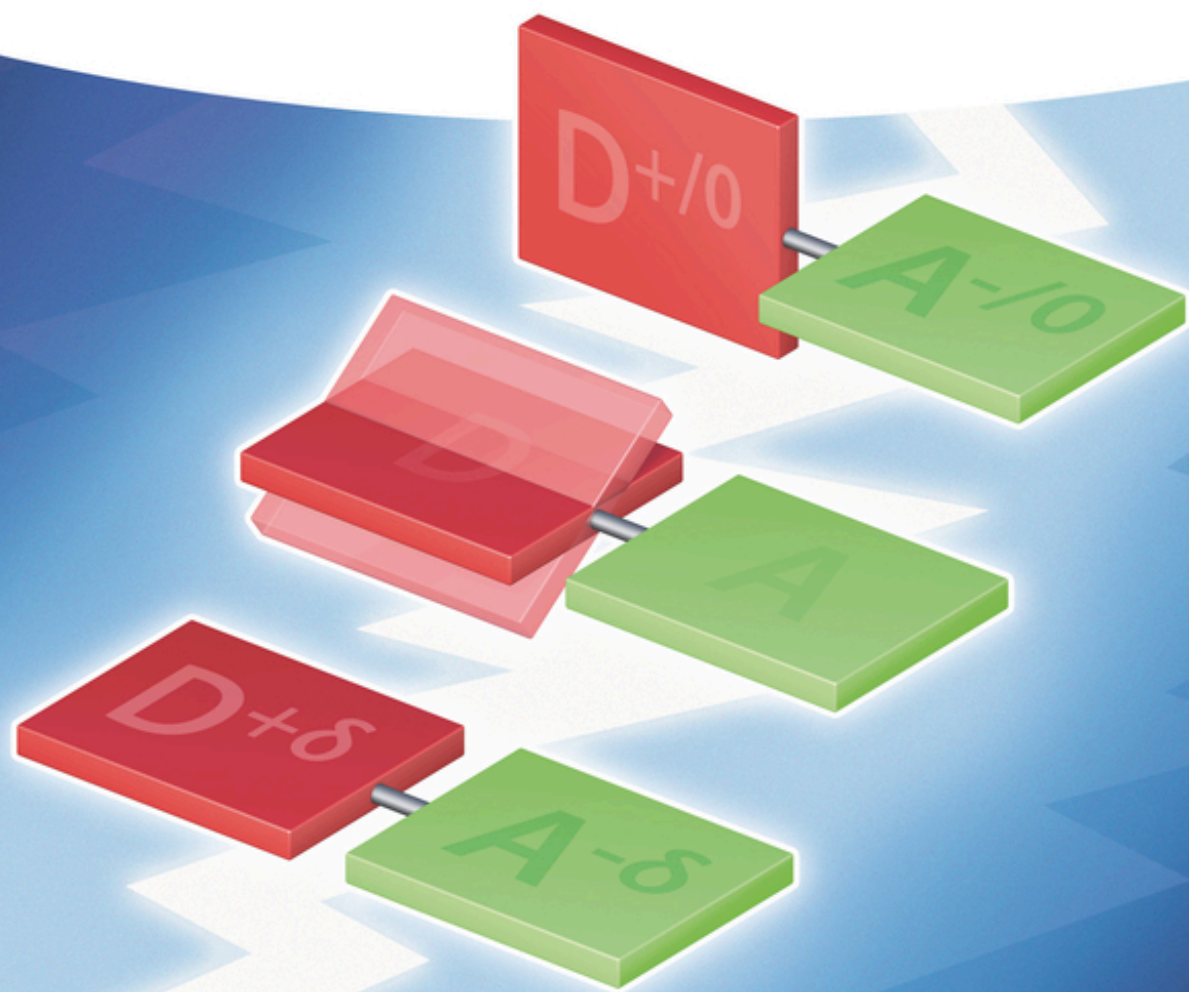


Ramprasad Misra and S.P. Bhattacharyya

Intramolecular Charge Transfer

Theory and Applications



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Preface

Over the last two decades, intramolecular charge transfer (ICT) molecules have been receiving wide-spread attention of scientists in view of their potential for technological applications in molecular electronics, solar cells, quantum optics, sensors, and so on. Organic ICT molecules in particular have been at the primary focus as they provide better stability and flexibility in design than the standard inorganic molecules. A large number of research publications dealing with different aspects of these molecules have been added to the literature over the recent years. We felt that a wide gap already exists between information available in books and monographs accessible to the graduate and Masters students as well as beginners in research and those available in specialized journals, and the gap is increasing by the day. A researcher interested in designing new organic nonlinear optical (NLO) material or ICT based sensor or molecule based materials for organic electronics, or a general reader curious to understand the ICT phenomenon more completely would welcome a book that bridges the that gap seems to exist. This book attempts to address the issue by providing a pedagogical description of the different stages and facets of ICT phenomenon and what goes behind the designing of ICT based materials for technological applications; what problems are to be taken care of and how to leverage theory and experiments in a specific context, and so on. In addition to an overview of the recent theoretical and experimental developments relating to ICT molecules and the ICT phenomenon the book contains a brief history of past efforts in this area. Charge transfer is a rather ubiquitous process in nature and a fundamental step in many chemical and biological processes, like photosynthesis and metabolism, for example. The ICT in conjugated π -electronic systems has attracted serious attention in view of the immense technological applications that the process has for example, in organic electronics and photovoltaics. Materials based on such molecules are potential candidates for organic light-emitting diodes (OLEDs), field effect transistors, dye-sensitized solar cells, and so on. In fact the main impetus to study electron transfer (ET) process in organic molecules and materials came from the urge to understand the mechanism of photosynthesis in plants and bacteria with the hope that the knowledge gained in the process would help the scientists in designing artificial photosynthetic systems for efficient conversion and storage of solar energy. The search for such systems is still on with a long way to go. Regular stocktaking is therefore essential in such a critical field of research.

