

# **New Book Proposal**

## **Excited-State**

### **Hydrogen Bonding and Hydrogen Transfer**

**Edited by**

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## PREFACE

Hydrogen bonding is of universal importance in chemistry, biology, and physics. Hydrogen bonding is central to the understanding of the microscopic structures and functions in many complex systems, for example hydrogen-bonded water or alcohols networks, organic compounds in solution, crystal engineering, self-assembled supramolecular architectures, proteins, and DNA building blocks of the life. Moreover, hydrogen bonding structures and dynamics in the excited states play also important roles on determining many chemical, physical and biochemical processes. In general, fluorescence emission behaviors of the organic and biological chromophores can be significantly influenced by the intermolecular hydrogen bonding interactions between chromophores and the protic solvents or biological surroundings. Furthermore, ultrafast deactivation processes of photoexcited molecular and supramolecular systems can be remarkably facilitated by the excited-state hydrogen bonding. In particular, the excited-state hydrogen transfer is tightly related to the excited-state hydrogen bonding structures and dynamics.

Hydrogen bonding in the ground state for various types of molecular and supramolecular systems has been described systematically in an abundance of published monographs. However, to the best of our knowledge, there are no monographs on the hydrogen bonding in excited states until now. It has been found that the excited-state hydrogen bonding and hydrogen transfer play more and more important role on many photophysical processes and photochemical reactions. Therefore, a new book presenting the hydrogen bonding and hydrogen transfer in excited states is urgently needed. This scientific book will be very helpful for extensively understanding the nature of hydrogen bonding and its key roles on the photochemistry, photobiology, and photophysics.

This book gives an extensive description of the research progress on excited-state hydrogen bonding and hydrogen transfer in recent years. First of all, both the experimental and theoretical investigations on the excited-state hydrogen bonding structures and dynamics of many organic and biological chromophores are presented. Such as, coumarin and its derivatives, fluorenone and its derivatives, diazines, quinones,  $\beta$ -carboline, harmane derivatives, substituted phthalimides, 4-aminoindandiones, hydroxyphenacyl compounds, diazromatic betacarboline derivatives, imidazolium ionic liquids, supramolecular host-guest complexes, nano-confined systems, rhodopsins, hydrated DNA bases and base pairs, and so on. After that, several chapters will describe the influences of the excited-state hydrogen bonding on various photophysical processes and photochemical reactions. For example, hydrogen bonding effects on fluorescence emission behaviors and photoisomerization; intramolecular hydrogen-bond formation mediated de-excitation of curcuminoids; role of hydrogen bonding in photosynthetic water splitting; ultrafast catalytic processes in the light-driven enzyme protochlorophyllide oxidoreductase (POR); photoinduced electron transfer and solvation dynamics in room temperature ionic liquids; hydrogen bonding

barrier crossing dynamics at bio-mimicking surfaces; hydrogen bonding effects on intramolecular charge transfer, vibrational energy relaxation, and the ICT to TICT conversion; hydrogen bond basicity in excited states and dynamic heterogeneity. Finally, we will focus our attention on the excited-state hydrogen transfer in the last several chapters. Some experimental and theoretical studies on the excited-state hydrogen transfer in some isomeric naphthalene derivatives, benzoxazole derivatives, pyrido-indole and pyrrolo-quinoline derivatives, green and red fluorescent proteins, hydrated halides, o-hydroxy carbonyl compounds, hydroxyl aromatic dopants, photoactive yellow protein will be presented. Moreover, investigations on controlling excited-state hydrogen transfer along hydrogen-bonded wires, excited-state double proton transfer, *ab initio* QM/MM excited-state molecular dynamics, reaction volume for photoinduced proton transfer in aqueous solutions of 6-methoxyquinoline, conformational switching between acids and their anions by hydrogen bonding, molecular recognition and chemical sensing of anions utilizing excited-state hydrogen bonding, photodissociation of hydrogen-bonded clusters, proton transfer reactions for dynamic quenching of fluorescence are also reported.

The readers of this book will be faculties and researchers in the fields of molecular and supramolecular photochemistry, photobiology, and photophysics. It will also serve as a good reference book for graduate students for the study of recent topics and progress in the excited-state hydrogen bonding and hydrogen transfer.

Finally, we would like to sincerely thank all the authors that have contributed with their excellent chapters to the realization of this monograph. We greatly acknowledge the assistance of co-workers from the group in Dalian institute of chemical physics (DICP) in the editorial process. Also, we thank the team at WILEY-BLACKWELL, in particular Dr. Paul Deards and Dr. Mingxin Hou for their helpful guidance during the entire project.

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# Vibrational Dynamics of the Hydrogen Bonds in Nucleic Acid Base Pairs

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## Abstract

This chapter reviews recent results on the vibrational dynamics of hydrogen-bonded nucleic acid base pairs putting special emphasis on the signatures of hydrogen bonding in linear and nonlinear infrared spectroscopy. Hybrid QM/MM trajectory simulations are discussed as a means for obtaining information on geometric correlations and hydrogen bond fluctuations in the condensed phase. A detailed account is given for the Watson-Crick base pair composed of 9-ethyl-8-phenyladenine and 1-cyclohexyluracil in deuteriochloroform solution. Different approaches for obtaining the time-dependent transition frequencies of the two hydrogen-bonded NH stretching vibrations along a QM/MM trajectory are discussed. This includes an empirical mapping between hydrogen bond distance and transition frequencies as well as calculating snapshot potential curves for the high frequency motions at selected nuclear configurations. Within the framework of a cumulant expansion, the linear and nonlinear spectra are expressed in terms of a single set of lineshape functions. Results obtained for the absorption lineshape and the pump-probe spectrum are found to be in good agreement with experiments. Two-dimensional infrared spectra are presented to reveal dynamical correlations between the two hydrogen bonds.

*Keywords:* Hydrogen bonding; Vibrational dynamics; QM/MM; Electronic excited states; Nucleic acid.

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# Vibrational Energy Relaxation Dynamics of XH Stretching Vibrations of Aromatic Molecules in the Electronic Excited State

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## Abstract

Vibrational energy relaxation (VER) of isomer (cis- and trans-) specified 2-naphthol and its hydrogen(H)-bonded clusters in the excited ( $S_1$ ) electronic states is described. The cis- and trans- isomers of 2-naphthol H-bonded clusters are selectively excited to the XH (X = O and N) stretching vibration of  $S_1$  by stepwise UV – IR double resonance excitation, and fluorescence from the initially excited state as well as the relaxed state and fragment are observed. It is found that after the IR pulse excitation an intracuster vibrational energy redistribution (ICVR) immediately occurs, which is followed by vibrational predissociation (VP) and isomerization. The latter two processes compete with each other. At low energy, the isomerization effectively occurs and the barrier height of the cis  $\rightarrow$  trans isomerization is estimated to be  $2900\text{ cm}^{-1}$ . With the increase of the IR energy, the rate constant of VP rapidly increases and becomes a dominant process.

*Keywords:* Hydrogen bonding; Electronic excited states; VER.

### 3

## The Hydrogen-Bond Basicity in the Excited State, Concept and Applications

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#### Abstract

The photophysics of different hydrogen bond acceptor molecules has been investigated in the presence of aliphatic or fluorinated aliphatic alcohols in n-hexane and carbon tetrachloride solvents. Mostly, consecutive two-step hydrogen bonded complex formation is observed in the presence of alcohols. Equilibrium constants are determined for the formation of singly and doubly complexed species. The UV absorption and fluorescence spectra for the singly and doubly complexed species are derived from the measured absorption and fluorescence spectra, respectively, by means of the equilibrium constants. It is concluded from the results that the spectroscopic (singlet excitation energy, Stokes shift and dual luminescent characteristics) as well as photophysical properties (life time, triplet yields etc) of the complexed species are significantly influenced by the Gibbs energy change in the complexation reaction. Quantitatively, a linear relationship is found between the difference of S1 singlet excitation energy of the complexed and uncomplexed species on one hand and the Gibbs energy change in the complexation reaction on the other hand. This observation is explained by means of an energy cycle and Abraham's hydrogen-bond acidity – basicity model. On the basis of the model, hydrogen-bond basicity values are determined for singlet excited species and its singly complexed derivative. Such hydrogen-bond basicity values of excited states can be useful (if the appropriate conditions are fulfilled) for predicting

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equilibrium constants for complex formation of the given excited state with different hydrogen bond donors. By means of time resolved fluorescence decay measurements the reaction rate of singlet excited molecules with alcohols can be determined, which parameter may depends on the Gibbs energy change in the complexation reaction. The derived quantitative correlation between the rate coefficient of complexation of the singlet excited molecule with alcohols and the Gibbs energy change in the complexation process allowed us to estimate the unknown, but purposeful rate coefficient for the complexation of the ground state species with different alcohols. The knowledge of the excited state hydrogen-bond basicity makes possible to construct an unbiased Lippert – Mataga – plot from the fluorescence and absorption spectra of the complexed molecule. On the ground of that correlation one can calculate the excited state dipole moments of the complexed species.

