

Modulation of Excited State Processes inside Octa Acid Cavity

*A Thesis
Submitted in Partial Fulfillment of the Requirements
for the Degree of*

DOCTOR OF PHILOSOPHY

by

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to the

**Department of Chemistry
Indian Institute of Technology Kanpur
Kanpur, India**

March 2022

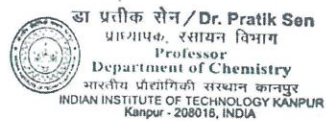
CERTIFICATE



It is certified that the work reported in the thesis entitled “**Modulation of Excited State Processes inside Octa Acid Cavity**” has been carried out by Mr. **Aritra Das** under my supervision and has not been submitted elsewhere for a degree.

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DECLARATION

This is to certify that the thesis titled “**Modulation of Excited State Processes inside Octa Acid Cavity**” has been authored by me. It presents the research conducted by me under the supervision of **Prof. Pratik Sen**.

To the best of my knowledge, it is an original work, both in terms of research content and narrative, and has not been submitted elsewhere, in part or in full, for a degree. Further, due credit has been attributed to the relevant state-of-the-art and collaborations (if any) with appropriate citations and acknowledgements, in line with established norms and practices.

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Dedicated to
Ma-Baba

Acknowledgements

It is just a matter of time before a rudderless boat gets lost in the ocean. At start, the field of research was truly like an ocean of endless possibilities to me. Getting lost was easy. Hopefully for me, unlike that boat, I have the perfect person, my supervisor Prof. Pratik Sen who has directed me to the right path so that I don't drift around and get lost. His lessons taught me how spectroscopy is the doorway to the elusive molecular world. Discussions with him on this subject helped me to build a clear and comprehensible understanding which later became beneficial during my research. There were times when I was stuck with my research. In these moments of trouble, he always supported me and found ways to motivate me. We used to solve those problems together through lengthy discussions. His philosophy was clear, all difficult problems are blessings in disguise, as the end results hidden behind them are usually special. By solving each problem, we learn something new. Because of that, after each fruitful discussion, he used to smile and say, "Learning will never end". These moments of joy shared with him will forever remain the source of motivation for me. A friend is the person to whom one can share his problems, ideas, and thoughts. A philosopher is the person who expounds his understandings on a subject to others and makes facing problems with equanimity easier. A guide is the person who nurtures one to a brighter future. My supervisor has been all of them for me in my PhD life. His many lessons will remain in my heart forever and will surely guide my way in the future. Without his guidance, neither would've I grew as a researcher, nor would this thesis be possible. I wish all the good fortunes for him and his family for the future.

It is my pleasure to express my sincere gratitude to Prof. V. Ramamurthy of University of Miami, USA. He is the person who has introduced me to octa acid and its immense potential. He also provided it to me for my research purposes, without which, this thesis wouldn't have been the same. The excitement I felt during our first ever meeting, I cannot express in words. Since then, every discussion with him have clarified my doubts and taught me something new. Since the start of my PhD days, his book "Principles of Molecular Photochemistry: An Introduction" has been my constant companion. There has not been a single research work, for which I did not had to turn its pages. I consider myself very fortunate to have been able to do some research works with him.

My sincere acknowledgement goes to Prof. R. N. Mukherjee and Prof. J. N. Moorthy for letting me use their laboratory facilities for my research purposes. I would also like to thank Prof. Rajeev Prabhakar of University of Miami, USA, for

the molecular dynamics studies and Dr. V. Srinivasan of IISER Bhopal, for the quantum mechanical calculations.

I want to take this opportunity to express my gratitude to Prof. A. Chandra, Prof. S. Gadre, Prof. k. Srihari, Prof. K. Poddar, Dr. M. Chandra for their insightful teaching during coursework. I would like to thank Prof. D. Goswami, Dr. M. Chandra, and Dr. M. Ranganathan for their constant encouragement during my time as their teaching assistant.

I express my whelming acknowledgement to the Department of Chemistry, IIT Kanpur for making a part of it and provide all the facilities. My sincere gratitude is due to the respected head of the departments Prof. S. Verma (former), Prof. A. Chandra (former) and Prof. J. K. Bera (current). Special thanks are due to Sudha mam and Geeta mam for their constant cooperation and generous helps.

I want to express my heartfelt gratitude to Dr. A. Halder of Presidency University, Kolkata. It was his teaching and discussions that made me love physical chemistry. I also want to acknowledge all my teachers from my childhood to my college days.

A special thanks goes to my senior in lab, Puspall Da. His lessons and training on the fluorescence up-conversion setup and the transient absorption setup has grown my confidence to handle them properly and use them for my research work. Thanks are due to my seniors Shradhey Da, Vaisakh Da, Vipin Da, Faizi Da, Vijaykant Da. I would like to thank Bhaswati Di, and Navin Da for welcoming me in the lab and sharing the enjoyable moments together. I am thankful to Nilimesh that he accompanied me from the start, I will never forget the day we first arrived at IIT Kanpur campus, such was its eventfulness. I would like to acknowledge my juniors Abhijit and Suman, working with them I really enjoyed. I also want to thank Arghya, Tanmoy, Kuldeep, Sandeep, Shubhendu, Arnab, Vishal for making my stay in the lab merrier. I would like to mention the M.Sc. Students worked in the lab during my tenure; Apala, Sukanta, Nisith, Sakil. I acknowledge Dr. Arunava Sengupta for helping with cyclic voltammetry experiments.

I had the good fortune to had three persons, Shovon, Pratyush, and Kanyashree, whom I cannot just mention as batchmates or labmates or friends. They were my family here. Words will not be enough to express their importance in my life. Shovon has been my friend since the M.Sc. days, and I am lucky to have him in my PhD life too. Together, we are the partners in crime. Pratyush came in our lab as a M.Sc. student and in time became a younger brother to me. He is such a person, that not loving him is difficult. Between Kanyashree and me, we have so many

common interests that we always have something to share, something to talk about. The sharing creates etched memories, remembering which never fails to put a smile in my face.

During my PhD tenure, I have come across a lot of affectionate friends without whom my stay in IIT Kanpur would have been dull and tiring. It is impossible to imagine a hostel life without the ‘tea adda’, ‘lunch/dinner table adda’, ‘late night adda’. I cherish these ‘adda times’ shared with Shubhashis, Biplab, Shovon, Nilimesh, Anubrata, Sabyasachi, How Da, Shubha Da and Bhut Da.

I am grateful to the Ministry of electronics and Information Technology, Govt. of India for providing me the prestigious Visvesvaraya fellowship. I acknowledge IIT Kanpur for the infrastructure and facilities. I also want to acknowledge HPC 2010 and HPC 2013 for the computational facilities.

It is the unconditional love, endless patience and unfathomable sacrifices of my mother and father, that made me what I am today. I dedicate this milestone in my career to them.

Aritra Das

Synopsis

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Degree for which Thesis is Submitted:	Ph. D.
Department:	Chemistry
Supervisor:	Prof. Pratik Sen
Thesis Title:	Modulation of Excited State Processes inside Octa Acid Cavity
Month and Year of Submission:	March, 2022

Under the current crisis of global warming, harvesting solar energy is the key to achieve the sustainability. Efficient solar energy harvesting demands fundamental knowledge on light-matter interaction, and thus a thorough study of light-matter interaction and its fate are relevant and contemporary topic of research. Interaction between light and matter can induce either physical or chemical changes in the system. Photon induced physical and chemical changes in molecules are known as photo-physics and photo-chemistry, respectively. In this thesis I have studied several photophysical phenomena in solution phase and under confinement. Photo-physical behaviour of a molecule present in a confined medium differs significantly from the properties when present in bulk solution. The existing knowledge along with the understanding presented in this thesis, can be used to map novel media that can be crucial for efficient solar energy harvest or mimicking cell environment.