The contents of the book have been divided among seven chapters as detailed in the following. In the introductory chapter (Chapter 1) the basics of the ICT process has been discussed laying the foundation for the next five chapters (Chapters 2–6). The rather long history of evolution of the idea of ICT process and ICT molecules has been presented in Chapter 2 to place the modern developments in a proper perspective. The ICT molecules most frequently studied with steady state and time-resolved spectroscopic techniques in the UV–visible range; specially, time-correlated single photon counting (TCSPC) and fluorescence up-conversion techniques have been found widespread use for time-resolved studies on ICT. Two other useful techniques for probing ICT have been femtosecond transient absorption (TA) and resonance Raman spectroscopy. A relatively recent and novel experimental tool to follow the ICT dynamics is the terahertz (THz) spectroscopy. The idea behind the THz spectroscopy is simple. The ICT process involves movement of electronic charge from one end of the molecule to the other. If the charge is accelerated, electromagnetic (EM) radiation will be emitted. Assuming that the ICT occurs on a timescale of picoseconds, the frequency of the EM radiation will be in the THz range that can be detected and monitored. It is, as if, the moving charge “broadcasts” its own dynamics opening up a direct route to follow the ICT dynamics. We have devoted some space to this new mode of studying the ICT process – the so called THz spectroscopy.

A lot of theoretical calculations (modeling as well as calculations) on ICT molecules are now available in literature. The calculations have been mostly done at the Hartree–Fock (HF) level and of late increasingly at the level of the complete active space self-consistent field (CASSCF) method or CASSCF with second-order correction incorporated (CASPT2) along with variants of density functional theory (DFT) and time-dependent density functional theory (TDDFT) methods. Although majority of such calculations have been done at the adiabatic level, there has been a “paradigm shift” in the sense that theoreticians are increasingly looking into the very important role played by non-adiabatic factors in shaping the ICT process. The Chapter 3 is devoted to the relatively newer theoretical and experimental techniques that are being used to unravel the mystery of the ICT process and model ICT rates.

It is now firmly established that the ICT process is critically affected by the properties of the medium in which it occurs. Not only are the spectral signatures of the ICT molecules modulated by the polarity and hydrogen bonding abilities of the solvents, the ICT rate is also affected by thermal effects (temperature) and friction (solvent viscosity). Several ICT molecules have therefore been exploited as polarity and viscosity sensors. Such media effects on the ICT process have been elaborately discussed in Chapter 4. As mentioned already, the ICT molecules have technological relevance and are being explored for fabricating new molecules based NLO or halochromic materials, materials for solar cells, for OLEDs, for viscosity and polarity sensors, and so on. In view of the importance of the field and diversity of issues, we have devoted two consecutive chapters to discuss technological applications of ICT molecules (Chapters 5 and 6). The NLO phenomena with emphasis on hyperpolarizabilities that the ICT molecules are

endowed with and several aspects of ICT based two-photon absorbing materials are dealt with in Chapter 5. Several issues with technological applications of ICT molecules in sensing, in OLEDs, and so on are examined in the penultimate Chapter 6 while Chapter 7 is devoted to consider future projection of research in ICT in backdrop of important developments that have already taken place.

This book is a review of studies of ICT process and related phenomena. We have reported results available in contemporary literature in good faith. Permissions for copyrighted materials have been duly obtained from the copyright holders. The book is primarily intended for the Masters and graduate (doctoral) students of chemistry and chemical physics. We hope that more specialized people too, will find the book useful. We have tried to strike a balance between experiment and theoretical aspects with the hope that it caters the need of the both theoreticians and experimentalists alike. In spite of our best efforts to make the compilation error-free, some unfortunate and unintended omissions might still be crept in. We sincerely regret any such blemishes.

We are happy to acknowledge the help and constant encouragement of colleagues and friends without which the book might not have seen the light of the day. A major part of the book was written while the authors were in the Indian Association for the Cultivation of Science (IACS). We thank all our colleagues in the Department of Physical Chemistry, IACS for providing the intellectual ambience needed for undertaking the project. We specially thank Prof. D.S. Ray and Prof. S. Adhikari for all the help and encouragements they extended to us. One of the authors (RM) wishes to thank his present mentor Prof. M. Sheves of the Weizmann Institute of Science for his constant support. RM is grateful to his parents, wife (Piyali), and other family members for their unfailing supports and encouragement. SPB wishes to express indebtedness to Bharati (wife), Rupsha (daughter), and Sayan (son) for their unfailing support and the colleagues in the Department of Chemistry, IIT Bombay for making his stay in the department (2012–2015) as Raja Ramanna fellow (DAE) fruitful.

August 21, 2017
Kolkata

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1

Introduction

1.1 An Overview of the ICT Process

Charge transfer is a fundamental step in many chemical and biological processes, including photosynthesis and metabolism [1–4]. The recent technological applications of charge-transfer-based materials include organic-light-emitting diodes (OLEDs), solar energy conversion, fluorescence sensing, nonlinear optical (NLO) materials, and so on [5–7]. The charge-transfer process may be divided into two broad categories. The transfer of charge from an electron-rich donor moiety to an electron-poor acceptor part located in different molecules is known as intermolecular charge-transfer process. However, if the donor and the acceptor belong to the same molecule, the phenomenon is called intramolecular charge-transfer (ICT) process. The ICT process generally occurs in the photoexcited state which a molecule reaches due to absorption of light of proper wavelength. The photoexcitation facilitates transfer of an electron from one part of a molecule/ion to its other part in the excited state, which makes the charge distribution in the excited state markedly different from that in the ground state. The through-bond ICT occurs in molecules in which the donor and the acceptor groups are connected through a π -electron bridge (Figure 1.1). In some rare cases, an intramolecular through-space charge transfer is observed, where the transfer of charge through the conjugative path is denied but donor and acceptor groups are in a favorable position for charge transfer. Although the intermolecular interaction mediated by through-space charge transfer dictates the properties of many π -stacked molecular systems, studies of intramolecular through-space charge transfer is scarce. In π -conjugated organic molecules comprising electron donor (D) and acceptor (A) subunits, the process has attracted a lot of attention due to their immense technological implications in organic electronics and photovoltaics [5–14]. Materials based on such organic molecules are potential candidates for use in OLEDs, field-effect transistors, dye-sensitized solar cells, to name a few. In this book, our focus is mainly on the excited-state ICT in stable organic molecules as well as in inorganic complexes. A few examples of the electron-transfer process in biomolecules have also been discussed. The signatures of ICT, spectroscopic techniques, and theoretical tools employed to study this process are also mentioned. It is now known that