*Keywords:* hydrogen-bond basicity; photophysics of aromatic molecules; dual luminescence; solvatochromism

## Solute–Solvent Hydrogen Bond Formation in the Excited State. Experimental and Theoretical Evidences

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### Abstract

Starting from the experimental effects observed in the excited state photophysical properties of organic molecules in different solvents and solvent mixtures, solute–solvent specific interactions are rationalized in terms of excited state hydrogen bond (H bond) formation. Several models that can be used to separate the polarity effect of the solvent from the H bond acceptor and/or H bond donor contributions (Lippert-Mataga, Dimroth-Reichardt, Kamlet-Taft, Catalán) are reviewed, and various of their applications are presented. The best experimental conditions required to evidence the presence of H bonds, i.e. choice of fluorescence probes, choice of solvents/solvent mixtures are discussed. Time-resolved fluorescence results are also presented as they can evidence the excited state H bond occurrence by way of two lifetimes assigned to the solute and to the H bonded solute–solvent species, respectively. The intramolecular charge transfer (ICT) character of the first excited singlet state has an important role in the solute–solvent H bond formation. We highlight some advances in studying the relation between the ICT character and the H bond formation by means of quantum chemical methods.

*Keywords:* Hydrogen bonding dynamics; charge transfer; excited states.

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## Effect of H-bonding on the photophysical behavior of Coumarin dyes

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### Abstract

Coumarin dyes are one of the most widely used fluorescence probes to study the dynamics and mechanism of different processes of both chemical and biological interest, including the characterization of different microenvironments. Many of these studies are based on the photophysical properties of the coumarin dyes, which are largely dependent on the nature of the microenvironments around the dye. Beside the most general long range dielectric interaction imparted by the surrounding solvent media, the short range specific interaction, like H-bonding, is also known to affect the photophysical characteristics of this class of dyes very significantly. In this chapter, a short review on our work on the effect of H-bonding, both intra and inter molecular, on the photophysical behavior of some of the coumarin dyes, that has been widely used as the fluorescence probe has been presented.

*Keywords:* Coumarin; Hydrogen bonding dynamics; Electronic excited states; Fluorescence probe; Photophysics

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# Insights from Singlet into Triplet Excited-State Hydrogen Bonding Dynamics in Solutions

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## Abstract

In the present work, the triplet electronic excited-state hydrogen bonding dynamics of fluorenone chromophore in alcoholic solvents was theoretically investigated using the time-dependent density functional theory (TDDFT) method for the first time. All the computational results of the triplet electronic excited state were compared with the corresponding results of the singlet electronic excited state reported in our previous works. Both the triplet excited-state spectral red-shift induced by intermolecular hydrogen bond and the frontier molecular orbitals analysis indicated that the intermolecular hydrogen bond formed between fluorenone and alcoholic solvents in the triplet excited state would be strengthened in comparison with that in ground state, which is similar to the case in the singlet excited state of fluorenone chromophore. The intermolecular hydrogen bond strengthening in the triplet excited state was confirmed by monitoring the calculated infrared (IR) spectral shifts of some characterized vibrational modes involved in the formation of intermolecular hydrogen bond in different electronic states. Moreover, we also demonstrated that the intermolecular hydrogen bond in the T1 state is weaker than that in the S1 state. The important deactivation processes for the S1 state of fluorenone in alcoholic solvents, such as internal conversion (IC), and intersystem crossing (ISC), etc. may be significantly influenced by the intermolecular hydrogen bonding dynamics in the singlet and triplet electronic excited states.

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*Keywords:* Hydrogen bonding dynamics; Electronic excited states; Fluorenone; Internal conversion (IC); Intersystem crossing (ISC).

## Hydrogen Bonding on Photoexcitation

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### Abstract

The solute-solvent interaction, especially involving the intermolecular hydrogen bonding, has been found to be very important in determining the molecular non-equilibrium process in solution. Intermolecular hydrogen bonding is a site-specific interaction that represents an important type of local interaction in which a hydrogen atom is linked to hydrogen donor and acceptor groups. Photoexcitation can induce a change in hydrogen bonding due to electronic redistribution in the excited states. This is termed as excited state hydrogen bonding dynamics, which occurs in an ultrafast time scale. This kind of dynamics is significantly associated with many important electronic excited state phenomena such as photoinduced electron transfer, internal conversion and fluorescence quenching, which have been understood by using diverse experimental and theoretical methods. The existence of more than one in-equivalent hydrogen bonds in hydrogen bond donating solvents like water or methanol has also been well documented. However, on photoexcitation some of these hydrogen bonds become strengthened whereas some become weakened or remain unchanged. Fast and very sensitive detections of intermolecular hydrogen bonding can be used not only as a calibrator of solvent properties but also as a unique sensor of hydrogen bonding potential in unknown media. Hydrogen bonds are essential for complementary base pairing and stabilization of double stranded DNA. Moreover, organic bi-functional molecules comprising both hydrogen bond donor and acceptor groups in close proximity may form an intramolecular H-bonded structure, which on photoexcitation leads to a massive intramolecular redistribution of electronic charge and proton gets translocated from hydrogen bond donor to hydrogen bond acceptor group. This phenomenon is commonly termed as excited state intramolecular proton transfer (ESIPT).

*Keywords:* Hydrogen bonding; ESIPT; excited states; photoexcitation.

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# Fluorescence Studies of the Hydrogen Bonding of Excited State Molecules within Supramolecular Host- Guest Inclusion Complexes

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## Abstract

Hydrogen bonding interactions can play an important role in the formation of supramolecular host-guest inclusion complexes. Such complexes, in which a relatively small guest molecule becomes included within the internal cavity of a larger, cage-like host molecule, can be stabilized by hydrogen bonding between the host and guest, but in competition with guest hydrogen bonding to the solvent. Fluorescence spectroscopy provides a useful and sensitive technique for studying the formation and stability of such complexes, based on measured changes in the guest fluorescence spectrum upon inclusion within the host cavity. However, when the guest is excited by the absorption of light, its electronic characteristics change, resulting in potentially significant changes in its hydrogen bond donor or acceptor properties. Thus, the hydrogen bonding between an electronically excited guest and the host in which it is included can be different than that between the guest in the ground state and the host. This chapter will review steady-state fluorescence studies of hydrogen bonding between excited state guests and the molecular hosts in which they are included (and in a few cases, between guests and excited state hosts), and discuss the effects of hydrogen bonding on the stability of the host-guest inclusion complex, and on the fluorescence properties of the guest (or host). Excited states of guests involved include singlet, triplet and charge transfer states.

*Keywords:* Hydrogen bonding; excited states; Host-guest; Inclusion complex.

## 9

# Electronic Excited State Structures and Properties of Hydrated DNA Bases and Base Pairs

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### Abstract

Nucleic acid bases are the building blocks of deoxyribonucleic acid (DNA), the genetic carrier, which stores information in the form of specific pattern of hydrogen bonding among complementary bases. Nucleic acid bases absorb ultraviolet (UV) radiation efficiently, but the quantum efficiency of radiative decay is very poor. Most of the absorbed radiation is released during the ultrafast nonradiative deactivation processes where conical intersection between the ground and excited state potential energy surfaces plays a vital role. DNA in vivo is heavily hydrated and the degree of its hydration depends upon various factors. Experimentally, the ground state molecular geometries of nucleic acid bases have been determined long time ago. But, corresponding details in the electronic excited states is yet not available; only qualitative information such as excited state structural nonplanarity among some bases has recently been revealed. High level theoretical calculations, on the other hand, can play significant role in this area. This review is devoted to the computational description of ground and electronic singlet excited states of nucleic acid bases and base pairs in the gas phase and effect of degree and mode of hydrations for these species. The possible role of hydration on the nonradiative deactivation processes is also discussed.

*Keywords:* Nucleic acid bases; base pairs; excited states; hydration; hydrogen bonding; nonradiative decay; excited state geometry; structural deformation

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## Effect of Intramolecular H-Bond-Type Interactions on the Photochemistry of Aza-Stilbene-Like Molecules

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### Abstract

This short review article describes the role of intramolecular hydrogen bonding (IHB) on the internal rotation around single and double bonds through some typical examples met in the framework of the research work of the author's laboratory on the radiative and reactive relaxations of some photoisomerizable aza-derivatives of 1,2-diarylethenes and related compounds (aza-1,4-diarylbutadienes and aza-1,n-distyrylbenzenes). In several of these compounds it has been found that IHB-type interactions between the heteroatom and the nearby located ethenic hydrogen atom in non-polar solvents may stabilize a specific conformational isomer thus affecting its relative abundance and its behaviour under irradiation. Moreover, stabilization of one of the geometrical (trans/cis) isomers by IHB may induce energy inversion of their excited states, thus controlling the photoreaction mechanism. In protic solvents, stronger intermolecular HB-type interactions may invert the situation thus prevailing on the intramolecular ones.