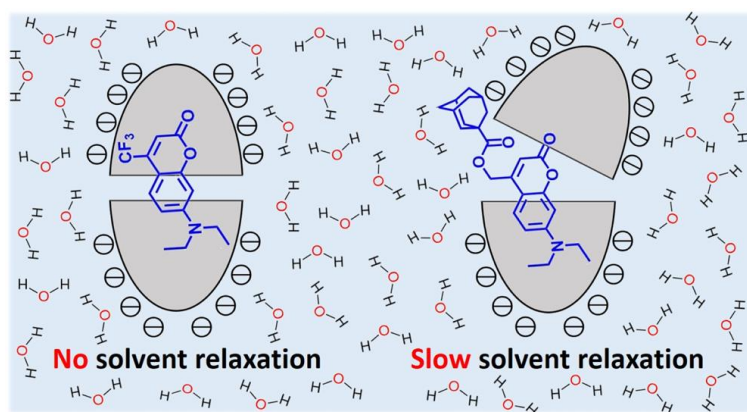
In this thesis, I have taken a water-soluble synthetic organic molecule (Octa acid, OA) as the confined medium. It is known to form capsuleplex in aqueous medium by encapsulating guest molecules. Depending on the stoichiometric ratio between the guest and OA, 1:2 or 2:2 capsuleplex can form. I have used solvation dynamics around the encapsulated host molecules to probe the cavity environment

of the guest-OA capsuleplex. Lack of solvation of the photo-excited guest suggests that the OA cavity is dry. I have also explored the effect of this confinement on some photophysical phenomena, namely excimer formation, intersystem crossing (ISC), and photo-induced electron transfer (PET). By incorporating two anthracene molecules inside OA cavity, I have been able to observe the excimer formation dynamics for the first time. Triplet stabilizing property of the OA cavity helped me to unravel the mechanism of intersystem crossing in halogen substituted coumarins. I have also proved the existence of Marcus inverted region for PET from encapsulated donor to acceptor partitioned by molecular wall of OA. This has helped me to understand the mechanism of PET across molecular wall.

Summary of work done

(1) Ultrafast Solvation Dynamics Reveal that Octa Acid Capsule's Interior Dryness Depends on the Guest

Steady state spectroscopic data of solvatochromic probes like pyrene and coumarin-1 encapsulated inside OA cavity (1:2 guest-host complex) suggests that the environment inside OA cavity is non-polar

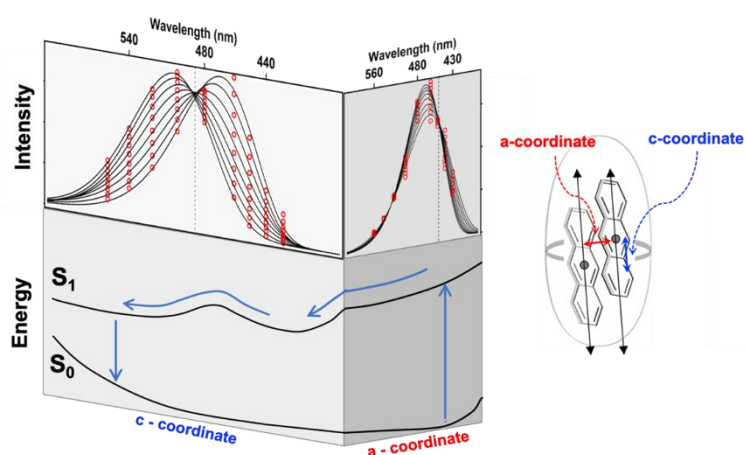


in nature. The immediate question is, how is the dynamics of solvation around these guest molecules and how does it vary with changing the shape and size of the guests. I have used two sets of coumarins as guests, one small that fits well within the capsule and the other larger that fits within an enlarged capsule, to answer this question. Coumarin-152, coumarin-153 and coumarin-152A are in the first set and the second set contains three coumaryl esters with different sizes and shapes depending on the substitutions. I have constructed the time-resolved emission spectra (TRES) for these six guest molecules encapsulated inside OA cavity by

recording their fluorescence transients using both the femtosecond fluorescence up-conversion and the time-correlated single photon counting (TCSPC) technique. For all the three large coumaryl esters, a time-dependent fluorescence Stokes shift (TDFSS) is observed. I have also determined the combined solvent response functions ($C(t)$) from the constructed TRES by the two methods, and same were fitted with tri-exponential functions to get the corresponding solvation times. For smaller coumarins, I did not observe any TDFSS, implies a dry OA cavity without any water loading in presence of small guests. This result was astonishing. As these coumarins were smaller in size, they have formed tight capsules with OA. As a result, we have managed to completely turn off solvent relaxation of photo-excited molecules present in aqueous medium by trapping them inside OA cavity. However, in case of coumaryl esters, I observed sufficient Stokes shift and the dynamics become faster as the size of the guest increased. This suggests that for large guest molecules water penetrates the OA cavity. Molecular dynamics (MD) simulation also supported this observation.

(2) Dynamics of Anthracene Excimer Formation within a Water-soluble Nanocavity at Room Temperature

In literature, the excimer formation dynamics could not be seen in bulk solution as it has always been diffusion controlled. In this work, I have managed to observe such a dynamics for anthracene (AN), by



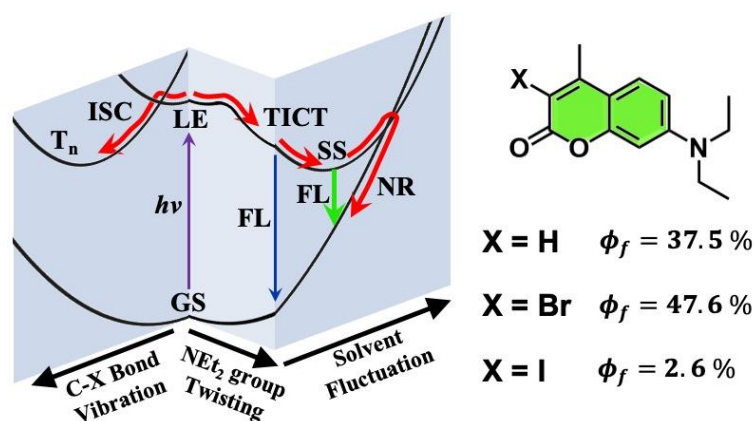
incorporating two of them in the OA cavity. AN forms 2:2 complex with OA when mixed in equal stoichiometry in aqueous medium. The steady state emission spectra of the 2:2 AN:OA complex ($AN_2@OA_2$) shows a broad emission band, centered

around 520 nm, that corresponds to the excimer. The fluorescence lifetime at 520 nm was found to be 263 ns. On the other hand, the 1:2 AN:OA complex (AN@OA₂) showed only a structured monomer type emission. I recognized that observation of excimer formation dynamics is a possibility in AN₂@OA₂, as the role of diffusion is nullified. Fluorescence titration confirmed that in an aqueous solution of AN and OA, an equilibrium among AN in bulk water (AN@bulk), AN@OA₂, AN₂@OA₂ is present. A particular species could be populated by choosing a desired ratio of AN and OA. The emission spectra of AN₂@OA₂ also characterized by a low intensity structured emission around 400-420 nm along with the broad excimer emission centered at 520 nm. I recorded the excitation spectra at 520 nm and 400-420 nm region and found they are different. A comparison of the excitation spectra at the 400-420 nm of AN₂@OA₂ with that of AN@bulk and AN@OA₂ reveals that the low intensity structured emission has not originated from the AN₂@OA₂ complex, rather from the residual AN@OA₂ or AN@bulk present in the solution. Because of this, I excluded the 400-420 nm region from the time-resolved fluorescence studies of AN₂@OA₂. A close inspection of the TRES of AN₂@OA₂ represents an unprecedented red shift of excimer emission with time. The zero-time spectrum was found at 458 nm, which is broad and structureless. It indicates that unlike in the bulk medium, AN exists in a pre-excimer type geometry inside the OA cavity, that gradually forms the excimer. However, the time-dependent frequency shift was not monotonous, which is interpreted to the involvement of more than one step in the excimer formation process. To confirm the suspicion, I constructed time-resolved area normalized emission spectra (TRANES). In the TRANES, there were two isoemissive points at two different wavelengths at two different time windows. The first isoemissive point was observed in between 0.0 ns to 0.1 ns at 448 nm. The second isoemissive point was found at 487 nm in between 0.1 ns to 16.0 ns. This observation confirmed the involvement of two steps involving three states. I plotted the time-dependent evolution of the ratio of the intensity of the initial state (initial peak position) and the final state (final peak position) for each of these two steps. They were fitted exponentially. Among the two, the second step was much slower,

which indicates the presence of a significant barrier in its path. The first step has a time constant of 0.06 ns. The time constant for the slower step is 2.65 ns. I assigned three possible coordinates of inter-molecular movements between the two anthracenes. Potential energy curves (PEC) along these three coordinates were calculated using TDDFT method. One of these coordinates involved slipping of one anthracene over the other along their long axis. PEC shows the presence of a barrier along this coordinate and thus supports the experimental observations. Combining experimental observations with theoretical support, I have presented a plausible scheme depicting the whole excimer formation process for AN₂@OA₂.