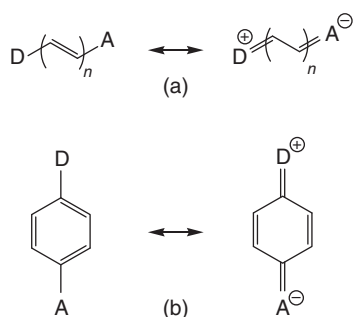


Figure 1.1 The intramolecular charge-transfer processes (a) in a (poly)ene system and (b) in an aromatic donor–acceptor molecule. Donor (D) to acceptor (A) charge transfer occurs in the excited state through the π -electron bridge to form an ICT state of higher dipole moment.

excited-state ICT in organic molecules may give rise to dual emission in its electronic spectrum. The peak seen at the blue end of the emission spectrum is generally believed to be arising from a locally excited (LE) state of the molecule, while the peak at the red end is generally assumed to bear the signature of an ICT species formed in the excited state. The ICT process generally occurs in polar solvents and the Stokes-shifted ICT fluorescence is observed due to solvent stabilization in the excited state [15]. In Figure 1.2, the potential energy surfaces (PES) for the ground state S_0 and the first two excited states (S_1 , S_2) have been depicted along with the LE and ICT states. The vertical coordinate represents energy, while the horizontal coordinate (ξ) comprises all molecular changes accompanying the LE \rightarrow ICT reaction, such as changes in bond lengths and bond angles. In the given example, excitation of the molecule leads it to the S_2 state, which relaxes through internal conversion to the equilibrated LE state. The ICT reaction proceeds from the LE to the ICT state that has a

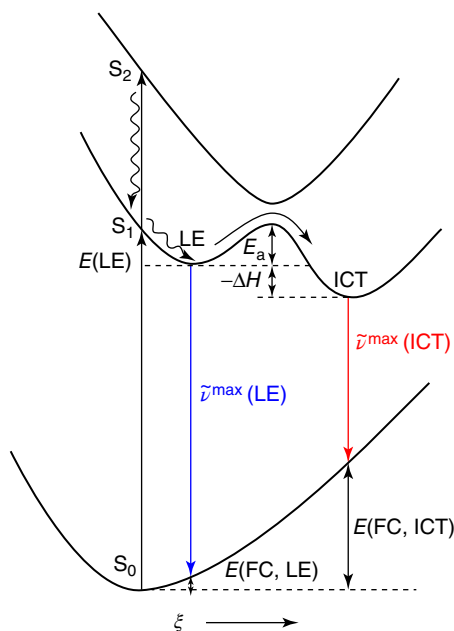


Figure 1.2 Schematic representation of intramolecular charge transfer (ICT) process in a model system. In the given scheme, excitation leads the molecule to the S_2 state from which it reaches the S_1 -LE state through internal conversion. The ICT state is accessible through the S_1 -LE state. Emission from both the LE and ICT states leads to dual emission from the molecule. (Druzhinin *et al.* 2010 [15]. Reproduced with permission of American Chemical Society.)

reaction barrier E_a and an enthalpy difference of ΔH . Fluorescence from the LE and ICT states reaches the corresponding Franck–Condon states $E(\text{FC}, \text{LE})$ and $E(\text{FC}, \text{ICT})$. This gives rise to dual fluorescence with emission maxima of $\tilde{\nu}_{\text{max}}(\text{LE})$ and $\tilde{\nu}_{\text{max}}(\text{ICT})$, respectively. Lippert and coworkers reported the dual fluorescence in 4-*N,N*-dimethylaminobenzonitrile (DMABN) for the first time in 1962 [16]. The debate continued regarding the origin of the dual emission of DMABN for some years. Most of the studies accepted that the observed dual emission from DMABN is due to excited-state ICT from the dimethylamine to the cyano group through the π -electron bridge. Later on, many congeners of DMABN were put under the scanner for deciphering or decoding the nature of the ICT process and its dynamics. Many experimental or theoretical studies or both have been devoted to investigate the charge-transfer mechanism in different organic molecules. The early experimental and theoretical results on the ICT process support a twisted intramolecular charge-transfer state (called TICT state) [16]. In the framework of the TICT model, the dual emission of an ICT probe originates from the primary excited, called LE, state as well as from the ICT state. The ICT state is accessible only by an adiabatic photoreaction from the LE state that includes rotational motion around the bond connecting the donor and acceptor moieties. If there is no energy barrier between the LE and ICT states, the excited-state relaxation can occur extremely rapidly, resulting in emission from the ICT species only. Although the TICT mechanism is till date the most popular concept in describing the structure of the excited state, this model was challenged by several groups. Later on, several other models, like planar intramolecular charge transfer (PICT), rehybridized intramolecular charge transfer (RICT), and wagging intramolecular charge transfer (WICT), were proposed by several groups to explain their experimental results. For example, Domcke and coworkers put forward a RICT model to account for the formation of the ICT state of DMABN and its analogs. Later on, the formation of a charge-transfer state from a rigid molecule, *N*-phenylpyrrole (PP) and its free analog, fluorazene phenylpyrrole (FPP) put a question mark on the validity of the TICT model. The similarity in spectral signatures of these molecules could not be explained using the TICT model. This led to the proposal of a PICT mechanism to explain the spectroscopic response of the aforesaid molecules. There are several other examples that support the fact that the ICT state of the molecule does not need to be twisted. The origin and drawbacks of some of these models have been described in Chapter 2.

Another point regarding the formation of the ICT state that is still under intense debate is the pathways of the charge-transfer process, that is, the mechanism through which the ICT process in a molecule occurs. Several high-level calculations and state-of-the-art experimental techniques have been used to settle this issue. In spite of several studies that describe the PES of the ICT process, this issue is yet to be settled amicably. A current account of this topic has been described briefly in Chapter 2. The charge-transfer studies in some other molecules, including rhodamine derivatives, coumarin, oxazine, flavin, Nile red, and so on, are discussed in Chapter 2.