*Keywords:* Intramolecular hydrogen bonding; photochemistry; excited states; trans-cis.

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## Hydrogen Bonding Barrier Crossing Dynamics at Bio-mimicking Surfaces

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### Abstract

The physicochemical properties of water molecules are considerably modified by the nature of their homomolecular as well as heteromolecular hydrogen bonding. Water molecules in confined bio-mimicking systems (especially in micelles and in reverse micelles) provide a useful platform for understanding the complex nature of water within biological environment. The water molecules in the close vicinity of biological membrane (commonly termed as “biological water”) are physically different from those of bulk water and these two types of water remain in thermodynamic equilibrium. This equilibrium is associated with an Arrhenius type energy barrier crossing model in which the bound-type water molecules (biological water) get converted into the bulk-type as the temperature of the system increases. The validity of such a model at the real biological surfaces is still an unsolved problem. Particularly, there has been a controversy of its applicability in bio-mimicking self organizing systems. Our group has recently carried out a series of studies involving temperature dependent ultrafast solvation dynamics using picosecond-resolved fluorescence spectroscopic technique to understand the implication of hydrogen bond dynamics as well as to establish the validity of the Arrhenius model in such systems. In the present contribution we have summarized the results obtained in our previous studies concerning the applicability of barrier energy crossing model in micellar, reverse micellar and mixed surfactant reverse micellar systems. We have also presented our results on the importance of such barrier crossing transition in the binding of a well known DNA marker Hoechst 33258 at reverse micellar interface.

*Keywords:* Hydrogen bonding; Crossing dynamics; Excited states.

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# Formation of Intermolecular Hydrogen Bonds in the Fluorescence Excited State of Organic Luminophores Containing Simultaneously Carbonyl and Amino Group

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### Abstract

The steady - state and dynamic photophysical characteristics of carbonyl containing organic luminophores, namely isobenzofuranones, indan-diones, acridones and chalcones, in solvents of different polarity and proton donating ability are investigated. It is found that when an amino group is present in their conjugated system, the dependences of the fluorescence Franck-Condon transition energy and the fluorescence quantum yield on the ET(30) constant of the solvent, as well as the fluorescence decay curves, are strongly influenced by the proton donating ability of the media. The obtained experimental results indicate that the nature of the emitting state is different in protic and aprotic solvents, due to formation of intermolecular hydrogen bonded solute - solvent complexes in the excited state of the studied compounds at room temperature. These conclusions are confirmed also by the observed deuterium isotope effect and matrix effect, as well as by the results from the quantum chemical calculations.

*Keywords:* Intermolecular hydrogen bonds; Excited state complexes; Fluorescence; Carbonyl containing organic luminophores

## Hydrogen-Bonding Effects on Excited States of Para-Hydroxyphenacyl Compounds

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### Abstract

There is much interest in developing efficient phototriggers that can be utilized for real-time monitoring of physiological responses in biological systems. The p-hydroxyphenacyl (pHP) protecting group has gained particular interest because it has demonstrated practical potential as a very fast and efficient “cage” for the release of various biological effectors. The photodeprotection reaction of pHP caged compounds appears to occur only in aqueous or aqueous containing solutions and does not appear to occur in neat organic solvents like acetonitrile (MeCN). In aqueous or aqueous containing solvents, in addition to the photodeprotection reaction, the photolysis also leads to a photosolvolytic rearrangement of the pHP cage into a p-hydroxyphenylacetic acid (HPAA) final product. Although the products and conditions for the pHP deprotection have been determined in previous work, the reaction mechanism is not well understood and there is still some uncertainty about the events and reactive intermediates involved in the photochemical pathway for the deprotection of pHP phototriggers. In this book chapter we present experimental results from a combination of ultrafast time resolved spectroscopy and time-resolved resonance Raman spectroscopy on the picosecond and nanosecond time scales as well as *ab initio* and density functional theory computational results to better elucidate the photodeprotection reaction of these important phototriggers. We found that explicit hydrogen bonding effects on the excited states of p-hydroxyphenacyl compounds plays a key role in their photochemistry and photodeprotection and rearrangement reactions. We examine the effects of hydrogen bonding on the structure and properties of the excited states of p-hydroxyphenacyl compounds and their role in the photodeprotection reactions. The results presented here enable us to better understand the overall mechanistic details of the pHP photochemistry and the role of the hydrogen bonding effects of water molecules in the photodeprotection reactions of this important class of phototrigger compounds.

Keywords: hydrogen bonding effect, excited states, photochemistry

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## Hydrogen Bonding Effects on Intramolecular Charge Transfer

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### Abstract

Intramolecular charge transfer (ICT) is an important process for the investigation of primary function of photoelectric devices and also a possible mechanism for chemical energy storage and a number of important photochemical and photobiological processes. In most of the studies the formation and stabilization of the twisted intramolecular charge transfer (TICT) state is attributed mainly to polarity and viscosity, suggesting that energy barrier for the formation of TICT process decreases with increase in polarity and decrease in viscosity of the medium. However recent investigations clearly established not only the polarity and viscosity, specific hydrogen bonding also plays a major role in the formation and stabilization of the ICT states including TICT states in numerous cases. Even in some molecules hydrogen bonding of solvent is absolutely essential for the molecule to emit from TICT state. Few literature reports suggested that hydrogen bonding of solvent with donor plays the role in the formation of TICT state, but most of the studies supported the role of hydrogen bonding of the solvent with acceptor in the formation and stabilization of TICT state. Time resolved studies indicated that the equilibrium between the locally excited and TICT states was not established in few molecules in protic solvents due to greater stabilization of TICT by hydrogen bonding that increases the barrier for reverse process.

Keywords: TICT, dual emission, hydrogen bond effect, specific interactions, intramolecular charge transfer

## Chemical Dynamics in Room Temperature Ionic Liquids: The Role of Hydrogen Bonding

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### Abstract

In this short article we have described our recent dynamical studies in room temperature ionic liquids. We have divided the section into two parts. In the first part we have reported the Photoinduced electron transfer in room temperature ionic liquid and the second part we have reported the solvation dynamics study in mixed solvents.

*Keywords:* Hydrogen bonding; Ionic liquid; Photoinduced electron transfer; solvation dynamics.

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## Vibrational Spectroscopy for Studying Hydrogen Bonding in Imidazolium Ionic Liquids and their Mixtures with Co-solvents

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### Abstract

Ionic liquids (ILs) are substances consisting of anions and cations, but in contrast to ordinary salts, ionic liquids are liquid at temperatures below 100°C. They are characterized by extremely low vapor pressures, non-flammability, electric conductivity and unique solubility properties, which explain the growing interest in this class of liquid material from both the science and engineering community. Within the last years numerous concepts for IL applications have been developed for, e.g., catalysis, separation technology, electrochemistry, analytics and particle synthesis. Since ILs are interesting for so many different fields they are nowadays intensively studied by means of all different kinds of experimental and theoretical methods. Among these, spectroscopic techniques play an important role to better understand the special nature of ionic liquids and their interactions with dissolved components or interfaces.

A large and important class of ILs is based on cations involving an imidazolium ring. In this ring structure the hydrogen atom at the C2 position is moderately acidic and therefore has a strong tendency to form hydrogen bonds either towards anions or towards polar co-solvent molecules that are present in the system. Such inter-ionic and inter-molecular hydrogen bonds exert influences on the vibrational structure of the participating molecules. Therefore, in turn this hydrogen bonding can be studied by means of vibrational spectroscopy.

In this contribution the vibrational spectroscopic studies of hydrogen bonding in imidazolium based ionic liquids will be reviewed. In most of these works well established methods like infrared absorption and Raman spectroscopy have been employed. However, also other techniques, e.g.

utilizing nonlinear optical effects, will be mentioned briefly. In addition, the potentials, challenges and possible future applications of vibrational spectroscopy for studying ionic liquids are discussed.

*Keywords:* Hydrogen bonding; Ionic liquids; Vibrational spectroscopy.