(3) Vibration-Assisted Intersystem Crossing in the Ultrafast Excited-State Relaxation Dynamics of Halo-Coumarins

Spin-orbit coupling (SOC) is always necessary for intersystem crossing (ISC). Insertion of heavy atom in molecule should enhance the SOC and hence the ISC. However, I have found some reported data which suggested



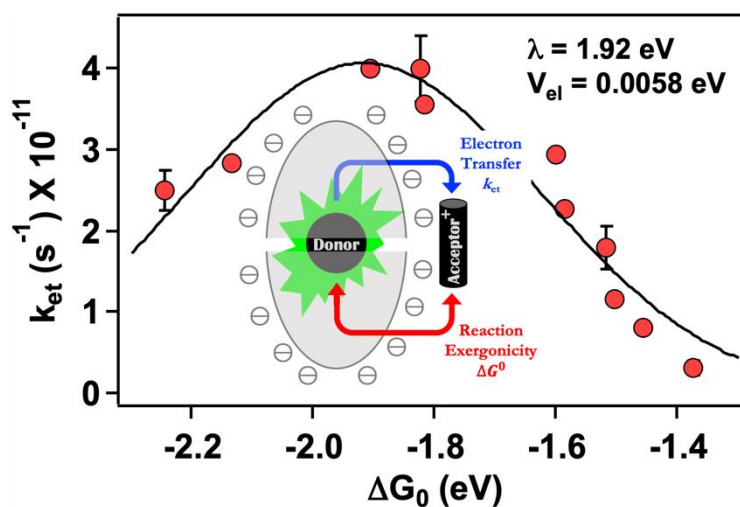
that in some cases the heavy atom incorporation underperformed to facilitate ISC. By comparing the ratio of the square of spin-orbit coupling (SOC) factor and the ratio of the experimentally obtained rate constant of intersystem crossing (ISC) between 1-bromonaphthalene and 1-iodonaphthalene, I found that for some unknown reason, ISC for the Br-derivative is less effective than expected from the square of SOC values. Furthermore, I experimentally determined the fluorescence quantum yield (ϕ_f) of coumarin-1 (C1), 3-bromocoumarin-1 (3Br-C1) and 3-iodocoumarin-1 (3I-C1) in methanol and found that though ϕ_f decreases sufficiently from C1 to 3I-C1, it slightly increases for 3Br-C1 compared to C1. I performed

extensive photophysical studies using steady state and time-resolved spectroscopy on these three coumarins to establish a mechanism that can explain the unusual trend. For all three coumarins in methanol, the global fitting of the femtosecond broadband transient absorption (TA) spectra yields three global time constants. The decay associated spectra (DAS) for the solvated state (SS) of 3I-C1 has a very low amplitude. This clearly suggested the presence of a non-radiative channel from S_1 in case of 3I-C1. However, I could not confirm the participation of triplets as no TA signals was observed that could be assigned as triplet. PEC calculation using TDDFT along the $-NEt_2$ group rotation could not differentiate between the three coumarins. I calculated the vibrational spectra for the excited states of 3I-C1 and found that there are resonating normal modes between S_1 , T_1 and T_2 . Close inspection of the two resonating modes between S_1 and T_2 revealed that the C3-I bond vibration is much more prominent in the T_2 mode compared to the S_1 mode. This indicated that S_1 to T_2 transition must involve the C3-I bond length variation coordinate. I have calculated the PEC along the C3-X (X=H, Br, I) bond length variation coordinate for all the three molecules. The PECs were distinct for these three molecules. For C1, all the electronic states were bound. For 3I-C1, the S_1 and T_2 surfaces crosses with the slightest of the bond elongation and the crossing is barrierless. Most importantly, for 3Br-C1, I found that for the S_1 and T_2 surfaces to cross, $\sim 6\%$ of bond elongation is necessary and the path to the S_1 - T_2 crossing point has a significant barrier (0.11 eV). I recalculated the PECs by incorporating the SOC. The SOC-incorporation did not change the main features of the PECs. Presence of the barrier was assigned as the plausible reason behind the observation of high ϕ_f for 3Br-C1. To confirm the involvement of triplet states, I decided to use the triplet stabilizing property of OA cavity. I recorded the steady state emission spectra at room temperature for the 1:2 complex (3Br/I-C1@OA₂) between 3Br/I-C1 and OA. For 3Br-C1@OA₂, there is only one emission band. Whereas for 3I-C1@OA₂ apart from the normal emission band, another low-intensity red-shifted band appeared around 580 nm, which intensifies with a decrease in the temperature. This new band matches with the phosphorescence of 3I-C1 recorded at 77 K. I assigned this new band as the

room temperature phosphorescence band of 3I-C1@OA₂. Global fitting of the TA response of both 3Br-C1@OA₂ and 3I-C1@OA₂ yield two time constants. TA spectra of 3I-C1@OA₂ consisted of a very short-lived stimulated emission (SE) signal and a long lived (> 10 ns) broad excited state absorption (ESA) signal. This long-lived broad ESA signal confirmed the triplet formation in 3I-C1. On the other hand, no such signal was observed in case of 3Br-C1. Combining the experimental and theoretical findings, I constructed a general scheme of excited state relaxation dynamics for halogen substituted C1. This model also successfully predicted the photophysical behaviour of the halogen substituted naphthalenes. I also calculated the PECs to predict the effect of halogen-substitution at the other available position of C1.

(4) Marcus Relationship Maintained During Ultrafast Electron Transfer Across a Supramolecular Capsular Wall

It was found that a transfer of electron can takes place from a photo-excited donor molecule trapped inside the OA cavity to an acceptor present outside the cavity. However, the role of the molecular wall between the donor and the acceptor has not been understood. In this



connection, I intend to understand (i) if electron transfer (ET) takes place via orbital overlap or not (ii) if orbital overlap was present, is it quantifiable and (iii) what is the role of the OA molecular wall in the mechanism of ET. I chose selective donor molecules that could form 1:2 complex with OA when mixed in proper stoichiometry, and methyl viologen (MV²⁺) and benzyl viologen (BzV²⁺) were chosen as the acceptors. The acceptors are expected to stay at the negatively charged

outer wall of the OA cavity, as they are positively charged. Such an arrangement resulted in electron transfer proceeding without a diffusion. I have experimentally determined the rate constant of ET (k_{et}) of eleven donor-acceptor pairs by following the time-dependent evolution of the viologen radical cation spectra in femtosecond broadband transient absorption (TA) spectroscopy. The oxidation potentials of the donor molecules and the reduction potentials of the acceptors were determined by cyclic voltammetry. Using the Rehm-Weller equation, I calculated the free energy change (ΔG_0) for all the pairs. I plotted k_{et} against ΔG_0 and observed a Marcus type bell-shaped dependence of k_{et} on ΔG_0 . From the fitting to the Marcus equation, I found the values of reorganization energy ($\lambda = 1.92$ eV) and the electronic coupling ($V_{el} = 0.0058$ eV). The value obtained for V_{el} is significant and suggests that despite presence of a molecular wall between the donor and acceptor, electronic overlap is present. It was speculated that the role of OA wall in the ET is similar to the C-clamp-trapped solvent molecules.

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Chapter 1

Introduction

In this chapter, I have summarized the general theories behind four photophysical process viz. intersystem crossing, photoinduced electron transfer, excimer formation and solvation dynamics. These four processes have been studied throughout this thesis in bulk solvents and inside Octa acid (OA) cavity.

1.1. Fate of an Excited State

Interaction between light and matter makes the existence of life possible in this world. Every aspect of life on the earth, from photosynthesis to the harvest of solar energy, is a consequence of light-matter interaction, which converts light energy into chemical energy. Upon interacting with light, fate of a molecule can be of two types. Either absorption of light will lead to some physical changes, or it will impose chemical changes via bond breaking and making. Phenomena of the first kind are categorized as photo-physics of the molecule and the second one is known as photochemistry of the molecule.¹⁻⁴ This thesis only covers the photophysical aspect.