1.2 Experimental and Theoretical Studies of the ICT Process

As we mentioned earlier, several studies have been devoted to explore the structure and mechanism of formation of the ICT state. Initially, steady-state UV–visible absorption and emission spectroscopy have been widely used for studying the ICT phenomenon in several organic molecules as dual fluorescence is a major observation of the ICT process. Later on, time-resolved spectral techniques, including, picosecond (ps) time-resolved fluorescence, femtosecond transient absorption (TA) and fluorescence upconversion spectroscopies are used by the scientific community to study the ICT process. Recently, Fleming and coworkers [17] have used a combined ultrafast electronic pump and infrared (IR) probe spectroscopy to study the excited-state CT. Gaffney and coworkers [18] have used polarization-resolved UV pump–mid-IR probe spectroscopy, in conjunction with time-dependent density functional theory (TDDFT) calculations to investigate the dynamics of charge-transfer–induced intramolecular rotation in julolidine malononitrile (JDMN), an ICT probe. Of late, Terahertz (THz) spectroscopy [19] is being used to measure the ICT in a molecule directly. When the ICT process occurs in a molecule, electronic charge moves from one end to another, which will undergo acceleration, resulting in radiation of electromagnetic (EM) pulses. If the charge-transfer process occurs on ps timescale, the radiated EM pulse will fall in the THz region of the spectrum. There are some phenomena similar to ICT, like energy transfer, intramolecular proton transfer (IPT), and so on that has similarity to this process but are different in nature. Dual fluorescence has also been observed in molecules undergoing excited-state intramolecular proton transfer (ESIPT). Although ESIPT is also a charge-transfer process, it is sometimes necessary to distinguish between the ICT and IPT processes occurring in a molecule. It has been seen that the IPT process occurs on a much faster timescale compared to the ICT process. On the other hand, in an ESIPT process, the hydrogen donor and acceptor groups must be present within a certain distance of each other, while ICT can occur even if the donor and the acceptor groups in a molecule are placed quite a distance apart either by a “through-bond” process mediated by a π -electron bridge or by a “through-space” interaction. It is now known that both the ICT and ESIPT processes are dependent on the solvents. One can therefore distinguish these two processes by changing the medium, which in turn will affect their spectroscopic properties.

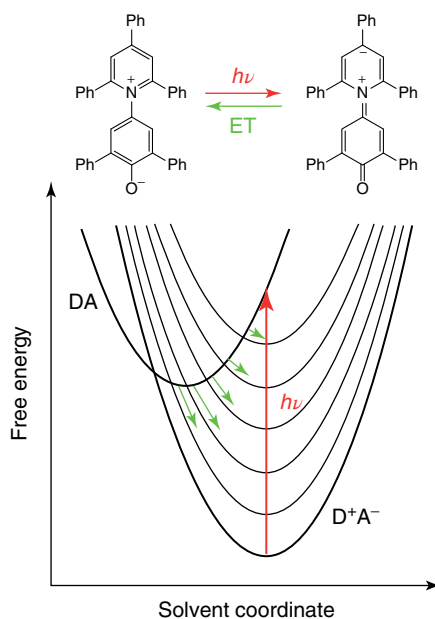
During the ICT process, the electronic charge distribution of a molecule changes, generally resulting in an ICT species with higher dipole moment compared to its ground-state counterpart. The idea of the formation of a higher dipole moment species has also been supported by the fact that in polar solvent the ICT reaction becomes faster due to better stabilization of the polar ICT species in polar medium. The formation of the ICT process in a molecule is also indicated through the redshifted emission as one goes from a nonpolar to a polar solvent. Although many of the ICT molecules show dual emission in polar solvents, not all of them show dual emission. It is believed that due to ICT the non-radiative

deactivation channels (like solvent relaxation) become active, finally decreasing the emission quantum yield. The properties of the medium play a crucial role in determining the rate of formation of the ICT state as well as its structure.

It is worth mentioning here that not all ICT molecules show redshifted emission maxima upon photoexcitation. Molecules with zwitterionic ground state gets charge transfer in the excited state, generally resulting in a species with lower dipole moment than that in the ground state. This may result in a blueshift in their emission maxima. For example, betaine-30, also known as Reichardt's dye (Figure 1.3) shows negative solvatochromism [20]. This was explained by the change in its dipole moment in the ground state to that in the excited state. The molecule remains in a charge-transferred zwitterionic (D^+A^-) state in the ground state that turns into a D-A state upon photoexcitation. The dipole moment of the betaine-30 is reported to be about 15 D and 6.2 D in the ground and excited states, respectively.

Several theoretical calculations have been employed to study the ICT process. Initially, semiempirical methods were used by several groups to explore the structure of the ICT state. Later, Hartree–Fock (HF), density functional theory (DFT), complete active space self-consistent field method (CASSCF) and second-order correction to CASSCF (CASPT2) level of theories were employed either alone or in conjunction with experimental studies to explore the ICT process in the excited state. Many of these theories now can reproduce the experimental results on the ICT process accurately. It is now known that standard DFT functional like B3LYP in many cases failed to reproduce the spectral properties of charge-transfer-based molecules. Therefore, several studies have devoted to propose new DFT functional and basis set combinations to study the ICT process. Some of these studies are discussed in the following

Figure 1.3 The free energy curves of the ground (S_0) and first excited (S_1) states of betaine-30. The vibrational levels and possible ET mechanism are also shown. (Kumpulainen *et al.* 2017 [20]. Reproduced with permission of American Chemical Society.)



chapters of this book. Initial theoretical studies involved optimization of the ground state, followed by calculation of spectroscopic properties using the ground-state geometry with certain approximation. Of late, optimization of the excited-state geometry using configuration interaction singles (CIS), TDDFT, and CASSCF level of theories has been undertaken to understand the physical nature of the charge transfer in specific organic molecules. It is apparent that in a molecule the formation of the ICT state from the LE state competes with the radiative deactivation process. These states occupy different regions of the PES of the relevant molecule. To understand and interpret the phenomenon unambiguously, the details of the PES of these molecules in the ground and excited states are therefore necessary. Of late, theoretical calculations at the CIS, TDDFT, CASSCF, and CASPT2 level of theories and femtosecond pump-probe spectroscopy have been essential tools in such endeavors. A detailed description on theoretical studies on ICT can be found in Chapter 3.