## Intramolecular H-Bond Formation Mediated De-Excitation of Curcuminoids: a Time-Resolved Fluorescence Study

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### Abstract

Many fluorescent aromatic compounds (photosensitizers) display light-induced biological activities, that is, they use the excitation energy in order to undergo reactions which are thermodynamically forbidden in the ground state. As the primary step of photosensitization is excitation to first excited singlet state,  $S_1$ , the excited-state reaction leading to the therapeutic effect occurs in competition with the other de-excitation mechanisms. The therapeutic potential of any photosensitizer would thus be enhanced by the inhibition of all  $S_1$ -quenching pathways that compete with the one responsible for photoactivity. Such inhibition may be pursued by both the choice of the environment most suitable for  $S_1$ -stabilization with respect to any decay mechanism, except the biologically relevant one, and a rational design of synthetic analogues of the photosensitizer.

Excited state intramolecular proton transfer (ESIPT) frequently is a relevant  $S_1$ -decay mechanism. ESIPT can occur on time scales ranging from hundreds of femtoseconds to tens of microseconds, thus it can be very fast. The rate and efficiency of the process are dramatically enhanced by intramolecular H-bond formation between the proton donating and the proton accepting moieties. In turn, the strength of intramolecular H-bonds is strongly dependent on the physical/chemical properties of the environment.

In solution, solvent polarity and H-bonding capabilities, as well as molecular charge distribution, are of major importance in determining the H-bonding affinity between the proton donating and accepting groups. In turn, the molecular charge distribution is sensitive to the substituents on the aromatic rings and to the formation of secondary intramolecular H-bonds. In the case of  $\delta$ -diketones, such as the tentative photosensitizer curcumin, also the rate and efficiency of reketonization (enol-diketo

tautomerization in  $S_1$ ) strongly depend on the strength of intramolecular H-bonds in the excited state.

Time-resolved fluorescence detection is a powerful tool to study the  $S_1$  dynamics. In the time domain, each  $S_1$ -decay mechanism is signalled by an exponential component in the acquired fluorescence decay pattern. The higher is the decay rate, the smaller is the measured time constant,  $\tau_i$ , of the  $i$ -th component. Moreover, the relative initial amplitude of a decay component in the decay pattern quantifies the probability of deactivation of  $S_1$  by the decay mechanism associated to that component. When intramolecular H-bonding is strong, decay mechanisms such as ESIPT and reketonization, whose efficiency is enhanced by H-bond formation, lead to  $\tau_i$  values of the order of hundreds of picoseconds at most. The comparison with the radiative decay time, normally several nanoseconds, shows that a very weak fluorescence signal is to be expected. Thus, the time-resolved pattern of the fluorescence decay is most conveniently measured by applying time-correlated single-photon counting (TCSPC). Nevertheless, extreme temporal resolution, frequently below the actual capabilities of conventional TCSPC apparatuses, must be granted in order to measure such a fast decay.

In the present Chapter a short overview on the ESIPT and reketonization processes is given and the principles of TCSPC are explained. The optimized TCSPC setup that allows our group to perform decay time measurements with 60% detection quantum efficiency and <30 ps temporal resolution is also described in details. Finally, the role of H-bonds in the excited state in determining the  $S_1$  dynamics is discussed for selected curcuminoids. Namely, fluorescence decay studies on native curcumin and its non-substituted analogue dicinnamoylmethane, that exhibits enhanced intramolecular H-bonding affinity, are presented. The effects of both phenolic substituents and solvent properties on the H-bond strength are assessed.

*Keywords:* H-bond-mediated excited-state dynamics, Fluorescence decay, Time-correlated single-photon counting, Photosensitization, Curcumin, Dicinnamoylmethane, Intramolecular proton transfer, Reketonization

## Hydrogen Bonds of Protein-Bound Water Molecules in Rhodopsins

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### Abstract

In many rhodopsins, a positively charged retinal chromophore is stabilized by a negatively charged carboxylate, and water molecules are observed by X-ray crystallography in the Schiff base region of various rhodopsins. It is thus believed that a water-mediated hydrogen-bonding network plays an important role in the structure and function of rhodopsins. How are the charged groups stabilized by water molecules in the hydrophobic protein interior? Are there any roles of water in the function of rhodopsins? Low-temperature Fourier-transform infrared (FTIR) spectroscopy can directly monitor hydrogen-bonding alterations of internal water molecules of rhodopsins, and we found that a bridged water molecule between the Schiff base and Asp85 in bacteriorhodopsin (BR), a light-driven proton-pump protein, forms an extremely strong hydrogen bond. It is likely that a hydration switch of the water from Asp85 to Asp212 plays an important role in proton transfer in the Schiff base region of BR. A time-resolved FTIR study of BR revealed that hydrogen bonds of water in the M intermediate are similar at low and room temperatures. The hydrogen bond of water plays different but also important roles in the light-driven chloride-ion pump. Comprehensive studies of archaeal and visual rhodopsins have revealed that strongly hydrogen-bonded water molecules are only found in proteins exhibiting proton-pump activities. Strongly hydrogen-bonded water molecules and their transient weakening may be essential for the proton-pump function of rhodopsins. Hydrogen bonds of protein-bound water molecules in rhodopsins are reviewed.

*Keywords:* Hydrogen bonding; Infrared spectroscopy; Rhodopsins.

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## Ground and Excited State Hydrogen Bonding in the Diazaromatic Betacarboline Derivatives

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### Abstract

In this chapter, we analyse in this review the ground and excited state hydrogen bonding and proton transfer reactions of betacarboline, 9H-pyrido[3,4-b]indole, and its derivatives. These molecules possess an acidic pyrrolic nitrogen and a basic pyridinic nitrogen. Thus, they belong to the interesting group of molecules having both proton acceptor and donor sites. Moreover, upon excitation by light absorption, the charge density on the nitrogen atoms changes considerably, the pyridinic nitrogen becoming more basic and the pyrrolic nitrogen more acidic in the first singlet excited state than in the ground state. As a consequence, the prototropic equilibria of these molecules are considerably modified in the first singlet excited state giving rise to the formation of prototropic species under the appropriate conditions. The dynamics of these excited state reactions is, therefore, usually complicated by the fact that multiple equilibria and different hydrogen bonded species can appear. This is the main reason why there is not a complete description of the dynamics of these processes and even controversy between different authors.

In our opinion, the reasons why the interpretation of the photophysical behaviour of betacarbolines is so complicated lie in the fact that the different authors have mainly worked with the parent compounds. Thus, because the donor and acceptor centres are free to interact through hydrogen bonds, different hydrogen bonded complexes can be formed. In this sense, and within our interest in the betacarboline photophysics, we designed a distinct strategy to broach the study of the ground and excited state proton transfer reactions of these compounds. It consisted in the selective blocking of the pyrrolic and pyridinic nitrogen atoms by methylation of the centre. This allowed us to independently analyse the hydrogen bond interactions through the pyridinic or the pyrrolic nitrogen, respectively. With this in mind, we have analysed the hydrogen bond interactions of the betacarboline derivatives, N9-methyl-9H-pyrido [3,4-b]indole, N9-methyl-1-methyl-9H-pyrido[3,4-b]indole and N2-methyl-9H-pyrido[3,4-b]indole. The studies have been carried out in the low polar aprotic solvent cyclohexane using 1,1,1,3,3,3-hexafluoro-2-ol as the donor compound. Moreover, we have also carried out measurements on the influence of the temperature on the BC photophysics. As it is well known, upon decreasing temperature self-aggregation of organic molecules can be observed. In this particular case the simultaneous presence of donor and acceptor centres in the BC skeleton has allowed to analyse the proper hydrogen bond interactions among BC molecules itself. Although in these last cases the photophysical behaviour is somewhat different to the observed with HFIP as the donor, the same



mechanism for the hydrogen bond complex formation can be used to explain the experimental results.

All the results of these investigations have allowed us to establish a general mechanism for the ground and excited state hydrogen bond formation and proton transfer reactions of betacarbolines and to characterise the adducts responsible for such processes.

*Keywords:* Hydrogen bonding dynamics; excited state ; proton transfer reactions.

## Probing Dynamic Heterogeneity in Nano-confined Systems: Femtosecond Excitation Wavelength Dependence and FCS

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### Abstract

Confined liquids in a nano-cavity plays a key role in many natural processes. Prominent examples of nano-confined liquids are water in the hydrophobic pocket of a protein or in biological cell and many liquids nano-porous catalysts. In recent years, femtosecond spectroscopy and computer simulations have generated considerable amount of new knowledge on the dynamics in a nano-cavity. In this review, we will concentrate on ultrafast solvation dynamics and fluorescence resonance energy transfer (FRET) in several nano-confined systems. The latter includes protein, micelles, ionic liquids, cyclodextrin host-guest complex and others. The nano-assemblies are heterogeneous in molecular length scale. As a result the spectra and dynamics of a fluorescent probe in different regions of such a nano-assembly are distinctly different. Recently, we have applied excitation wavelength (ex) variation to study dynamics in different regions of such assemblies. This method is based on the simple fact that molecules in different environments are spectrally distinct and as a result, at different ex different sub-sets of molecules are excited. Using this strategy, we have been able to delineate the difference in solvation dynamics and FRET in different regions of micelle, reverse micelle, gel, and lipid vesicles. The most interesting observation is that ex shows even a neat ionic liquid is heterogeneous. Note, the dimension of a micelle is much smaller than spatial resolution of a microscope. Thus spatial resolution in the nano-water pool achieved by ex variation exceeds the spatial resolution of a microscope.