Light is an electromagnetic radiation. Among the whole frequency range of electromagnetic spectrum, UV-visible region infests electronic excitation of molecules. Electronic excitation is of main interest in this thesis. The fate of a molecule, following electronic excitation is described by Jablonski diagram.¹⁻⁴

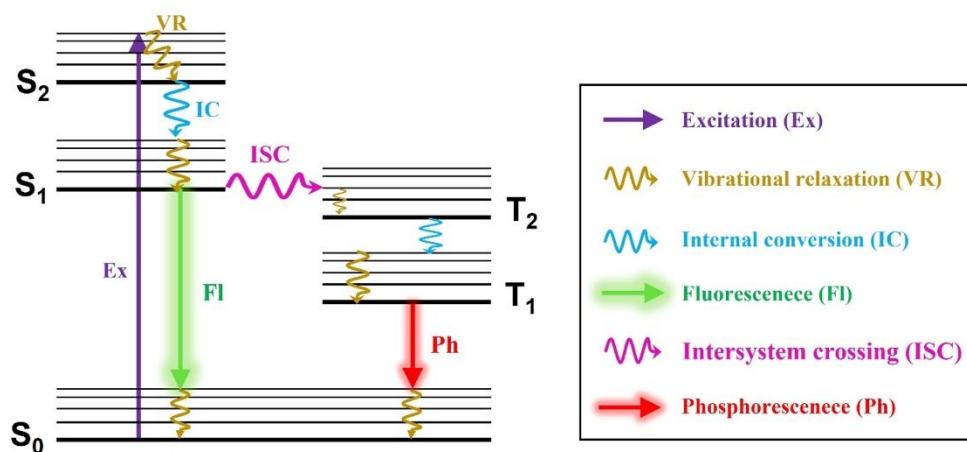


Figure 1.1.1. Jablonski diagram. Electronic excitation (straight purple arrow) sends the molecule from S₀ to the higher vibrational levels of S₂. Vibrational relaxation (VR; wavy yellow arrow) brings the molecule to the ground vibrational level of S₂. Internal conversion (IC; wavy blue arrow) followed by VR brings it to the ground vibrational level of S₁. From S₁, the molecule can reach S₀ by radiative transition known as fluorescence (straight green arrow). Alternatively, it can end up in the triplets (here T₂) via intersystem crossing (ISC; wavy pink arrow). After that VR and IC brings the molecule to the T₁. From T₁, the molecule can reach to S₀ by the radiative transition called phosphorescence (straight red arrow). Note: Fluorescence and phosphorescence are usually accompanied by the simultaneous non-radiative transitions between S₁ to S₀ and T₁ to S₀.

A typical Jablonski diagram is given in figure 1.1.1. The ground electronic state is designated as S_0 . The 'S' stands for the singlet spin multiplicity of the state. The following higher excited states are noted as S_1 , S_2 , etc. The first excited triplet state is represented as T_1 where T stands for triplet spin multiplicity. Each electronic states consists of a bunch of vibrational levels represented as 0, 1, 2, etc. The gap between the S_0 and S_1 is much larger than the available thermal energy at room temperature. For excitation of molecules from S_0 to S_1 light energy is required. Electronic transition is an instantaneous process with respect to the nuclear motions. Essentially, timescale of electronic transitions is as small as 10^{-14} s. Because of this instantaneous nature of electronic transitions, transitions are represented by vertical arrows in the Jablonski diagram. It is known as the Frank-Condon principle. After the excitation to the S_1 or S_2 state, the molecule can undergo several intermediate processes to ultimately reach the ground state (S_0). Usually, absorption of photon excites the molecules to a higher vibrational level of S_1 or S_2 . Just after the excitation, the molecules rapidly relax to the ground vibrational level of S_1 . The relaxation between the vibrational levels is known as vibrational relaxation (VR) and the non-radiative transition from S_2 to S_1 is called internal conversion (IC). In the figure 1.1.1 both the processes are depicted. The timescale of the VR and IC is $\sim 10^{-12}$ s. Energy gaps between singlet states gradually decreases with increasing energy. Therefore, the vibrational coupling between the higher singlet states (higher than S_1) is very efficient making the IC process very fast. Because of that usually we do not observe emission from higher singlet states. After reaching the ground vibration level of S_1 , the molecule can reach S_0 via non-radiative IC or via radiative emission, which is known as fluorescence. Typical fluorescence lifetimes are in the order of $10^{-9} - 10^{-8}$ s. The gap between S_1 and S_0 is sufficiently large and in that case, fluorescence competes with the IC process. Because of fast IC from higher singlet to S_1 followed by rapid VR, fluorescence always occurs from the ground vibrational level of S_1 . This is the Kasha's rule. Apart from this path to reach S_0 , the excited molecule can follow an alternate path. Molecules in excited singlet states may undergo spin change to reach the triplet states. This process is called intersystem crossing (ISC).

Being spin forbidden, ISC is an unfavorable process. In some molecules though, efficient spin-orbit coupling make ISC feasible. Molecules for which ISC is facile, it acts as an extra channel of relaxation for S_1 , which eventually quenches its fluorescence. IC between triplet states leads the molecules to the lowest energy triplet state (T_1). From T_1 , the molecule can reach S_0 by non-radiative transition (ISC) or it can reach S_0 by radiative transition. Radiative transition from T_1 to S_0 is known as phosphorescence. Phosphorescence is a lower energy emission compared to fluorescence as T_1 is energetically lower than S_1 . Transition between states of different spin is generally forbidden, which also makes the phosphorescence lifetime much longer than that of fluorescence.¹⁻⁴

1.2. Solvation Dynamics

Photoexcitation may accompany with a change in the dipole moment of the molecule, which acts as an electric field. Solvation dynamics is the response of the dielectric medium towards this electric field.³⁻¹⁷

Figure 1.2.1 depicts an electric dipole ($\vec{\mu}$) present in a uniform electric field ($\vec{R}$). The angle between $\vec{\mu}$ and $\vec{R}$ is given by θ . $\vec{R}$ exerts an electric force $+q\vec{R}$ on the positive end of the dipole. As it is a uniform electric field the negative end of the dipole feels a force of same magnitude but in opposite direction ($-q\vec{R}$). As a result, $\vec{\mu}$ experiences a torque ($\vec{\tau}$) which tries it to align it along $\vec{R}$.

$$\vec{\tau} = \vec{\mu} \times \vec{R} = \mu R \sin \theta \quad (1.2.1)$$

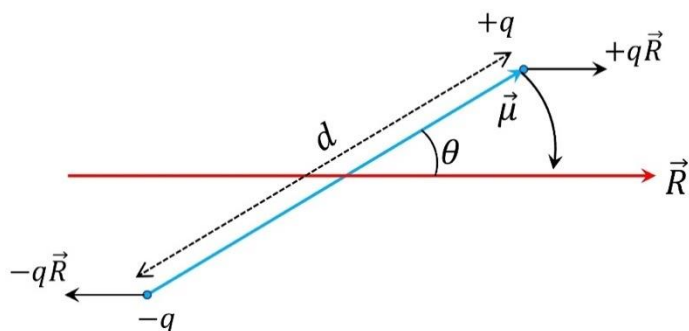


Figure 1.2.1. Effect of a uniform electric field ($\vec{R}$) on an electric dipole ($\vec{\mu}$). The length of the dipole is d . The angle between $\vec{\mu}$ and $\vec{R}$ is θ . $\vec{R}$ applies a torque on $\vec{\mu}$ to align it parallel.

The magnitude of $\vec{\tau}$ is maximum when $\theta = \pi/2$. $\vec{\mu}$ feels the $\vec{\tau}$ exerted by $\vec{R}$ until θ decreases to 0. For an infinitesimal decrease in θ (i.e., $-d\theta$), the work done by $\vec{R}$ is given by,

$$dw = -\tau d\theta \quad (1.2.2)$$

As electric field is conservative in nature, the work done is negative of the potential energy. Thus,

$$dE = \tau d\theta = \mu R \sin \theta d\theta \quad (1.2.3)$$

Integrating both side we obtain at

$$\begin{aligned} \int_{E(\pi/2)}^{E(\theta)} dE &= \mu R \int_{\pi/2}^{\theta} \sin \theta d\theta \\ \Rightarrow E(\theta) - E(\pi/2) &= -\mu R \cos \theta \end{aligned} \quad (1.2.4)$$

Description of potential energy always requires a reference point. In this case we take $\theta = \pi/2$ as that reference point and $E(\pi/2) = 0$. Hence

$$E(\theta) = -\mu R \cos \theta = -\vec{\mu} \cdot \vec{R} \quad (1.2.5)$$

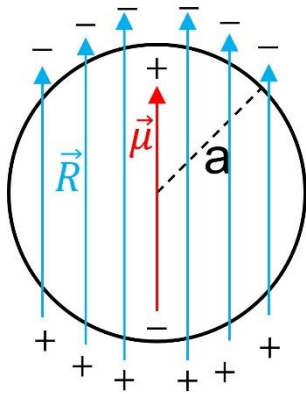


Figure 1.2.2. Dipole ($\vec{\mu}$) and the reaction field ($\vec{R}$) induced by the dipole in a uniform dielectric medium.

