



Photoacid as an Efficient ICT Probe for Understanding the Ground State Proton Transfer (GSPT) Process from Solute to Solvents

ANAS D. FAZAL, TRUPTI D. SOLANKY, ABHISHEK R. PATEL and SUMIT K. PANJA*

Tarsadia Institute of Chemical Science, Uka Tarsadia University, Maliba Campus, Gopal Vidyanagar, Bardoli, Mahuva Road, Surat, Gujarat, India.



Article History

Published on: 20 October 2023

Intermolecular interaction via H-bonding interaction plays important role on generation of functional material, biological recognition and drug design etc. Photoacid shows interesting intermolecular proton transfer process in excited & ground state from solute to solvent. Solute-solvent interaction is also important factor for excited & ground state proton transfer process (GSPT). Photoacid as ICT probe is excellent for monitoring GSPT from solute to solvent. Further, effect of substituent on photoacid also shows tuning the effective GSPT from solute to solvent in solution.

Intermolecular interactions play a crucial role for the generation of physiologically active compounds, novel functional materials, and mechanisms for chemical and biological recognition and rational drug design.¹⁻² The creation of useful novel materials and enhanced understanding of mechanism of formation of cluster in solution depend greatly upon the research of fundamental intermolecular interactions.² The intermolecular interaction between solvent & solute can be described by intermolecular H-bonding interaction at ground and excited state.³⁻⁴ Excited state intermolecular proton transfer (ESPT) process of photoacid has been comprehensively examined so far.⁵⁻⁷ However ground state proton transfer (GSPT) process from solute to solvents are infrequently pragmatic. Photoacid have unique characteristic feature to exhibit microsolvation behavior with protic solvent via intermolecular H-bonding interactions.⁸⁻⁹

Upon electronic excitation, photoacids has shown significant changes of their acidity and exhibit distinct pKa values in ground & excited state.¹⁰ Solute-Solvent interaction via intermolecular H-bonding interaction

CONTACT Sumit K. Panja ✉ sumitkpanja@gmail.com 📍 Tarsadia Institute of Chemical Science, Uka Tarsadia University, Maliba Campus, Gopal Vidyanagar, Bardoli, Mahuva Road, Surat, Gujarat, India.



© 2023 The Author(s). Published by Oriental Scientific Publishing Company

This is an Open Access article licensed under a Creative Commons license: Attribution 4.0 International (CC-BY).

Doi: <https://dx.doi.org/10.13005/OJPS08.02.01>

& degree of photoacidity of photoacids are responsible for efficiently GSPT transfer process from solute to solvent.¹¹⁻¹² The microsolvation behavior of photoacid in protic solvents depends upon strength of intermolecular H-bonding interaction & degree of photoacidity at ground and excited state. It is also pragmatic that electron withdrawing group enhances photoacidity of photoacid in solutions and makes photoacids as ICT probe for GSPT and ESPT process from solute to solvents.⁸⁻⁹

Microsolvation is a key phenomenon and has been widely studied in protic solvents, especially in water.¹³ The microsolvation of photoacids provides better understanding for proton transfer phenomena from solute to solvents, considering solute molecule enclosed by solvent molecule.¹³⁻¹⁴ Photoacid is an important class of molecule used as molecular probe for determining structural transitions of proteins & water accessibility in biological surfaces.¹⁵⁻¹⁶ Electronic structure of hydrated cluster has been calculated to provide molecular level understanding about hydration process of photoacid.¹⁷⁻¹⁸ Phenol is considered as simplest photoacid and also works as chromophore in aromatic amino acid in biological system.¹⁹⁻²⁰ The interaction between phenol & solvent molecule is considered as model system for understanding the molecular level microsolvation behaviour of phenol clusters.^{14, 21-22} In neutral condition, phenol behaves as weak ICT probe but in basic solutions, it shows strong ICT probe due to the enhancement of intermolecular charge transfer (ICT) process in solution.²³ In homogeneous clusters such as water/aliphatic alcohol, water/aromatic alcohol, aliphatic alcohol/aromatic alcohol and other similar complicated systems are also inspected via UV and IR spectroscopic methods.¹² Precise disturbance of the clusters can lead to red shift of O-H vibrational stretching by alternation of H-bonding interaction which happens between solute & solvent in solution.²⁴

Recent studies indicate that microsolvation of photoacids can have a considerable impact on solute in the ground state proton transfer in solution.²⁵ Photoacid has a great importance in different chemical, pharmaceutical and fragrant industries etc. It can also be used for the conformational changes of complex biological systems and in many complex reactions. Further, degree of photoacid related to efficient ICT probe to investigate GSPT from solute to solvent & impact of electron withdrawing group on photoacidity should be studied further applications in complex chemical, pharmaceutical and biological systems.