*Keywords:* Hydrogen bonding; Dynamic heterogeneity; fluorescence resonance energy transfer; Host-guest; Fluorescence correlation spectroscopy.

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## Role of Hydrogen Bonds in Photosynthetic Water Splitting

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### Abstract

This contribution is an attempt to briefly summarize our current knowledge on the role of hydrogen bonds in photosynthetic water splitting leading to molecular dioxygen and hydrogen chemically bound to plastoquinone (PQ). The overall process, which takes place in Photosystem II (PS II), comprises three different reactions sequences [1]: i) light induced generation of the strongly oxidizing chlorophyll cation radical P680<sup>+</sup> and moderately reducing anion radical Q<sub>A</sub><sup>-•</sup>, ii) four-step oxidation of the water oxidizing complex (WOC) by P680<sup>+</sup> via tyrosine residue Y<sub>Z</sub> of polypeptide D1 acting as redox mediator, and iii) two-step reduction by Q<sub>A</sub><sup>-•</sup> of PQ at the Q<sub>B</sub> site.

Sequence i) is not accompanied by deprotonation/protonation reactions, whereas the reactions of ii) and iii) are multi-site proton (PT) and electron (ET) transfer redox steps.

Hydrogen bonds play a key role for the oxidation of Y<sub>Z</sub> by P680<sup>+</sup>. The properties of this reaction (activation energy, kinetic H/D isotope exchange effect, dependence on the redox states) are described and the possible existence of a low barrier hydrogen bond (LBHB) configuration is considered and critically discussed. Marked changes of the reaction coordinates emerge when PS II complexes are deprived of an intact WOC. In addition to Y<sub>Z</sub> also the hydrogen bonding of tyrosine residue Y<sub>D</sub> of polypeptide D<sub>2</sub> is briefly described.

Only limited information is available on the functional role of hydrogen bonding for oxidative water splitting at the Mn<sub>4</sub>O<sub>x</sub>Ca cluster. Therefore the description of the coupling between ET and PT steps and of the mechanistically most relevant steering effect of proton shift(s) on O-O bond formation will be mainly restricted to a few general considerations.

Likewise our knowledge on hydrogen bonding related to protonation pathways coupled with PQ reduction is also rather fragmentary. A brief summary will be presented.

*Keywords:* Hydrogen bonding; Photosynthetic water splitting

## Proton Transfer Reactions in the Excited Electronic States

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### Abstract

Proton transfer reactions are known to be one of the simplest and important transformations in chemistry which can occur both in the ground and excited states of molecular species. Excited state proton transfer (ESPT) reactions belong to one of the main kinds of reactions in photochemistry and refer to relatively new class of reactions. The understanding of ESPT is obviously an essential building block of photochemistry and now also of some fields of nanotechnologies and technologies of bio- and chemical sensing. Extremely important field is study and application of PT reactions in biology. Proton transfer at the surfaces of biological systems is one of the most prevalent reactions in the biosphere - it is used in the aerobic generation of ATP and oxygen. Proton transfer into and out of proteins is important, both for many enzyme reaction mechanisms and proton pumping across membranes.

ESPT reactions can be divided on two large groups: intermolecular and intramolecular ones which often abbreviated in literature as ESIPT. ESIPT is usually observed for systems that are linked already in the ground state by hydrogen bonding between proximate groups participating in reaction. The majority of reaction of this type involve the transfer of a proton from an oxygen donor to an oxygen or nitrogen acceptor. Usually an intramolecular hydrogen bond between the two moieties of molecule facilitates PT. Therefore, hydrogen bonding may be considered as very important intrinsic property of the molecule appearing in ESIPT state.

In this chapter we will focus on results of our study of ESIPT in 3HF and some its derivatives at variation of physical conditions in solutions and use different energies of fluorescence excitation. Herein, we will demonstrate some new original results obtained at selective excitation of fluorescence in different singlet bands of absorption, at different temperatures and employing method of dynamic quenching of fluorescing states of molecules. We describe also study of ESIPT reaction from higher excited states and new methods based on ratiometric approach for

evaluation the rates of this reactions using spectra of fluorescence and excitation of fluorescence.

There will be presented the theory describing effects of dynamic quenching in the frame of two-state excited-state reaction formalism that predicts interesting, non-trivial behavior of two bands in steady-state spectra and carried out experiments the quenching by TEMPO the fluorescence of several 3-hydroxyflavone dyes that exhibit ESIPT reaction and on which the two types of reaction mechanism are observed. In line with predictions of the theory, the quenching changes strongly the distribution of intensities between bands of dual fluorescence for kinetic type of reaction (3-hydroxyflavone) but does not change it for the novel compounds (FA, F) whose excited states exhibit strong charge transfer character. Based on these findings one may suggest that the quenching of fluorescence by an efficient collisional quencher can be a simple and convenient method using only the steady-state experiment for distinguishing the excited-state reactions occurring under thermodynamic or under kinetic controls. The developed theoretical description is not limited to ESIPT; it can be useful in analysis of quenching effects on other photochemical reactions that can be described by two-state excited-state reaction formalism. Based on these findings a simple test can be suggested for the mechanisms of these reactions allowing discrimination of two important cases, of thermodynamic and of kinetic control.

The effects of high-lying excited states and quenching on the fluorescence intensity of both forms of ESIPT dye and on the peculiarities of the definition of the constants of bimolecular quenching and Stern-Volmer constants of initial reagents and products are considered. For products arising in a result of photoreaction in the excited state, these constants could not be correctly obtained from characteristics of product emission at different contents of quencher; new methods for determining collisional characteristics of dyes in solution, which differ from methods commonly used in the case of single-band fluorescence, are substantiated.

It is shown that, generally, upon excitation of molecular objects via high-lying singlet states, the yield of photoreaction products can increase in a number of cases. Then, if fluorescence of fluorophors and their photoproducts is detectable, the probabilities of reactions via high-lying singlet states can be determined by means of fluorescence measurements. Experimental data are presented that demonstrate the roles played by high-lying singlet states at various temperature and dynamic quenching of fluorescence in a solutions of 3-hydroxyflavone.

ESIPT reaction from the  $S_2$  state of 3HF in solutions found recently are discussed in detail. Results of our experiments obtained by means of steady state and picosecond laser spectroscopy methods are presented.

Spectra of the dual fluorescence of 3-hydroxyflavone in different solvents and with picoseconds time resolution were obtained at excitation by tunable picoseconds pulses of the optical parametric generator within  $S_1$  and  $S_2$  bands of absorption. Spectra dynamics reveals time development of the internal proton transfer in the excited state of molecule from the hydroxyl to the carbonyl group. The relative contribution of the tautomer form to integral emission remains essentially higher during all interval of emission observation. The obtained data directly evidence an additional channel of the internal proton transfer from the  $S_2$  singlet state of 3-hydroxyflavone with high kinetic rate.

ESIPT reaction from the  $S_2$  singlet state may take place also for other compounds undergoing the ES IPT process. Some of them are specially synthesised and tested as multiparametric sensors and possess by unique properties in determination of polarity of environment, local electric fields, detection of single molecules of water in membranes and vesicles, various properties of H-bonds. It is possible with their help to detect molecular oxygen in alive cells, the different subdomains of DNA, the ions of different metals, the cholesterol in proteins, apoptosis of cells. It is worth to mention at last that the creation of photoreaction products through the  $S_n^N$  states may concern and some other primary photoreactions, such as redistribution of the electronic density (charge transfer) in the excited state, the protolytic reactions, the H-bond creation, the creation of excimer and exiplexes. Some new applications of ES IPT reaction from  $S_n$  states are discussed.

*Keywords:* Hydrogen bonding; Excited state proton transfer.

# Controlling Excited-State Proton/H-Atom Transfer along Hydrogen-Bonded Wires

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## Abstract

Over the last decade, the use of gas phase experiments and high level calculations has revealed a new possible competitive pathway to Excited-State Proton Transfer (ESPT) along a hydrogen-bonded wire: the Excited-State H-Atom Transfer (ESHAT). The fundamental difference between the two processes is that an electron closely accompanies the proton during the transfer in the latter process. We have been able to build prototype systems in which a Grothuss-like excited-state H-atom transfer occurs along a unidirectional hydrogen-bonded wire connected to an aromatic chromophore that is used as a scaffold. Our work is based on experimental measurements using supersonic expansions and one- or two-color pump-probe experiments, and *ab initio* calculations to model the experimental observations. Here we review some of our investigations of ESHAT and highlight the necessity of closely relating experiment and theory. In particular, we discuss some aspects which either favor or block ESHAT and the need to define a new quantity to characterize the affinity of a system to this kind of reaction. The influence of properties like solvent type or solvation will be illustrated mainly by describing the investigations of clusters of 7-hydroxyquinoline chromophore with ammonia or water wires and the fluorescent moiety of the green fluorescent protein consisting of a serine-tyrosine-glycine derived chromophore and its close hydrogen-bonded environment.