Generally, a fluorophore is considered as a point dipole in a medium of uniform dielectric constant (i.e., the solvent). Figure 1.2.2 represents dipole ($\vec{\mu}$) in a dielectric medium. Energy of the dipole in an electric field ($\vec{R}$) is given by the equation 1.2.5.^{3,18-20} In our case, the electric field is a reaction field in the medium, induced by the dipole itself. The direction of a dipole moment is from the negative end to the positive end of the dipole. On the other hand, the direction of an electric field is from the positive end towards the negative end. Consequently, $\vec{\mu}$ and $\vec{R}$ are parallel to each other as shown in figure 1.2.2. Thus, $\theta = 0$. Consequently, the energy of the dipole (E_{dipole}), in this case, will be³

$$E_{dipole} = -\mu R \cos \pi = -\mu R \quad (1.2.6)$$

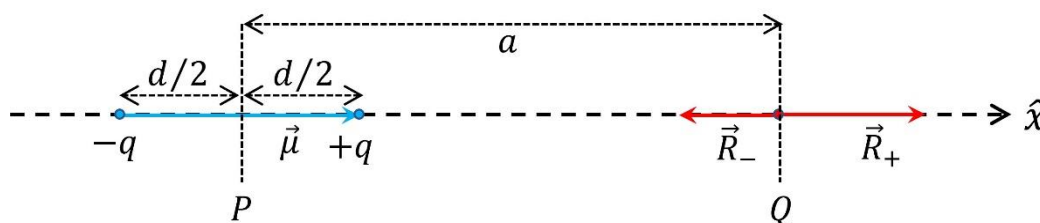


Figure 1.2.3. Schematic representation of the reaction fields generated by a dipole.

To determine the reaction field due to a dipole, in figure 1.2.3 a dipole of length d and moment $\vec{\mu}$ has been depicted. The dipole is situated at P . Q is a point situated at a distance a from P . In the above figure, $\vec{R}_+$ and $\vec{R}_-$ are the reaction fields at Q , generated due to the positive and the negative ends of the dipole respectively. The direction of $\vec{R}_+$ is away from the positive charge of the dipole and $\vec{R}_-$ is directed towards the negative charge of the dipole. $\vec{R}_+$ and $\vec{R}_-$ are given by,

$$\vec{R}_+ = \frac{1}{4\pi\epsilon_0} \frac{q}{(a-d/2)^2} (\hat{x}) \quad (1.2.7)$$

$$\vec{R}_- = \frac{1}{4\pi\epsilon_0} \frac{q}{(a+d/2)^2} (-\hat{x}) \quad (1.2.8)$$

Therefore, the total reaction field ($\vec{R}$) will be

$$\begin{aligned}\vec{R} &= \frac{1}{4\pi\epsilon_0} \frac{q}{(a-d/2)^2} (\hat{x}) + \frac{1}{4\pi\epsilon_0} \frac{q}{(a+d/2)^2} (-\hat{x}) \\ \Rightarrow \vec{R} &= \frac{1}{4\pi\epsilon_0} \frac{1}{a^4} \left[\frac{2aqd}{\left(1-\left(\frac{d}{2a}\right)^2\right)^2} \right] (\hat{x})\end{aligned}\quad (1.2.9)$$

For a point dipole, $d \ll a$. Consequently, $\left(\frac{d}{2a}\right)^2 \ll 1$. Neglecting $\left(\frac{d}{2a}\right)^2$ and putting $qd(\hat{x}) = \vec{\mu}$ in the above equation we obtain

$$\vec{R} = \frac{1}{4\pi\epsilon_0} \frac{2\vec{\mu}}{a^3} \quad (1.2.10)$$

This is the reaction field induced by the dipole in a uniform dielectric medium. The value of the coulomb constant ($\frac{1}{4\pi\epsilon_0}$) can be taken as a unity when considered in atomic units.

However, for a real solvent medium, there is another important factor that needs to be considered. It is the polarizability (f). In that case the expression of the reaction field (R) modifies into^{3,18,19}

$$R = \frac{2\mu}{a^3} f \quad (1.2.11)$$

In the above equation, a is the cavity radius of the solute dipole. The solvent polarization can be divided into two parts, namely electronic (f_{el}) and orientational (f_{OR}) polarizability. f_{el} depends on the motion of the electrons. It is an instantaneous process and originates the high frequency polarization, which is a function of refractive index (n) of the solvent.^{3,18,19}

$$f_{el} = \frac{n^2-1}{2n^2+1} \quad (1.2.12)$$

f_{OR} depends on the orientation of solvent molecules and is a much slower process. This is known as the low frequency polarization. f_{OR} can be represented as a function of the dielectric constant (ϵ) and refractive index (n) of the medium^{3,18,19}

$$f_{OR} = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1} \quad (1.2.13)$$

When $\varepsilon \simeq n^2$, orientation polarization (f_{OR}) becomes 0, which means that orientation of solvent molecules has no influence on the solute dipole. The only possible reason behind this is that the solvent has no permanent dipole moment. Hence smaller f_{OR} values indicate toward solvents of lesser polarities.

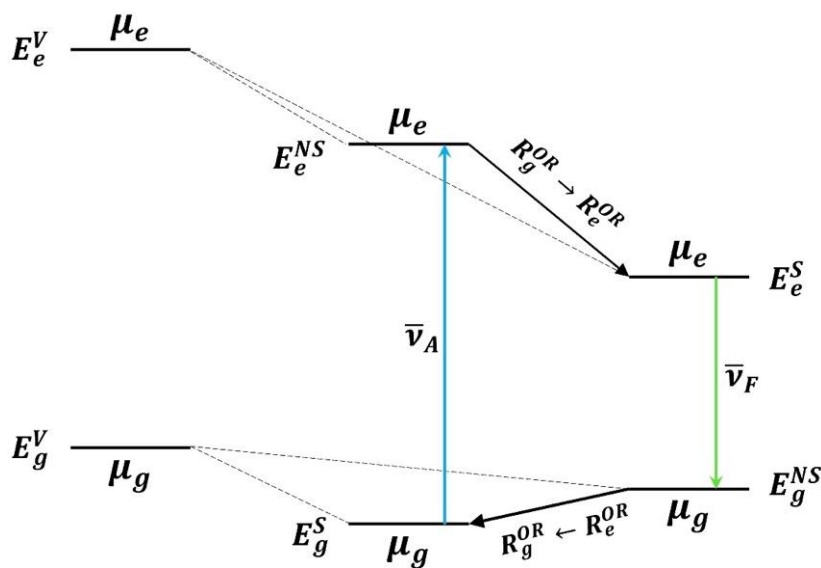


Figure 1.2.4. Solvent effect on electronic energy levels of a solute molecule which is a fluorophore. Ground state dipole moment of the fluorophore is μ_g and excited state dipole moment of it is μ_e . E_g^V and E_e^V are the energy of the ground and excited electronic level if the fluorophore was in vacuum instead of the solvent. E_g^S and E_e^S are the energy of the ground and excited electronic level when the fluorophore is in the solvent and properly solvated. E_g^{NS} and E_e^{NS} are the energy of the ground and excited electronic level when the fluorophore is in the solvent but not solvated. R_g^{OR} and R_e^{OR} are the favorable orientational reaction fields for the fluorophore in ground and excited state respectively.

Let us consider the ground and excited state dipole moments for the fluorophore are μ_g and μ_e , respectively. As photoexcitation is instantaneous, only the electronic polarization can response to this sudden change in dipole moment. The orientation polarization remains same as in the ground state. As time progress, the solvent molecules reorient themselves around the dipole in the excited state to stabilize it. This phenomenon is called solvation dynamics. Let us denote the ground state

reaction field for electronic and orientational polarization respectively as R_g^{el} and R_g^{OR} . They are given by^{3,18,19}

$$R_g^{el} = \frac{2\mu_g}{a^3} f_{el} \quad (1.2.14)$$

and

$$R_g^{OR} = \frac{2\mu_g}{a^3} f_{OR} \quad (1.2.15)$$

Similarly, the reaction fields in the excited state are^{3,18,19}

$$R_e^{el} = \frac{2\mu_e}{a^3} f_{el} \quad (1.2.16)$$

$$R_e^{OR} = \frac{2\mu_e}{a^3} f_{OR} \quad (1.2.17)$$

Where R_e^{el} and R_e^{OR} are the electronic and orientational components of the reaction field in the excited state.

