

EXCITED STATE DEACTIVATION VIA SOLVENT TO CHROMOPHORE PROTON TRANSFER IN ISOLATED 1:1 MOLECULAR COMPLEX: EXPERIMENTAL VALIDATION BY MEASURING THE ENERGY BARRIER AND KINETIC ISOTOPE EFFECT

RAMESH JARUPULA, SAURABH KHODIA, MD SHABEEB, BAWEJA SIMRAN, BHAVIKA KALAL, SURAJIT MAITY, *Chemistry, Indian institute of technology Hyderabad, Hyderabad, Telanagana, India.*

We have experimentally demonstrated conclusive evidence of solvent-to-chromophore excited state proton transfer (ESPT) as a deactivation mechanism in a binary complex isolated in the gas phase. The above was achieved by quantitatively determining the energy barrier of the ESPT processes, qualitatively analyzing the quantum tunneling rates, and evaluating the kinetic isotope effect. The 1:1 complexes of 2,2'-pyridylbenzimidazole (PBI) with H₂O, D₂O, and NH₃, produced in a supersonic jet-cooled molecular beam, were characterized spectroscopically. The vibrational frequencies of the complexes in the S₁ electronic state were recorded using a resonant two-color two-photon ionization method coupled to a Time-of-Flight mass spectrometer set-up. In the PBI-H₂O, the ESPT energy barrier of 431±10 cm⁻¹ was measured using UV-UV hole-burning spectroscopy. The exact reaction pathway was experimentally determined by isotopic substitution of the tunneling-proton (in PBI-D₂O) and increasing the width of the proton transfer barrier (in PBI-NH₃). In both cases, the energy barrier was significantly increased to > 1030 cm⁻¹ in the PBI-D₂O and to > 868 cm⁻¹ in PBI-NH₃. The heavy atom in PBI-D₂O decreased the zero-point energy in the S₁ state significantly, resulting in the elevation of the energy barrier. Secondly, the solvent-to-chromophore proton tunneling was found to decrease drastically upon deuterium substitution. In the PBI-NH₃ complex, the solvent molecule formed a preferential hydrogen bonding with the acidic (PBI)N-H group. This led to the formation of a weak hydrogen bonding between the ammonia and the pyridyl-N atom, thus, increasing the proton transfer barrier width (H₂N-H...N_{pyridyl}(PBI)). The above resulted in both an increase in barrier height and a decrease in the quantum tunneling rate in the excited state. The experiment, aided by computational investigations, demonstrated the variation observed for both the energy barrier and the quantum tunneling rate by substituting NH₃ in place of H₂O can be directly correlated to the drastically different photochemical and photo-physical reactions of biomolecules under various microenvironments. To validate the above methods in different chemical environments, such as PBI-CH₃OH and PBI-CH₃OD complexes show a similar mechanism.