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## Excited State Proton Transfer via Hydrogen Bonded Dimers and Complexes in Condensed Phase

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### Abstract

Contemporary progress regarding the excited-state proton transfer (ESPT) in condensed phase has been reviewed via three aspects: (1). Biprotic transfer within doubly H-bonded homo- or hetero- dimer, (2). Proton transfer through a host/guest types of hydrogen bonded complexes and (3). Proton transfer through solvent relay, and solvation dynamics coupled proton transfer. For (1), of particular emphases are ESPT of 7-azaindole (7-AI) and its various corresponding analogues. As for 7-AI (and analogues) homodimer, the concerted versus stepwise ESPT process has raised intensive debate during the past decade. Review will be on the basis of both experimental and theoretical approaches, in which roles of experimental parameter, hydrogen-bonding strength and configuration (i.e. geometry) on reaction dynamics are discussed. The results are then fairly compared with ESPT in heterodimer. In addition to the dynamical concern, as for the aspect (2), excited-state thermodynamics are of importance to fine-tune the proton transfer reaction. Relevant fundamental and applications will be reviewed and discussed. For (3), various mechanisms of protic solvent assisting ESPT will be reviewed, among which plausible resolution will be deduced and discussed. Particular attention is given to reaction dynamics in alcohol and aqueous solutions, aiming at its future perspective in biological applications. Finally, the differentiation in mechanism between solvent diffusive reorganization and solvent relaxation to affect the ESPT dynamics will be made and discussed.

*Keywords:* Hydrogen bonding; excited state proton transfer; dynamics.



# Ab initio QM/MM Excited-State Molecular Dynamics Approach Using the Effective Fragment Potential Method

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## Abstract

We have recently developed an ab initio molecular dynamics (AIMD) code for examining excited-state reaction processes in solution, by utilizing QM/MM (quantum mechanics / molecular mechanics) methodology. A state-averaged CASSCF method is applied to describe the electronic structures of target molecules (QM part), while the effective fragment potential (EFP) is employed to represent the solvent water molecules (MM part). In this review, we give a brief description of the AIMD-QM/MM-EFP method, and introduce two illustrative applications on (1) the excited-state hydrogen transfer reaction of 7-azaindole in water solution, and (2) the excited-state dynamics of coumarin 151 in water solution.

*Keywords:* Hydrogen bonding; QM/MM; ab initio molecular dynamics; excited state.

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## Excited States Intramolecular Proton Transfer Processes on Some Isomeric Naphthalene Derivatives – a DFT Study

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### Abstract

Potential energy (PE) curves for the intramolecular proton transfer in the ground (GSIPT) and excited (ESIPT) states of 1-hydroxy-2-naphthaldehyde (1H2NA) and 2-hydroxy-3-naphthaldehyde (2H3NA) were studied using DFT/B3LYP(6-31G) and TD-DFT/B3LYP(6-31G) level of theory respectively. Our calculations suggest the non-viability of ground state intramolecular proton transfer for both the compounds. Excited states PE calculations support the ESIPT process to both 1H2NA and 2H3NA. The wide difference in ESIPT emission process of 1H2NA and 2H3NA have been explained in terms of HOMO and LUMO electron density of the enol and keto tautomer of these two compounds.

*Keywords:* GSIPT, ESIPT, 1H2NA, 2H3NA, DFT, B3LYP, PE.

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## Conformational Switching Between Acids and Their Anions by Hydrogen Bonding

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### Abstract

Weak acids, such as thiols, phenols, and carboxylic acids under hydrophobic conditions, exhibit low  $pK_a$  values because of neighboring amide NH. Anions formed upon the deprotonation of RXH (R = alkyl or aryl; X = S, O) are stabilized by  $NH\cdots X$  hydrogen bonds between X- and amide NH. In metal-anion complexes, these hydrogen bonds increase the formation constant because of  $pK_a$  shift and  $p\pi-d\pi$  interaction. A hydrogen bond does not form between XH and the neighboring amide NH in the ground state; rather, an extremely stabilized structure with  $NH\cdots X$  hydrogen bonding formed by deprotonation is subject to a large conformational change between acid without prelocated amide NH and its anion. Thus, deprotonation-driven conformational switching is achieved using a cyclohexane skeleton in amidated Kemp's acids, unsymmetrically linked phenolic oligoamides, Asp-containing oligopeptides, and photo-induced  $pK_a$  shifting compounds. P-450 peptide model complexes exhibit various exchangeable properties with competition between  $NH\cdots S$  hydrogen-bonding structure and  $\alpha$ -helix. The prelocation of the neighboring amide NH toward acids shifts the  $pK_a$  value.

*Keywords:* Hydrogen bond; Thiol; Carboxylic acid; Phenol; Prelocated amide NH;  $pK_a$  shift, Metal-ligand bond; Formation constant; Metal-ligand covalency

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## Charge Transfer in Excited States: ab initio Molecular Dynamics Simulations

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### Abstract

During past few years, the study of excited state phenomena has gained momentum due to its importance in atmospheric chemistry and photochemistry by new developments in experimental and theoretical methods. This book chapter summarizes our current knowledge of theoretical methods used to study photoexcitation phenomena of hydrated halides, water clusters, hydrated iodic acid, and pyrrole-water clusters by using excited state ab initio molecular dynamics simulations employing the complete-active-space self-consistent-field method. We are able to explain charge-transfer-to-solvent driven femtosecond-scale dynamics by the time evolution of geometrical parameters, kinetic energies, and charges during the excited state simulations. In the case of hydrated halides (I-(H<sub>2</sub>O)<sub>n=2-5</sub>), an excess electron is transferred from the iodine anion to the solvent and is stabilized by the water cluster which results in the dissociation of hydrated halides into halide radicals and electron-water clusters. In the case of water clusters, two different but complementary mechanisms of photoexcitation and photoionization for water photolysis have been proposed. For hydrated iodic acids, hydrogen radicals (or molecules) and iodine radicals are released upon excitation. In the case of pyrrole-(H<sub>2</sub>O)<sub>1-2</sub> clusters, upon excitation the charge density is located over the farthest water molecule which is repelled by the depleted  $\pi$ -electron cloud of pyrrole ring, resulting in a highly polarized complex. Hence, ab initio excited state dynamics has been proven to be very promising in explaining photoexcitation reactions in real time.

*Keywords:* Hydrogen bonding; Charge Transfer; Dynamics simulations.

## Competitive ESIPT in o-hydroxy Carbonyl Compounds: Perturbation through Solvent Modulation and Internal Torsion

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### Abstract

Excited State Intramolecular Proton Transfer (ESIPT) is a direct manifestation of transfer of a proton (rather hydrogen atom) through a preformed intramolecular hydrogen bond (IHB) between the adjacent donor and acceptor groups upon excitation and leading to the formation of a tautomeric species, often characterized by largely Stokes shifted fluorescence emission. ESIPT processes are important both from scientific and technological point of view, like in the fields of ESIPT laser, memory storage devices etc. However, any perturbation in IHB, either through the involvement of another component (e.g. solvent etc.) or through the internal rotation of the participating groups, can lead to a competition between the formation of ESIPT product or relaxation through “normal” emission. Understanding the ESIPT process and its perturbation through external influence in different systems can lead to important conclusions about their practical use as well as the nature of several other prototropic species those can be formed in the reaction media. In this present contribution, we review the recent literature on ESIPT of o-hydroxy carbonyl compounds and its perturbation through solvent participation as well as torsional motion of the neighboring groups leading to the formation of multiple species in the excited state.

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*Keywords:* Hydrogen bonding; Electronic excited states; ESIPT.

## Excited State Double Hydrogen-Bonding Induced by Charge Transfer in Isomeric Bifunctional Azaaromatic Compounds: Pyrido-Indole and Pyrrolo-Quinoline Derivatives.