Figure 1.2.4 depicted the energetics behind the whole excitation and deexcitation process of a fluorophore in a dielectric medium. In the ground state, the solvent molecules remain in equilibrium with the fluorophore of dipole moment μ_g . Therefore, the reaction field around it are R_g^{el} and R_g^{OR} . Thus, the energy of this state with proper solvent orientation can be written as,^{3,18,19}

$$E_g^S = E_g^V - \mu_g R_g^{el} - \mu_g R_g^{OR} \quad (1.2.18)$$

Where E_g^V is the ground state energy of the molecule in the vapor state. It is noted that the whole energetics of the fluorophore in a dielectric medium is calculated with respect to the energy of the corresponding states in vapor state. As we bring a dipole from vapor state to a dielectric medium, it induces a reaction field (R) and the energy stabilizes by an amount μR as described in equation 1.2.18. 'S' in the superscript of E_g^S indicates that it is a properly solvated state. Using the expressions of R_g^{el} and R_g^{OR} given in equation 1.2.14 & 1.2.15, we get^{3,18,19}

$$E_g^S = E_g^V - \mu_g \frac{2\mu_g}{a^3} f_{el} - \mu_g \frac{2\mu_g}{a^3} f_{OR} \quad (1.2.19)$$

Just after excitation by a light of wavenumber $\bar{\nu}_A$, the dipole moment changes from $\mu_g \rightarrow \mu_e$ so does the electronic reaction field from $R_g^{el} \rightarrow R_e^{el}$. Whereas the orientation reaction field remains same as that of the ground state i.e., R_g^{OR} as the excitation is instantaneous. This state is therefore not solvated properly. The energy of this state is given by^{3,18,19}

$$E_e^{NS} = E_e^V - \mu_e \frac{2\mu_e}{a^3} f_{el} - \mu_e \frac{2\mu_g}{a^3} f_{OR} \quad (1.2.20)$$

The excitation energy can be written as the difference between E_e^{NS} and E_g^S .^{3,18,19}

$$hc\bar{\nu}_A = (E_e^V - E_g^V) - \frac{2(\mu_e^2 - \mu_g^2)}{a^3} f_{el} - \frac{2\mu_g(\mu_e - \mu_g)}{a^3} f_{OR} \quad (1.2.21)$$

As time progress after photoexcitation, the solvent molecules reorient themselves around μ_e to reach the most stable orientation. Hence the reaction field gradually changes from $R_g^{OR} \rightarrow R_e^{OR}$. The energy of the solvated excited state (E_e^S) can be written as^{3,18,19}

$$E_e^S = E_e^V - \mu_e \frac{2\mu_e}{a^3} f_{el} - \mu_e \frac{2\mu_e}{a^3} f_{OR} \quad (1.2.22)$$

The molecule eventually reaches the ground state by radiative transition (fluorescence) and the dipole moment changes from μ_e to μ_g . Accordingly, the reactive field due to electronic polarization also changes rapidly from $R_e^{el} \rightarrow R_g^{el}$. Whereas the orientational reactive field again fails to react to the change and remains R_e^{OR} . That makes this newly generated ground state not solvated and its energy E_g^{NS} is given by^{3,18,19}

$$E_g^{NS} = E_g^V - \mu_g \frac{2\mu_g}{a^3} f_{el} - \mu_g \frac{2\mu_e}{a^3} f_{OR} \quad (1.2.23)$$

The difference between E_e^S and E_g^{NS} gives the fluorescence.^{3,18,19}

$$hc\bar{\nu}_F = (E_e^V - E_g^V) - \frac{2(\mu_e^2 - \mu_g^2)}{a^3} f_{el} - \frac{2\mu_e(\mu_e - \mu_g)}{a^3} f_{OR} \quad (1.2.24)$$

Subtracting equation 1.2.21 and 1.2.24 we get^{3,18,19}

$$\bar{\nu}_A - \bar{\nu}_F = \frac{1}{hc} \left[\frac{2\mu_e(\mu_e - \mu_g)}{a^3} - \frac{2\mu_g(\mu_e - \mu_g)}{a^3} \right] f_{OR} \quad (1.2.25)$$

Using the form of f_{OR} given in equation 1.2.13, doing algebraic simplification, and finally adding the inherent Stokes shift (C) between excitation and fluorescence wavenumber due to vibrational relaxation (VR) we obtain^{3,18,19}

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hca^3} (\mu_e - \mu_g)^2 \left[\frac{\epsilon-1}{2\epsilon+1} - \frac{n^2-1}{2n^2+1} \right] + C \quad (1.2.26)$$

This is the Lippert-Mataga equation.

It is thus clear that the formation of the E_e^S state from the E_e^{NS} state needs finite amount of time that depends on the solvent properties. Usually, the E_e^{NS} state is denoted as the Frank-Condon (FC) state and the E_e^S state is known as the solvated state (SS).

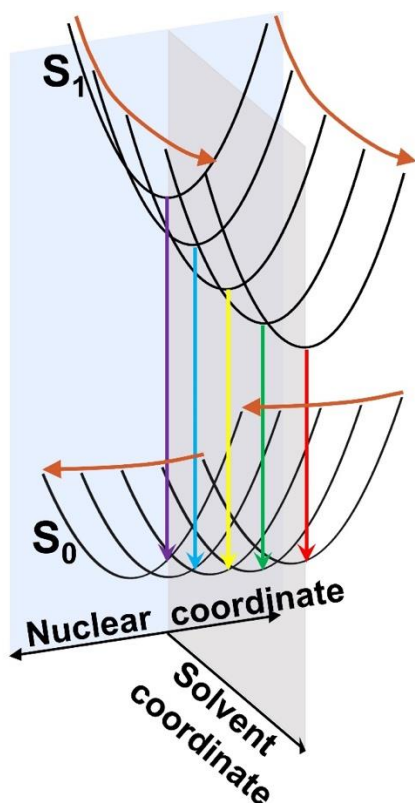


Figure 1.2.5. Depiction of solvation dynamics process. The electronic states are parabolic along the nuclear coordinate. These whole parabolic states of the molecule stabilize or destabilizes along the solvent coordinate depending on solvent orientations around the molecule.

In figure 1.2.5 a schematic representation of the said process has been depicted. As shown in the figure, the solvation is a continuous process and consist of numerous intermediate states between FC and SS state. If the excited probe molecule is fluorescent in nature, then as solvation progress the fluorescence should redshift with time. This is known as time-dependent fluorescence Stokes shift (TDFSS).^{3-17,21-35} Using time-resolved fluorescence measurement, it is possible to capture each step of solvation and determine the time constant of solvation. In figure 1.2.5, we have schematically presented the relaxation of electronic states along the solvent coordinate which represents the solvent orientations around the fluorophore.

When time-resolved fluorescence measurements at different wavelength (λ) are done with exact same peak counts, we obtain i number of time constants (τ_i) and corresponding amplitudes (a_i). These amplitudes and time constants vary with λ . For such a case we can write the intensity at λ at time t by^{3,4}

$$B(\lambda, t) = \sum_i a_i(\lambda) e^{-t/\tau_i(\lambda)} \quad (1.2.27)$$

Where $\sum_i a_i(\lambda) = \text{peak count}$

If $B(\lambda, t)$ was the actual intensity at λ at time t , then time integration of $B(\lambda, t)$ would have provided us the steady state spectra ($I_{ss}(\lambda)$). However, as decays are collected at same peak counts for all λ , the intensity obtained at different λ at different times are wrongly estimated by a factor which is also a function of λ . Let us take this correction factor as $A(\lambda)$. Multiplication of $A(\lambda)$ with $B(\lambda, t)$ will give the actual intensities at λ at time t . Let us express this corrected intensity at λ at time t as $I(\lambda, t)$.^{3,4}

$$I(\lambda, t) = A(\lambda) B(\lambda, t) \quad (1.2.28)$$

Combining equation 1.2.27 and 1.2.28, we get

$$I(\lambda, t) = A(\lambda) \sum_i a_i(\lambda) e^{-t/\tau_i(\lambda)}; \text{ Where } \sum_i a_i(\lambda) = \text{peak count} \quad (1.2.29)$$

Now the time-integral of $I(\lambda, t)$ over $0 \rightarrow \infty$ will give the $I_{ss}(\lambda)$

$$\begin{aligned}
I_{SS}(\lambda) &= \int_0^\infty I(\lambda, t) dt \\
&= \int_0^\infty A(\lambda) \sum_i a_i(\lambda) e^{-t/\tau_i(\lambda)} dt \\
&= A(\lambda) \sum_i a_i(\lambda) \tau_i(\lambda)
\end{aligned} \tag{1.2.30}$$

$$\therefore A(\lambda) = \frac{I_{SS}(\lambda)}{\sum_i a_i(\lambda) \tau_i(\lambda)} \tag{1.2.31}$$

Using this form of $A(\lambda)$ in equation 1.2.29 we get

$$I(\lambda, t) = \frac{I_{SS}(\lambda)}{\sum_i a_i(\lambda) \tau_i(\lambda)} \sum_i a_i(\lambda) e^{-t/\tau_i(\lambda)} \tag{1.2.32}$$

This is the working formula to construct time-resolved emission spectra (TRES).^{3-17,21-35}

Let us consider another case where the fluorescence decays at different λ were recorded without fixing the peak counts but based on acquisition time. In that case, the amplitudes of decays at different λ would have been according to their fluorescence quantum yields. In this case $B(\lambda, t)$ has a same expression as equation 1.2.27, but $\sum_i a_i(\lambda) \neq 1$. Moreover $A(\lambda) = 1$. Hence

$$I(\lambda, t) = \sum_i a_i(\lambda) e^{-t/\tau_i(\lambda)} \tag{1.2.33}$$

And

$$I_{SS}(\lambda) = \sum_i a_i(\lambda) \tau_i(\lambda) \tag{1.2.34}$$

In this method, equation 1.2.33 is the expression for TRES.