Electron transfer (ET) reaction can be considered as one of the simplest chemical reactions occurring in nature. Initially, the classical Marcus theory, proposed during the mid-fifties of the previous century became very popular. In the model described by Marcus theory, the free energy of the reactant (R) and product (P) goes along the reaction coordinate, comprising both solvent and intramolecular modes [21]. The horizontal displacement, as shown in Figure 1.4, accounts for the difference in equilibrium geometries of the reactant and product states and is quantized by the reorganization energy (λ). On the other hand, the vertical displacement represents the driving force of the reaction and is denoted as $-\Delta G_{\text{ET}}$. The reorganization energy can be further divided into contribution from the solvent and intramolecular modes. In classical Marcus theory, the ET reaction is considered as a thermally activated process and the rate of this reaction (k_{ET}) can be expressed in an Arrhenius-type equation, as shown in Equation 1.1.

$$k_{\text{ET}} = A \exp \left[-\frac{(\Delta G_{\text{ET}} + \lambda)^2}{4\lambda k_{\text{B}} T} \right] \quad (1.1)$$

where k_{B} is the Boltzmann constant and T is the absolute temperature.

From Equation 1.1, three conditions can arise: (i) In the normal region, $-\Delta G_{\text{ET}} < \lambda$, the values of k_{ET} increases with the driving force. (ii) In the

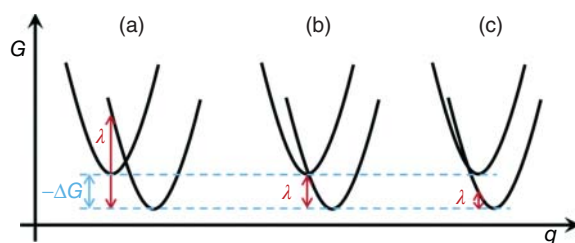


Figure 1.4 Potential energy curves along the reaction coordinate, q , for the reactant and product states. The curves a, b, and c represent the normal, barrier-less and inverted Marcus regions, respectively (see text for details). (Pelzer and Darling 2016 [22]. Reproduced with permission of Royal Society of Chemistry.)

barrier-less region $-\Delta G_{\text{ET}}$ is almost equal to λ , the k_{ET} value reaches the maxima. (iii) In the inverted region, $-\Delta G_{\text{ET}} > \lambda$, the values of k_{ET} decreases with increasing driving force.

Later, several semiclassical and quantum mechanical descriptions of the ET process were considered [20, 22]. Fermi Golden rule [23] is one of the popular models to study the ET process. Sumi–Marcus theory [24] of ET considers the possibility of the ET process taking place faster than the solvent relaxation by splitting the reaction coordinate into fast and a slow coordinates, where they are associated with the relaxing intramolecular modes and with the solvents, respectively. Some of the methods to find the rate of electron-transfer process are discussed in Chapter 3. Recently, Manna and Dunietz [25] studied the rate of photoinduced charge-transfer processes within dyads consisting of porphyrin derivatives in which one ring ligates a zinc (Zn) metal center and where the rings vary by their degree of conjugation.

The separation of charge that follows the ICT process generally enhances the dipole moment of the system in the excited state with some exceptions, like betaine-30 (discussed in this chapter). So, it is quite likely that the ICT species will be stabilized progressively with increase in the polarity of the medium as polar solvents surround the polar probe to exert stability to the probe molecule. The signatures of the ICT process are therefore expected to be more recognizable in strongly polar solvents. A solute (probe) interacts with the solvent in different ways. In suitable cases, it can form molecular clusters of specific sizes and stoichiometries through specific interaction (mostly through hydrogen bonding) with the solvent molecules. On the other hand, the solute molecules may be solvated through the dielectric property of the solvent. This process is called macroscopic or bulk solvation. Both specific or microscopic solvation and macroscopic solvation in dielectric continuum could shape the photophysics of the solute. Many experimental, quantum chemical studies and simulations have been therefore undertaken by the scientific community to unravel the microscopic details the solvent effects on the ICT process [26–38]. It is now known that investigations of structure and dynamics of hydrogen-bonded molecular clusters provide us with the opportunity to understand the effect of the bulk solvation systematically. The studies of cluster formation between solvent and solute molecules also enable one to understand many complex physical and chemical processes from a molecular point of view, which is not possible in the study of bulk solvents. The investigations on the formation of molecular clusters have been fueled due to advent of experimental methods like the mass-selective resonance two-photon ionization (R2PI), rotational coherence spectroscopy (RCS), two-photon ionization and IR ion depletion (IR/R2PI) spectroscopy, among others [39]. A large volume of research has been devoted to explore the molecular clusters in the ground state. Of late, invention of many state-of-the-art time-resolved spectroscopic techniques, like femtosecond TA spectroscopy, femtosecond time-resolved fluorescence spectroscopy, time-resolved vibrational spectroscopy, and so on, have enabled the scientific community to study hydrogen bonding in the excited states. The effect of the medium polarity and hydrogen bonding ability on the ICT process on some molecules is discussed in Chapter 4. Studies of the ICT process is

generally done in solution. However, a few studies of ICT have been reported in literature either in the gas phase or in solid state. A few representative examples of ICT studies in the gaseous and solid states can be found in Chapters 2 and 4.

As mentioned earlier, several new ICT molecules are being reported in literature to understand the ICT process in detail that could be useful in using them for technological applications. Zhao *et al.* [40] have reported the photoinduced ICT process in thiophene- π -conjugated donor-acceptor compounds. As thiophene has lower delocalization energy than benzene, the authors hoped that the former could be a better spacer for π -conjugation in ICT molecules. In fact, several compounds containing thiophene ring have been investigated for possible use in optoelectronic devices, such as NLO, OLEDs, and dye-sensitized solar cells [41–43]. To test their hypothesis, the authors compared the spectral properties of QTCP with its benzene-bridged analog QBTP (Figure 1.5). They assigned the large Stokes shift and strong solvatochromism of these molecules to the formation of the ICT state. They also found that the electron-withdrawing ability of the substituents at the thienyl 2-position affected the ICT process of the molecules studied. In addition to this, they also observed emission from the S_2 state of these molecules, which they confirmed through their fluorescence excitation spectra.