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### Abstract

In this review, we analyze ground and excited state effects induced by hydrogen bonding compounds in two series of isomeric bifunctional azaaromatic chromophores based on pyrido-indole [betacarboline and methylene-bridged 2-(2'-pyridyl)indoles] and pyrrolo-quinoline derivatives. These families possess both a hydrogen bond donor (N-H pyrrolic group) and a hydrogen bond acceptor (pyridine-type nitrogen atom). In addition, these compounds present photo-induced changes in the electronic distribution, which alter the acid/basic properties in both groups in the excited state. This charge transfer originates a variation of their reactivity. These groups can originate an intermolecular double hydrogen bond altering completely the excited-state behaviour of the chromophore, provoking phototautomerization phenomena. Depending on the spatial separation between the functional groups, this phototautomerization can occur directly by formation of dimeric species or by an appropriate protic partner acting simultaneously as a proton donor and an acceptor. Hence, photophysics of these compounds shows a high sensitivity to solvent and environment.

*Keywords:* Hydrogen bonding; Excited states double hydrogen bonds; phototautomerization phenomena.

# Unusual Rheology of Hydrogen Bonded Large Molecular Aggregates of Charged Amphiphiles: Photochemistry and Photophysics of Hydroxy Aromatic Dopants

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## Abstract

The self-assembly of amphiphilic molecules often develops a variety of interesting structures of different shapes and sizes. Among the most fascinating of these are the 'wormlike micelles', which are flexible cylindrical chains with radii of a few nanometers and contour lengths up to several micrometers. These attractive structures are similar to polymer chains in their ability to entangle into viscoelastic networks but, unlike polymers they display shear induced unusual rheology if formed at low amphiphilic concentrations in presence of hydrotropic organic salts.

Recently it has been shown that neutral aromatic molecules with hydrogen bonding functionalities (e.g., substituted phenols and naphthols) are also efficient promoters, which not only form long wormlike micelles in charged amphiphiles but also trigger transition from wormlike micelle to vesicle as well. Vibrational, electronic absorption and emission spectroscopies demonstrate the role of hydrogen bond in such microstructural transitions.

The shear induced non-linear rheological changes of wormlike micellar solutions bring about problem in viscosity measurement because torsional shear rheometers apply considerable stress during measurement and the zero-shear viscosity becomes obscure. On the other hand, the quantum yield of emission of naphthols in wormlike micelles are very sensitive to the solution viscosity and this offers an interesting route of fluorescence monitoring of unperturbed solution viscosity as a function of applied shear. It is indeed interesting that the

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systems display identical emission intensity vs shear rate changes as that of the viscosity-shear profile and the photochemistry and photophysics of naphthols in organised media control the phenomena via excited state proton transfer (ESPT) and hydrogen bonding. Naphthols possess two strongly overlapped bands in the near uv region viz., the longitudinally polarised  ${}^1L_a \leftarrow {}^1A$  band and the transversely polarised  ${}^1L_b \leftarrow {}^1A$  band. The solvent water induces a strong coupling between the reactant excited states prior to excitation, two new adiabatic potential energy surfaces are formed. These no longer are well described as only  $L_a$  or  $L_b$  and be more generally denoted as  $S_1$  and  $S_2$  states. The barriers for motion of the proton can as a result, be low enough for the first vibrational eigen states to be above the barrier, permitting the ESPT to occur spontaneously. The fast deprotonation process of hydroxy aromatic compounds are significantly retarded in micelles. This results in a marked increase in the intensity and life time of the neutral emission and the rise time of the anion emission. Many ambiguous results have been reported and the explanations were not unequivocal. Attempt has been made to explain these results by means of making and break of hydrogen bonds.

*Keywords:* Hydrogen bonding; Excited states; Self-assembly of amphiphilic molecules; Excited state proton transfer (ESPT); Photochemistry and Photophysics

## Excited-State Intramolecular Proton Transfer in Benzoxazole Derivatives

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### Abstract

The mini review discusses the fundamental aspects of 2-(2'-hydroxyphenyl)benzoxazole (HBO) system, whose fluorescence characteristics is influenced by various environmental changes such as substitution, solvent polarity and temperature. The discussion is based on the influence of those environmental changes on the pKa of the chromophore in excited state, which has direct impact on the proton transfer. Comparison is made with 2,5-bis(benzoxazole-2'-yl)benzene-1,4-diol derivative, bis(HBO) system, in which two benzoxazole rings are locked into a coplanar structure. Specific attention is paid to correlate the H-bonding characteristics (strength & bond length) with the observed fluorescence.

*Keywords:* Hydrogen bonding; Excited-state intramolecular proton transfer.

## Ultrafast Dynamics of the Excited States of Hydrogen-Bonded Complexes and Solvation

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### Abstract

Intermolecular hydrogen bond formed between two molecules is a 'site-specific' local interaction and determines the structure and reactivity of a large variety of molecular systems. In solution, while the solute molecule (called the *probe*) undergoes a change in charge distribution following photoexcitation, the solvent molecules associated with it need to reorganize themselves to minimize the free energy of the excited state of the probe, called the solvation. The dynamic aspect of polar solvation, which arises due to the long-range coulombic interaction, has been studied extensively over the last three decades. In case the probe and the solvent molecules are associated via hydrogen-bonding in the ground state, the hydrogen bond needs to be reorganized in the excited state and the relaxation dynamics of the hydrogen bond has a very important role to play in the dynamics of solvation of the excited state of the probe. It has a special significance to photochemists, since the hydrogen bond acts as an efficient accepting mode for nonradiative energy in the excited state. Hydrogen bond dynamics also play an important role in the intramolecular charge transfer process. Although the effect of intermolecular hydrogen bonding interactions on the electronic states of a probe molecule has been extensively studied by steady state spectroscopy, a few studies have been perceived on the dynamic aspects of solvation by specific hydrogen-bonding interaction only in recent times. Femtosecond time-resolved electronic absorption spectroscopic technique has been shown to be a useful technique to reveal useful information regarding the dynamics of hydrogen bond reorganization process in a few carefully chosen probe molecules, such as, an aromatic molecule containing a carbonyl group, which form hydrogen-bonded

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complex with the solvent. Significant differences observed in the evolution of the spectroscopic properties of the S1 state of the probe molecule in protic and aprotic solvents following photoexcitation, obviously suggested the role of hydrogen bond reorganization process in the relaxation dynamics of the excited state of the probe molecule. This has been confirmed by the similarities in the dynamics using different kinds of probe molecules. Linear correlation between the lifetimes of the equilibration process occurring because of repositioning of the hydrogen bonds and Debye or longitudinal relaxation times of the normal alcoholic solvents establish the fact that, the hydrogen bond dynamics can be described as merely a solvation process. However, recently developed femtosecond time-resolved infrared absorption technique provides mode specific and site-specific information and are capable of recording real-time snapshots of the hydrogen bond motions, both in the ground and excited states of the hydrogen bonded complexes. In the present article, the recent studies on the ultrafast dynamics of hydrogen bond investigated using femtosecond visible and IR absorption spectroscopic techniques have been reviewed.

*Keywords:* Hydrogen-bonded complex, Steady-state and time-resolved visible and IR absorption spectroscopy, Excited state of hydrogen-bonded complex, Hydrogen bond reorganization.

## Reaction Volume for the Photoinduced Proton Transfer in Aqueous Solutions of 6-Methoxyquinoline

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### Abstract

In this work we report the time-resolved determination of the volume changes for the excited (and ground) state proton transfer reactions of aqueous solutions of the aromatic ethersubstituted compound 6-methoxyquinoline. Photoinduced proton abstraction from the solvent is accompanied by a fast contraction due to the solvation of the newly formed ions, and is followed by an expansion of equal amount, associated with reestablishment of the pre-pulse equilibrium. From the pH dependence of the measured volume changes we could estimate the excited state  $pK_a^*$  as  $11.8 \pm 0.1$ . In addition we could also determine the quantum yield for proton abstraction from water as  $0.33 \pm 0.04$ .

*Keywords:* Hydrogen bonding; Reaction Volume; Photoinduced Proton Transfer.

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## Molecular Recognition and Chemical Sensing of Anions Utilizing Excited-State Hydrogen-Bonding Interaction

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### Abstract

Hydrogen-bonding interaction plays crucial roles at the interface between physics, chemistry, biology and various multidisciplinary areas of science. Upon photo-excitation, an excited-state molecule changes the charge distribution and consequently dipole moment and its intermolecular interaction with solvent molecule(s)/guest that determines the outcome of the excited molecular species. Some molecules have larger dipole moment in electronic excited state than in the ground state and this dynamic change of dipole moment induces strong hydrogen bonding interaction in the excited state. After electronic excitation, basic part (proton acceptor) of a molecule becomes more basic and acidic part (proton donor) becomes more acidic because of redistribution of electronic charges. When basic and acidic parts/groups are in close proximity with suitable geometry in such a way that hydrogen bond formation are possible and, therefore, the excited state inter/intramolecular proton transfer may take place. This excited state proton transfer offers an opportunity for molecular recognition and signal transduction by judicious choice of functionality in artificial receptors. With complementary functionality, an artificial receptor molecule recognizes suitable guest and the “molecular information” is remained in the interacting partners, which may be transduced into signal output after redistribution of  $\pi$ -electrons of host-guest complexes through excited-state proton transfer reaction. This transduced signal can be further enhanced by introducing multiple H-bonding interactions, which in turn will maximize recognition capacity and may be applied for chemical sensing.