Construction of TRES reveals the gradual shift of emission spectra with time following excitation. The time-dependent shift of emission spectra is the observable behind the excited state relaxation. Therefore, the extent of solvent relaxation is formulated as^{3-17,21-35}

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \tag{1.2.35}$$

$C(t)$ is the solvent response function, $\nu(t)$ is the frequency maxima of emission spectra at time t , $\nu(\infty)$ is the frequency maximum of emission spectra after infinite

time (i.e., at the end of solvation), $\nu(0)$ is the frequency maximum of emission spectra at time 0 (i.e., at the start of solvation).^{3-17,21-35}

The obtained value of $\nu(0)$ from time-resolved study is often not the actual $\nu(0)$ as it is limited by the instrument response function. Therefore, for most of the cases we miss a certain percentage of initial solvent relaxation. It became customary to determine the percentage miss in solvation following the procedure described by Fee and Maroncelli.^{3-17,21-35} After photoexcitation, all molecules reach the ground vibrational level of the first excited electronic state by vibrational relaxation. This amount of energy relaxation is not a part of solvation. Shift in emission spectra due to this relaxation is called the intrinsic Stokes' shift of the molecule. Solvation starts after that. This implies that the emission spectra at the start of the solvation, which is the so-called zero-time spectra, should match nicely with the emission spectra of the molecule in a completely non-polar medium like cyclohexane where solvent relaxation does not happen. The difference of frequency maximum of the molecule in cyclohexane to the estimated zero-time spectra from TRES gives the percentage miss of solvation.^{3-17,21-35}

According to the dielectric continuum model of solvation and linear response theory, temporal response of $C(t)$ should be exponential. Whereas in real case, it often deviates from the expectation and becomes multi-exponential. The involvement of various motions like translation, rotation, libration, vibration of solvent molecules around the solute having different timescales is the reason for this. All of these contributes to the multi-exponential nature of $C(t)$ decay.⁵⁻¹⁷

1.3. Excimer Formation

Excimer is a kind of dimer formed by the collision of two monomers, where one of them is in its electronically excited state and the other in electronic ground state. For two approaching ground state monomers there is only coulombic interaction acting between them. As the two ground state monomers approach one another via

diffusion, the coulombic repulsion between them increases rapidly, thus increasing the energy of the whole system steadily as a function of distance between them. On the other hand, when one of those monomers is in the excited electronic state, it has half-filled HOMO (or HOMO-i) and LUMO (or LUMO+j). Due to the lower ionization potential of half-filled LUMO and higher electron affinity of half-filled HOMO, the excited monomer possesses the ability to interact with any species having polarizable electron cloud. . In terms of MO interaction, the extra stabilization in case of excimer formation can be established. In the following figure we have shown the MO picture for the dimerization in ground state as well as for the excimer formation.^{1,2}

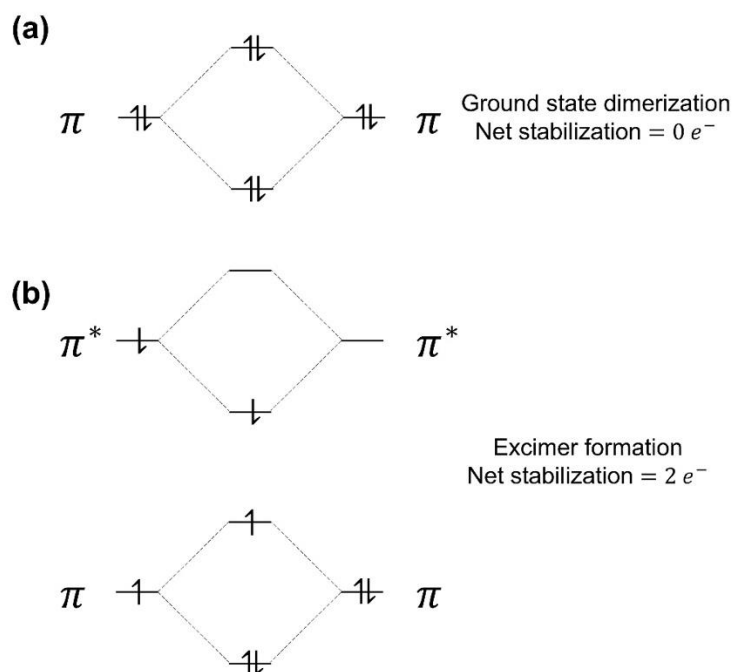


Figure 1.3.1. Qualitative understanding of the stabilizing effect for excimer formation using orbital interactions like the MO diagram.

From the figure 1.3.1, it is understandable that for dimer formation between two ground state monomers, there is no net energy stabilization available. Whereas, when one of the monomers are photo-excited, MO interaction leads to net stabilization of 2 electrons.^{1,2}

The availability of an extra stabilization energy in case of excited state dimer (excimer) formation can also be shown quantum mechanically. It is known as the exciton model. Let us first consider the case of ground state dimerization where the molecules are in ground state. Suppose ψ_1 and ψ_2 are the ground state wavefunction for the two molecules. Thus, the total ground state wave function is simply given by the product of the two individual wavefunction.

$$\psi_G = \psi_1\psi_2 \quad (1.3.1)$$

Therefore, the energy of the ground state will be given by

$$E_G = \iint \psi_1\psi_2 H \psi_1\psi_2 d\tau_1 d\tau_2 \quad (1.3.2)$$

Where H is given by,

$$H = H_1 + H_2 + V_{12} \quad (1.3.3)$$

In the above equation, H_1 and H_2 are the individual Hamiltonian of the monomers, V_{12} is intermolecular perturbation potential.

The energy for this system will come as,

$$E_G = E_1 + E_2 + \iint \psi_1\psi_2 (V_{12}) \psi_1\psi_2 d\tau_1 d\tau_2 \quad (1.3.4)$$

The third term on the right-hand side of the equation 1.3.4 gives the repulsion energy between the two molecules. It is a positive term and is destabilizing in nature. Its magnitude increases as the distance between two molecule decreases.

Now let us think about the case where one molecule is in excited state and the other is in the ground electronic state. If 1 and 2 designate the two molecules, then there are two possibilities, molecule 1 is in excited state and molecule 2 is in ground state and the vice versa. If ψ_1^* is the excited state wavefunction of molecule 1 and ψ_2 is the ground state wavefunction of molecule 2 then the total wavefunction of the system can be given as $\psi_1^*\psi_2$, whereas for the other case where molecule 1 is in ground state but molecule 2 is in excited state the total wavefunction will be $\psi_1\psi_2^*$. As the ground state and excited state wavefunction for the molecule are different hence any one of the above two product wavefunctions can represent the total

wavefunction of the state of interest. To properly represent the total wavefunction for the system we must take the linear combination of $\psi_1^*\psi_2$ and $\psi_1\psi_2^*$.

Therefore, the wavefunction that will represent the state of interest will be given by,

$$\psi_E = r\psi_1^*\psi_2 + s\psi_1\psi_2^* \quad (1.3.5)$$

Now we must determine the values of r & s.

To do so we can follow the exact same procedure as we do in case of Huckel MO theory e.g., determination of the Huckel MO for ethylene.