Studies of the ICT process led to the proposal of several theoretical models to mostly predict the rate of the ICT process. Some of these models have been discussed in Chapter 3. Recently, Ivanov and coworkers [44] have reported their simulation studies of ultrafast charge recombination in ion pairs formed through intramolecular electron-transfer process in the light of free-energy-gap law. They simulated the kinetics of charge transfer and ensuing ultrafast charge recombination within the framework of multichannel stochastic model that considers reorganization of both the solvents and a number of intramolecular high-frequency vibrational modes. They described the solvent relaxation in terms of two relaxation modes. The authors found that for ultrafast charge recombination the free-energy-gap law strongly depended on parameters like electronic coupling, reorganization energy of the intramolecular high frequency vibrational modes, as well as the vibrational and solvent relaxation times.

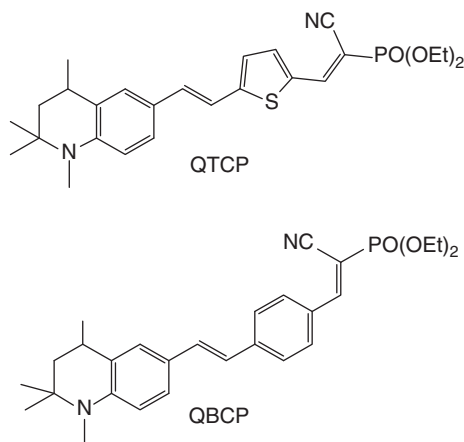


Figure 1.5 The chemical structure of QTCP and QBTP.

They also found that the semilog dependence of the charge recombination rate constant on the free-energy gap varied from a parabolic shape to an almost linear one, while the electronic coupling was increased and the vibrational relaxation time was decreased. The authors predicted that the dynamical solvent effect in charge recombination was large in the area of strong exergonicity, while the effect was small in the area of weak exergonicity.

As mentioned earlier, the properties of the medium play a crucial role in determining the properties of an ICT molecule. Dube and coworkers [45] have reported that the internal motions of hemithioindigo (HTI) photoswitches could be controlled through a change of solvent. The control of the internal motions of molecules using stimuli from outside is important for generation of responsive as well as complex molecular behavior and functionality. Photoswitches that react to light reversibly in a specific way are used as “engine” unit to trigger specific motion as well as events in functional molecular and biological systems [46–48]. HTI derivatives typically consist of a central double bond that functions as a bridge between the thioindigo fragment and a stilbene fragment via one additional single bond. After photoexcitation, unsubstituted HTI derivatives undergo de-excitation in which rotation of the double bond occurs, with additional pyramidalization of the corresponding carbon atoms. The presence of a single C—C bond in these molecules raises the possibility of rotation of this bond during the de-excitation process. Simultaneous rotation of the single and double bonds, called hula-twisting, is generally not considered to take place during de-excitation of unsubstituted HTI derivatives. To test the possible formation of TICT states, the authors considered four HTI derivatives acronymed Z-1 to Z-4 (Figure 1.6). HTI derivatives Z-1 to Z-3 possess substituents in both *ortho*-positions of the stilbene fragment. They used the planar derivative HTI

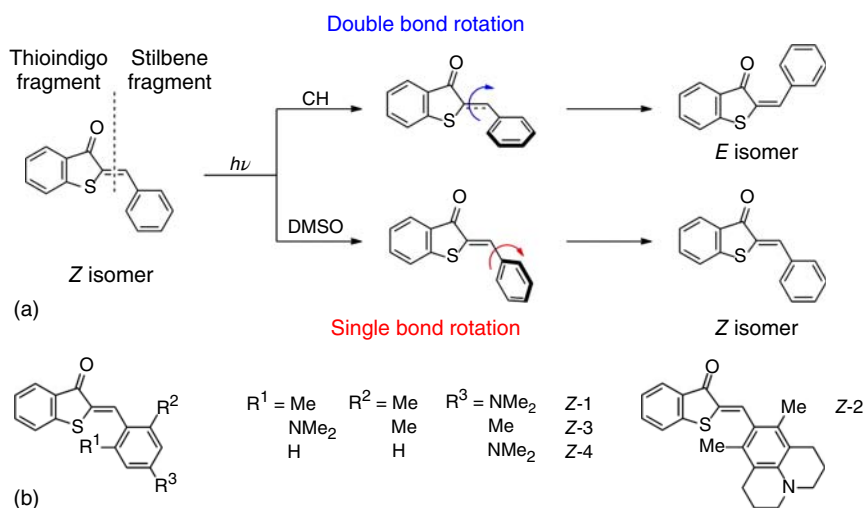


Figure 1.6 (a) Possible light-induced motions of the HTI derivatives, as proposed by Dube *et al.* (b) The chemical structures of the HTI photoswitches Z-1 to Z-4. (Wiedbrauk *et al.* 2016 [45]. Reproduced with permission of American Chemical Society.)