*Keywords:* Hydrogen bonding; Electronic excited states; Molecular recognition; Chemical Sensing.

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## Theoretical Studies of Green and Red Fluorescent Proteins

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### Abstract

The Green Fluorescent Protein (GFP) has caused a revolution in cellular and molecular biotechnology over the last two decades. In the GFP, excited state as well as ground state proton transfers occur via a hydrogen bond network of water and amino acid residues and play a vital role for conversion of the UV light absorbed at 395 nm into the green fluorescence emitted at 508 nm. This fluorescence is highly visible, efficiently emitting, and amazingly useful in scientific research, because it allows us to look directly into the inner workings of cells. In recent years the photophysical mechanism of the GFP has received considerable attention, including important theoretical work. Theoretical studies include ab initio calculations of the GFP chromophore and its immediate surrounding residues, mixed quantum mechanics/molecular mechanics (QM/MM) calculations and molecular dynamics (MD) simulations. In this chapter, we review our recent theoretical studies of mechanistic aspects of the GFP photocycle, including structures, energetics, proton transfer dynamics, spectral properties and reaction mechanism. For ground state proton transfers, we have employed density functional theory (DFT) initially, and then extend our investigations into the excited state proton transfers using high level ab initio methods including complete active space self-consistent field (CASSCF) and multi-reference configuration interaction (MRCI) methods. Exact nuclear quantum dynamics (QD) simulations have also been explored, through which we can predict the rate constants of proton transfer reactions and extract the kinetic isotope effects (KIE), and then compare the simulations with

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experimental results in order to understand the underlying reaction mechanisms. In addition, we review our recent work for related red fluorescent proteins (RFPs), with an emphasis on calculations aimed at exploring the relationship between the stability of different isomeric forms of the chromophore and fluorescence quantum yield, via both bare chromophore and whole-protein quantum mechanical / molecular mechanical (QM/MM) methods.

*Keywords:* Proton transfer; Kinetic isotope effect (KIE); Fluorescent protein; Hydrogen bonding network; Internal conversion.



## Changes in Active Site Hydrogen Bonding upon the Formation of the Electronically Excited State of Photoactive Yellow Protein

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### Abstract

Photoactive yellow protein (PYP) is a bacterial blue light photoreceptor that exhibits photochemistry based on its negatively charged *p*-coumaric acid (*p*CA) chromophore. In the initial dark state of PYP the *p*CA chromophore is in the *trans* configuration, and forms three functionally important hydrogen bonds with its protein binding pocket. First, the deprotonated phenolic oxygen of the *p*CA is strongly hydrogen bonded to the side chains of Glu46 and Tyr42. Secondly, the carbonyl oxygen of the *p*CA hydrogen bonds with the backbone NH group of Cys69. We review information on the kinetics of ultrafast transitions in the PYP photocycle obtained by various spectroscopic methods, and summarize available vibrational marker bands for molecular events in PYP. We use this information to evaluate current understanding of hydrogen bonding in the electronically excited state of PYP. Analysis of cryotrapped and time-resolved infrared and resonance Raman spectroscopic data has shown that during the first stage of the photocycle *p*CA *trans* to *cis* isomerization flips the position of the *p*CA carbonyl oxygen, disrupting its hydrogen bond with Cys69 while keeping the hydrogen bond to Glu46 intact. Sub-picosecond time-resolved and polarization sensitive infrared measurements indicate that in the electronically excited state of PYP the hydrogen bond between Glu46 and the *p*CA is weakened without the occurrence of a change in orientation of the Glu46 side chain. This shows that the phenolic ring of the *p*CA and the side chain of Glu46 do not undergo significant motions upon formation of the excited state. The concomitant weakening of the hydrogen bond between these two groups has been attributed to a large change in charge distribution upon

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formation of the electronically excited state of the *p*CA. Disruption of the *p*CA C=O – Cys69 excited state hydrogen bond has been reported to be a key step for the successful entry into the PYP photocycle. Further structural interpretation of the vibrational signals of the electronically excited state of the *p*CA in terms of hydrogen bonding interactions will require isotope-edited ultrafast infrared measurements and vibrational calculations.

*Keywords:* Hydrogen bonding; Photoactive yellow protein; Electronic excited states; Vibrational modes.

## Ultrafast catalytic processes in the light-driven enzyme protochlorophyllide oxidoreductase (POR)

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### Abstract

The enzyme protochlorophyllide oxidoreductase (POR) catalyses the reduction of protochlorophyllide (Pchl<sub>id</sub>), which is a key light-driven reaction in the chlorophyll biosynthetic pathway and triggers a profound transformation in plant development. As POR is light activated it can provide new information on the way in which light energy can be harnessed to power enzyme reactions and it presents us with a unique opportunity to study catalysis at low temperatures and on ultrafast timescales, which are not usually accessible for the majority of enzymes. The recent advances in our understanding of the catalytic mechanism of POR illustrate why it is an important generic model for studying enzyme catalysis and reaction dynamics. The reaction involves the addition of two protons and two electrons and catalysis is induced by the absorption of light by the Pchl<sub>id</sub> substrate. As the reaction involves the Pchl<sub>id</sub> excited state, a variety of ultrafast spectroscopic techniques have shown that significant parts of the reaction occur on the picosecond timescale. It has been suggested that the formation of a precursor species, in which Pchl<sub>id</sub> forms a strongly hydrogen-bonded complex with residues in its direct environment and/or NADPH, is essential for the subsequent hydride and proton transfer steps to proceed on a microsecond timescale. Herein, we provide a detailed review of spectroscopic investigations on POR, with a particular focus on recent time-resolved transient absorption and fluorescence experiments.

*Keywords:* Proton, hydride, femtosecond, conformation, activation, FTIR.

*Abbreviations used:* ps, picosecond; fs, femtosecond.

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## Photodissociation of Molecules in Hydrogen Bonded Clusters Probing the Excited State

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### Abstract

We review our recent results on the photodissociation of hydrogen bonded clusters. They are generated in supersonic expansion and subsequently photolyzed. Hydrogen atoms leaving the clusters are detected and the kinetic energy distributions (KEDs) of these outgoing fragments are determined. In the KED spectra, we distinguish three regimes with an increasing kinetic energy: those products which are slowed down by the cluster cage, those which leave it unperturbed and those which gain energy in processes following primary photodissociation. We have analyzed the shapes of the kinetic energy spectra and identified important reaction channels. Our experiments are accompanied and interpreted with theoretical calculations which are based on state-of-the-art *ab initio* methods.

Photoinduced processes in two classes of hydrogen bonded clusters are presented in this review: Photochemistry (1) in aqueous systems and (2) in hydrogen bonded heterocyclic clusters. In aqueous photochemistry, we have identified the hydronium radical  $\text{H}_3\text{O}^\bullet$  to be the central intermediate. This intermediate can be formed either in the excited state as is the case of pure water clusters or in a two step process involving acidic dissociation followed

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by a charge-transfer-to solvent absorption. The latter mechanism is found in water clusters doped with hydrogen halides (HCl, HBr). We have also shown in our studies that these hydrogen halides are very likely dominantly present in a form of contact ion pairs under our experimental conditions. These results are potentially relevant in the fields of atmospheric chemistry and also in radiation chemistry since it has been previously argued that the  $\text{H}_3\text{O}^+$  radical can serve as a model of the solvated electron.

In the second part of our review, we investigate the photochemistry of pyrrole, imidazole, and pyrazole clusters. While all these clusters consist of 5-membered nitrogen rings, their bonding is quite different. Pyrrole clusters are bound via  $\text{NH}\cdots\pi$  interactions, imidazole clusters via single hydrogen bonds and pyrazole clusters via double hydrogen bonds. The photochemistry of these rings is always characterized by a competition between direct dissociation of the N-H bond on the  $\pi\sigma^*$  state and regeneration of the ground state via the  $\pi\pi/S_0$  intersection, followed by a fragmentation of the molecule in the ground state. In cluster environment, the dissociation pathway is always suppressed. Furthermore, we discuss the possibility that a new reaction channel, excited state hydrogen transfer followed by a ground state recovery, appears in the hydrogen bonded systems. In this case, the excess energy is dissipated between two partner molecules. The photostability of these systems is thus guaranteed.

*Keywords:* photodissociation, hydrogen bonded clusters, pure and doped water clusters, clusters of 5-membered aromatic rings, hydronium radical, solvated electron

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