoacids were evaluated and found to correlate with the size of the water clusters as base; the number of molecules constituting the water clusters tend to decrease as the photoacid becomes acidic, i.e., with lower pK^{a*} values. From the comparison with our previous results reporting the size of alcohol clusters as Brønsted base in the ESPT of the same photoacids [2–4], it is found that water is less reactive in acid-base reactions than alcohol when hydrogen-bond network is limited to form small clusters.

References

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