Z-4 as control, which does not undergo the TICT process in the excited state. All the four derivatives have strong electron-donor dialkylamino substituent (the electronic effect of additional alkyl substituents in Z-1 to Z-3 was considered to be not much). The twofold *ortho*-substitution in Z-1 to Z-3 resulted in a significant twist along the single-bond axis that could be measured using crystal structure analysis. The authors found that the dihedral angle around the rotatable single bond was highest for Z-1, with a value of 75° . The aforesaid dihedral angles for Z-2 and Z-3 were found to be 60° and 32° , respectively. Their planar analog Z-4 showed the dihedral angle to be 7° in its crystal structure analysis. The authors studied the chemical shift of indicative proton signals in ^1H NMR spectra of Z-1 to Z-3 that showed a similar twist of these molecules even in solution phase. As expected, the planar molecule HTI Z-4 showed moderate solvatochromism in both absorption and fluorescence. The absorption spectra of HTIs Z-1 to Z-3 also showed moderate solvatochromism, although somewhat broader than their planar analog Z-4. The fluorescence spectra of HTIs Z-1 and Z-2 were affected significantly due to the change in the polarity of the medium. In polar solvents, those molecules showed Stokes shift of more than 200 nm. Dual emission of Z-1 and Z-2 were observed in polar solvents like dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) and acetonitrile. The steady-state absorption and emission behavior of HTI Z-3 was quite similar to HTIs Z-1 and Z-2, although the authors did not find any clear indication of dual emission of this probe. The authors undertook time-resolved absorption, time-resolved emission, and quantum yield measurements to understand the photophysics of the aforesaid molecules in detail. They followed the ultrafast kinetics taking place after photoexcitation of HTIs Z-1 to Z-4 in different media at 22°C by TA spectroscopy with 150 fs resolution. Although the fitting of the time-resolved absorption curve of HTI Z-4 resulted in several timescales, the authors identified the important processes to describe the excited-state dynamics of these molecules. For this molecule, very fast nuclear motions and solvent reorganization were observed due to photoexcitation to the Franck–Condon (FC) region before reaching the relaxed first excited state ($S_{1\text{Min}}$). The $S_{1\text{Min}}$ was identified in all the solvents studied through small redshifted ground-state bleaches and simulated emissions. The redshift increases with increasing solvent polarity. The authors argued that the decay of this electronic excited state to be related to the Z/E photoisomerization of this molecule (HTI Z-4). The rate of photoisomerization of HTI Z-4 was found to be solvent dependent, which decreased with increasing solvent polarity. The slowing down of photoisomerization with increase in the polarity of the solvents was attributed to the significantly polar nature of the $S_{1\text{Min}}$. However, no indication of formation of the TICT state was observed in HTI Z-4. For twisted HTI derivative Z-1, the initial absorption behavior in nonpolar solvents like cyclohexane was found to be quite similar to its planar counterpart HTI Z-4, although the decay of the excited-state features and appearance of E isomer absorption in this molecule was found to be faster than that in HTI-Z-4. The authors argued that the steric interactions imposed by the *ortho*-substituents in HTI Z-1 could be the reason for fast isomerization of this molecule in nonpolar solvents. In moderately polar solvents like dichloromethane (CH_2Cl_2), the time-resolved absorption profile of

HTI Z-1 varied significantly that of its planar counterpart. Dual emission of Z-1 and Z-2 were observed in polar solvents like DMF, DMSO, and acetonitrile. They also found that the excited electronic state had redshifted simulated emission and new excited-state absorption (ESA) features. This new excited state was found in HTI Z-1 in every polar solvent used for the study and the time constant of the relatively longer lived state was connected to the decay of $S_{1\text{Min}}$, while the amplitude is determined by the properties of the solvent as well as the specific decay time. The authors found that the new excited state (they call it T as it was only observed in the twisted HTI derivatives) got stabilized significantly with increase in solvent polarity. This indicated that the new excited state was highly polar and could possess significant charge-transfer character, a characteristic of the TICT state. Similar studies were carried out for HTIs Z-2 and Z-3, which also indicated the formation of TICT states in these molecules. The steady-state absorption and emission, time-resolved absorption and emission spectral studies, and quantum yield measurements of the probe led the authors to conclude the following. For planar HTI derivative Z-4, the de-excitation occurs through the photoisomerization of the double bond using the conical intersection (CoIn_{S_2}) between the second excited state (S_2) and the ground state (S_0). The excited population leaves the initially reached $S_{1\text{Min}}$ state and crosses a barrier to reach the S_2 hyperpotential surface. Finally, it reached the CoIn_{S_2} from which the transition to the S_0 state occurs. The behavior of HTI Z-4 is solvent independent. In twisted HTI derivative Z-1, the excited-state behavior is solvent dependent. In nonpolar solvent cyclohexane, the excited TICT state is not accessible and the de-excitation proceeds through the double-bond photoisomerization pathway. This led to fluorescence of HTI Z-1 from the $S_{1\text{Min}}$ of this molecule in cyclohexane. In solvents with medium polarity (CH_2Cl_2), the TICT state of HTI Z-1 is stabilized significantly and gets populated upon photoexcitation. A strong fluorescence of this molecule from the TICT state occurs in CH_2Cl_2 . Increasing solvent polarity further (e.g., DMSO) stabilizes the TICT more which leads to opening of another radiation-less de-excitation pathway through rotation around the single bond. The depopulation of the TICT state in DMSO becomes rapid and another blueshifted emission from $S_{1\text{Min}}$ is observed in this solvent. All these results are schematically shown in Figure 1.7. The results presented by the authors showed that an unprecedented control over the photoinduced intramolecular rotations could be achieved for the HTI photoswitches through change in solvent polarity.

It is worthwhile to note here that just connecting the donor and acceptor moieties through the π -electron bridge in a molecule is not enough for ICT to occur in the excited state. Dube and coworkers [49] have studied the structural and electronic factors required for formation of excited ICT state in a series of HTI dyes (Figure 1.8). These dyes have been studied extensively for possible use as photoswitches that have advantages like high thermal bistability, fatigue-resistant switching, and visible light responsiveness. The TICT process is reported to be a second de-excitation pathway that is complementary to photoisomerization in these molecules. Dube and coworkers have considered eight HTI derivatives with varying structural and electronic properties to decipher the parameters required to facilitate the ICT process in the excited state. The

