

Hydrogen Bonding Catalyzed Excited-State Double Proton Transfer Reaction between 2-aminopyridine and Acetic Acid

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Phototautomerization process involving a double proton-transfer reaction has been a hot topic in biochemistry and photochemistry in recent years. We have investigated the photo-induced tautomerization of 2-aminopyridine (2AP) to 2(1*H*)-pyridineimine(1H2PI) by experimental and theoretical methods. In solution 2AP and acetic acid could form a complex connected by intermolecular hydrogen bonding. With photo excitation intermolecular proton transfer reaction would happen along hydrogen bonding. The reaction mechanism is complex and still need to investigate. During the process of protons transferring, the hydrogen bonding plays an important role. The intermolecular hydrogen bonding in the electronically excited states has been strengthened significantly which induces the proton transferring. The reaction mechanism is determined by the unsymmetrical molecular structure and the strength of hydrogen bonding. The acetic acid acts as a catalyst, providing proton first and accepting proton later. The C=O dual bond has a shift from one side to the other side in the acid molecular, which accompanies the catalysis in the intermolecular double proton transfer reaction.

The steady-state absorption and fluorescence spectra are described both by experimental and theoretical methods. The time-dependent density functional theory (TDDFT) method with B3LYP hybrid functional is employed to study the excited-state hydrogen-bonding dynamics. The representative effect of hydrogen bonding has been put forward. The possible mechanisms of double proton transfer reaction have been discussed, the potential energy curves of the ground and excited states with different mechanisms have been shown. The stepwise mechanism expresses the superiority in view of the energy aspect. Herein the sequence of the asynchronous double proton transfer is theoretically confirmed for the first time.

This kind of hydrogen bonding catalyzed excited-state double proton transfer reaction has been investigated far and wide. It plays an important part in excited-state dynamics and appears significance and potential in the photocatalysis field.

References

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