References

1. E. A. Meyer, R. K. Castellano, F. Diederich. Interactions with aromatic rings in chemical and biological recognition. *Angew. Chem. Int. Ed.* 42 (2003) 1210-1250.
2. K. S. Kim, P. Tarakeshwar, J. Y. Lee. Molecular clusters of π -systems: theoretical studies of structures, spectra, and origin of interaction energies. *Chem. Rev.* 100 (2000) 4145-4186.
3. S. K. Panja, S. Verma, S. Saha. Probing phenol dimer in molecular complex: role of nitro group and stabilizing agent. *J. Mol. Struct.* 1193 (2019) 103-109.
4. P. Song, F.-C. Ma. Intermolecular hydrogen-bonding effects on photophysics and photochemistry. *Annu. Rev. Phys. Chem.* 32 (2013) 589-609.
5. J. F. Joung, S. Kim, S. Park. Effect of NaCl Salts on the Activation Energy of Excited-State Proton Transfer Reaction of Coumarin 18. *J. Phys. Chem. B* 50 (2015) 15509-15515.
6. O. Gajst, L. P. da Silva, J. C. G. Esteves da Silva, and D. Huppert. Excited-State Proton Transfer from the Photoacid 2-Naphthol-8-sulfonate to Acetonitrile/Water Mixtures. *J. Phys. Chem. A*, 30 (2018) 6166-6175.
7. N. Sülzner, B. Geissler, A. Grandjean, G. Jung, P. Nuernberger. Excited-State Proton Transfer Dynamics of a Super-Photoacid in Acetone-Water Mixtures. *ChemPhotoChem* 6 (2022) e202200041
8. K. M. Solntsev, D. Huppert, N. Agmon. Photochemistry of "Super"-Photoacids. Solvent Effects. *J. Phys. Chem. A* 103 (1999) 6984-6997.
9. L. M. Tolbert, K. M. Solntsev. Excited-State Proton Transfer: From Constrained Systems to "Super" Photoacids to Superfast Proton Transfer. *Acc. Chem. Res.* 35(2002) 19-27.
10. O. Gajst, L. P. da Silva, J.C.G.E. da Silva, D. Huppert, Excited-state proton transfer from the photoacid

- 2-Naphthol-8-sulfonate to acetonitrile/water mixtures. *J. Phys. Chem. A* 122 (2018) 6166–6175.
11. L. M. Oltrogge, Q. Wang, S. G. Boxer. Ground-State Proton Transfer Kinetics in Green Fluorescent Protein. *Biochemistry* 53 (2014) 5947–5957.
 12. R. Knochenmuss, O. Cheshnovsky, S. Leutwyler, Proton transfer reactions in neutral gas-phase clusters: 1-Naphthol with H₂O, D₂O, CH₃OH, NH₃ and piperidine. *Chem. Phys. Lett.* 144 (1988) 317–323.
 13. T. Sawamura, A. Fujii, S. Sato, T. Ebata, N. Mikami, Size dependence of intracuster proton transfer of phenol-(H₂O)_n (n = 1–4) Cations. *J. Phys. Chem.* 100 (1996) 8131–8138.
 14. P. Krishnakumar, R. Kar, D. K. Maity. Microhydration of 2-Naphthol at Ground, First Excited Triplet, and First Excited Singlet States: A Case Study on Photo Acids. *J. Phys. Chem. A* 122 (2018) 929–936
 15. G. J. Zhao, K. Li Han, Hydrogen Bonding in the Electronic Excited State. *Acc. Chem. Res.* 45 (2012) 404–413.
 16. N. Amdursky, Photoacids as a new fluorescence tool for tracking structural transitions of proteins: following the concentration-induced transition of bovine serum albumin. *Phys. Chem. Chem. Phys.* 17 (2015) 32023–32032.
 17. J. L. Perez-Lustres, F. Rodriguez-Prieto, M. Mosquera, T.A. Senyushkina, N.P. Ernsting, S.A. Kovalenko, Ultrafast Proton Transfer to Solvent: Molecularly and Intermediates from Solvation- and Diffusion-Controlled Regimes. *J. Am. Chem. Soc.* 129 (2007) 5408–5418.
 18. D. K. Deb, B. Sarkar, Theoretical investigation of gas-phase molecular complex formation between 2-hydroxy thiophenol and a water molecule. *Phys. Chem. Chem. Phys.* 19 (2017) 2466–2478.
 19. S. K. Panja, S. Saha, Temperature Sensor Probe Based on Intramolecular Charge Transfer (ICT) & Reversible Solute-Solvent Interaction in Solution. *Spectrochimica Acta Part A* 212 (2019) 128–131.
 20. A. Nilsen-Moe, C. R. Reinhardt, S. D. Glover, L. Liang, S. Hammes-Schiffer, L. Hammarström, C. Tommos. Proton-Coupled Electron Transfer from Tyrosine in the Interior of a de novo Protein: Mechanisms and Primary Proton Acceptor. *J. Am. Chem. Soc.* 142 (2020) 11550–11559.
 21. B. Brutschy, The Structure of Microsolvated Benzene Derivatives and the Role of Aromatic Substituents. *Chem. Rev.* 100 (2000) 3891–3920.
 22. S. K Panja. Photoacid as ICT Probe for Ground State Proton Transfer Process from Solute to Solvents. *J. Mol. Liq.*, 299 (2020) 112194-112201
 23. S. K. Panja, N. Dwivedi, S. Saha, Manipulating the proton transfer process in molecular complexes: synthesis and spectroscopic studies. *Phys. Chem. Chem. Phys.* 18 (2016) 21600–21609.
 24. M. Prémont-Schwarz, D. Xiao, V. S. Batista, E. T. J. Nibbering, The O–H Stretching Mode of a Prototypical Photoacid as a Local Dielectric Probe, *J. Phys. Chem. A* 115 (2011) 10511–10516.
 25. A. Shabashini, S. K Panja, A. Biswas, S. Bera, G. C. Nandi, ICT based photoacid probe for microsolvation and H-bonding assisted proton transfer process from solute to solvents, *J. Photochem. Photobiol. A*, 432 (2022) 114087-114092