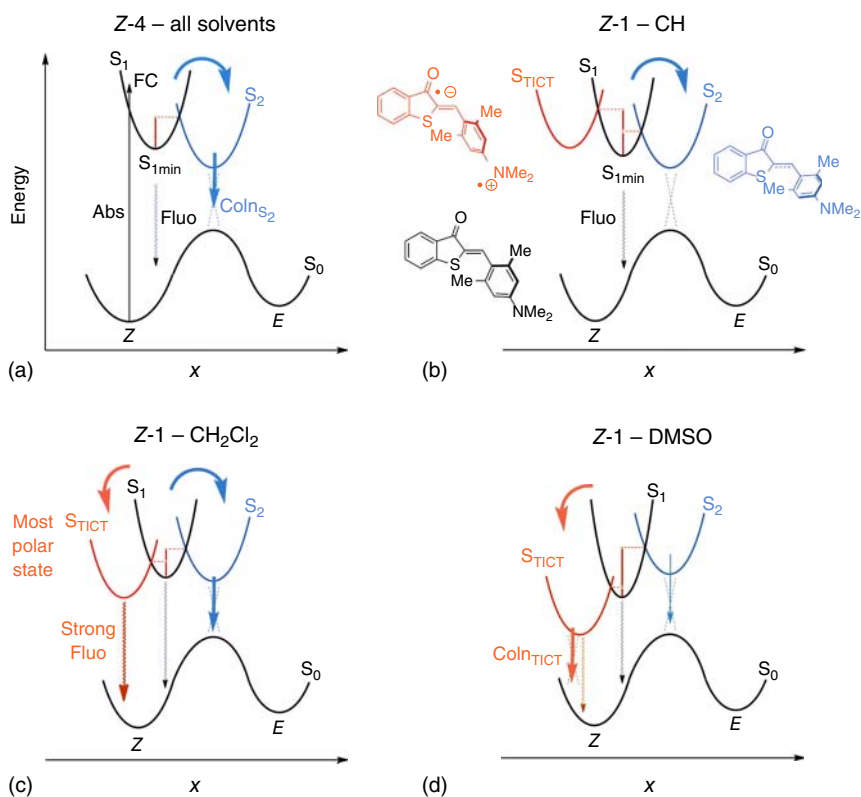


Figure 1.7 Schematic representation of excited-state deactivation mechanism of HTI derivatives: (a) Z-4 (in all solvents) and Z-1 (in cyclohexane, CH_2Cl_2 and DMSO). (Wiedbrauk *et al.* 2016 [45]. Reproduced with permission of American Chemical Society.)

HTI derivatives have different substitutions at the stilbene fragment and the twist angles around the rotatable single bond connecting the stilbene moiety with the photoisomerizable double bond are also different. HTI derivatives with acronyms Z-1 and Z-2 have strong donor units in conjugation with the photoisomerizable double bond. They also have large twisting of the stilbene fragment in the ground state. In all the HTI molecules used in this study, the thioindigo fragment with its strong electron-withdrawing carbonyl is used as the electron acceptor. HTI derivatives Z-3 and Z-4 possess strong donor groups but they are planar in the ground state. Z-5 and Z-6 do not possess strong electron-donating groups, although they are severely twisted around the rotatable single bond in their respective ground states. HTI derivatives Z-7 and Z-8 have substituents with moderate donating strength and they are twisted in the ground state. The authors argued that the varying donor strengths of the molecules studied can alter the push-pull character of the molecules, which is an important ingredient for formation of the ICT state. The steady-state electronic absorption spectra of Z-1 and Z-2 showed redshift in their absorption maxima with the increase in polarity of the media, although the effect is rather smaller than their

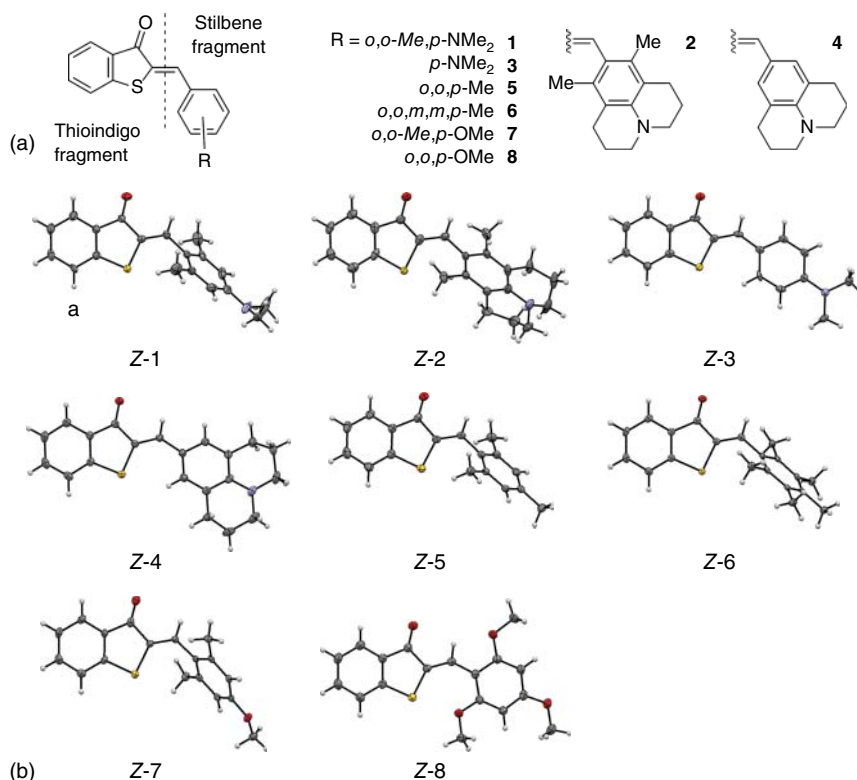


Figure 1.8 (a) Chemical structure of the HTI derivatives Z-1 to Z-8 studied by Dube and coworkers; (b) crystal structures of this Z-1 to Z-8. (Wiedbrauk *et al.* 2017 [49]. Reproduced with permission of American Chemical Society.)

corresponding emission spectra. The steady-state emission spectra of these derivatives showed strong bathochromic (red) shifts with increasing solvent polarity and occurrence of dual emission in solvents with large polarities. The planar derivatives Z-3 and Z-4 showed prominent solvent response, although much less compared to that of Z-1 and Z-2. The authors found that the effect of solvent polarity on the absorption and emission maxima of Z-5 and Z-6 are even smaller than that of Z-3 and Z-4. In spite of having twisted ground-state structures and donating groups with moderate strengths, the solvatochromic response of Z-7 and Z-8 are not very strong. Since the effect of solvent polarity on the emission energy is larger than the corresponding absorption energy of the molecules studied, the authors argued that the excited-state minima from which the fluorescence occurs are more polar than the FC region. As TICT is an alternative yet independent pathway of de-excitation along with the *Z/E* isomerization and the TICT process is highly dependent on the polarity of the solvents, it is expected that the quantum yield of *Z/E* photoisomerization will decrease significantly with increasing solvent polarity. In fact, the authors have used the quantum yield of *Z/E* photoisomerization ($\phi_{Z/E}$) as a tool for identification of the TICT process.