Corresponding secular equation will be

$$\begin{bmatrix} H_{11} - E_E & H_{12} \\ H_{21} & H_{22} - E_E \end{bmatrix} \begin{bmatrix} r \\ s \end{bmatrix} = 0 \quad (1.3.6)$$

Where H_{11} , H_{22} , H_{12} and H_{21} are given by

$$H_{11} = H_{22} = \iint \psi_1^*\psi_2 H \psi_1^*\psi_2 d\tau_1 d\tau_2 \quad (1.3.7)$$

$$H_{12} = H_{21} = \iint \psi_1^*\psi_2 H \psi_1\psi_2^* d\tau_1 d\tau_2 \quad (1.3.8)$$

If we work that calculation out, then we will end up with two different set of coefficients (r & s) and thus two different wavefunctions as follows

$$\psi'_E = \frac{1}{\sqrt{2}}(\psi_1^*\psi_2 + \psi_1\psi_2^*) \quad (1.3.9)$$

$$\psi''_E = \frac{1}{\sqrt{2}}(\psi_1^*\psi_2 - \psi_1\psi_2^*) \quad (1.3.10)$$

As these two wavefunctions are different, hence energy of these two states will be different.

$$E'_E = E_1^* + E_2 + \iint \psi_1^*\psi_2(V_{12})\psi_1^*\psi_2 d\tau_1 d\tau_2 + \iint \psi_1^*\psi_2(V_{12})\psi_1\psi_2^* d\tau_1 d\tau_2 \quad (1.3.11)$$

$$E''_E = E_1^* + E_2 + \iint \psi_1^*\psi_2(V_{12})\psi_1^*\psi_2 d\tau_1 d\tau_2 - \iint \psi_1^*\psi_2(V_{12})\psi_1\psi_2^* d\tau_1 d\tau_2 \quad (1.3.12)$$

The only difference between these two energy levels is the fourth term on the right-hand side of equation 1.3.11 & 1.3.12. The stabilizing effect for excited state dimer

comes from this energy splitting term, $\mathcal{E}$. That is why excimer emission comes at longer wavelength compared to the monomeric emission.

$$\mathcal{E} = \iint \psi_1^* \psi_2 (V_{12}) \psi_1 \psi_2^* d\tau_1 d\tau_2 \quad (1.3.13)$$

Now let us consider the other case where both monomer molecules got excited. For that case both the molecules 1 & 2 are in the first excited state hence the corresponding wavefunctions are ψ_1^* and ψ_2^* . As there are no other possible combination available hence the total wavefunction will be given by the product of the two excited state wavefunction, exactly like the case where both the molecules were in ground state. The total wavefunction will be given by,

$$\psi_{EE} = \psi_1^* \psi_2^* \quad (1.3.14)$$

And the energy calculation for this state will be exactly like that of the first case where both the molecules are in ground state. It is shown in the following equation.

$$E_{EE} = \iint \psi_1^* \psi_2^* H \psi_1 \psi_2 d\tau_1 d\tau_2 = E_1^* + E_2^* + \iint \psi_1^* \psi_2^* (V_{12}) \psi_1 \psi_2 d\tau_1 d\tau_2 \quad (1.3.15)$$

As there is no orbital mixing in this case like the ground state case, hence there is no possibility of energy splitting and excimer formation.

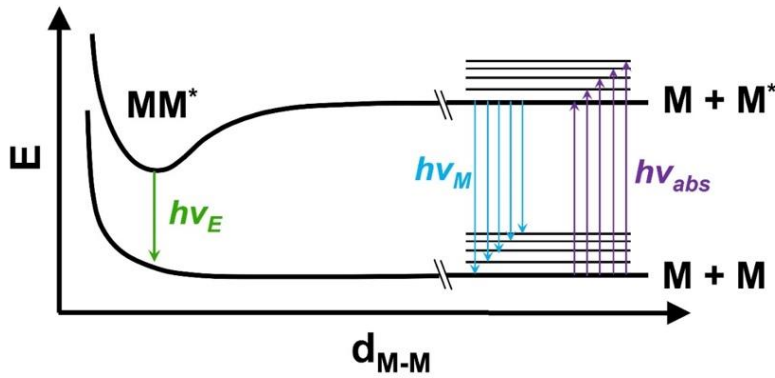


Figure 1.3.2. Potential energy curve (PEC) for excimer formation. When the distance between two monomers (d_{M-M}) is large, structured monomeric emission is observed. Two monomers come close to one another by diffusion and forms the excimer. As the ground state corresponding to the excimer well is not a stationary state, the vibrational structure for it is not well-defined. Therefore, excimer emission becomes structureless.

All experimental reports suggest that emission from the excimer state is broad in nature and red-shifted compared to the corresponding monomeric emission.^{1,2,36-39} This observation can be explained by the potential energy curve (PEC) along the distance between two approaching non-excited monomers and the PEC along the distance between two monomers when one of them is electronically excited (figure 1.3.2).

In the above figure, when both the monomers are in the ground state, closing the distance between them gradually increases the overall energy of the system. When one of the monomers is excited, beyond certain point while decreasing intermolecular separation between the excited and non-excited monomer, the stabilizing interactions between M and M* eventually decrease the overall energy. Further decrease in intermolecular separation will rapidly increase the energy. This way a potential well is formed along the intermolecular distance coordinate. This well represents the excimer formation. As at the intermolecular distance where excimer forms, the excited state is stabilized whereas the corresponding ground state is energetically destabilized, emission from the excimer state is usually red shifted compared to the monomeric emission. In the figure monomeric emission which is observed at large intermolecular separation, is shown by blue arrows. The excimer emission is shown in green arrow. When two monomers are well-separated from one another, the vibrational structure of each of them remains intact that is why we observe vibrationally structured monomer emission. Whereas the corresponding ground state of excimer is a very unstable state and rapidly dissociative in nature. That is why this ground state of excimer acts as a continuum and does not have any distinct vibrational feature. This justifies the broadband nature of excimer emission.

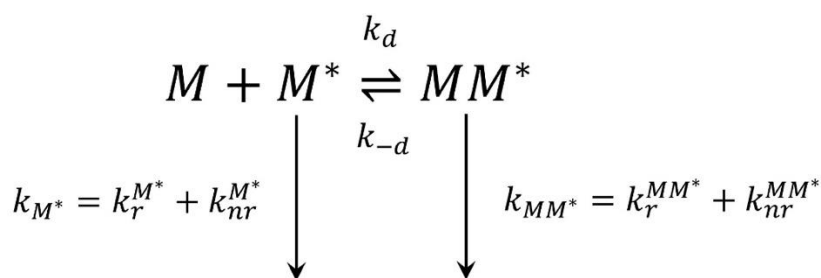


Figure 1.3.3. Equilibrium picture of the excimer formation process. M and M^* are the ground state and excited state monomer. MM^* denotes the excimer. k_{M^*} is the rate constant of decay of M^* and is a sum of the radiative ($k_r^{M^*}$) and non-radiative ($k_{nr}^{M^*}$) decay rate constants for M^* . Similarly, k_{MM^*} is the rate constant of decay of MM^* and is a sum of the radiative ($k_r^{MM^*}$) and non-radiative ($k_{nr}^{MM^*}$) decay rate constants for MM^* . k_d and k_{-d} are the diffusive rate constants.

The whole excimer formation process can be described by the following equilibrium scheme (see figure 1.3.3). Solving the differential equations associated with the change in excited monomer concentration and excimer concentration will give the dynamics of the monomer emission and excimer emission.

The two differential equations associated with the process are as follows

$$\frac{d[M^*]}{dt} = -k_{M^*}[M^*] - k_d[M][M^*] + k_{-d}[MM^*] \quad (1.3.16)$$

$$\frac{d[MM^*]}{dt} = -(k_{MM^*} + k_{-d})[MM^*] + k_d[M][M^*] \quad (1.3.17)$$

Solving equation 1.3.16 and 1.3.17 by using Laplace transform⁴⁰ provides the following solutions

$$[M^*] = [M^*]_0 \left[\frac{k_{MM^*} + k_{-d} - \alpha}{\beta - \alpha} e^{-\alpha t} + \frac{\beta - k_{MM^*} - k_{-d}}{\beta - \alpha} e^{-\beta t} \right] \quad (1.3.18)$$

$$[MM^*] = [M^*]_0 \left[\frac{k_d[M]}{\beta - \alpha} e^{-\alpha t} - \frac{k_d[M]}{\beta - \alpha} e^{-\beta t} \right] \quad (1.3.19)$$

where,

$$\alpha + \beta = k_d[M] + k_{-d} + k_{M^*} + k_{MM^*} \quad (1.3.20)$$

and

$$\alpha\beta = k_d k_{MM^*}[M] + k_{-d} k_{M^*} + k_{M^*} k_{MM^*} \quad (1.3.21)$$

Now let us consider the case when $k_{-d} \ll k_{MM^*}$, which means the dissociation of the excimer is very much slow compared to the lifetime of the excimer. In that case the modified differential equations will be

$$\frac{d[M^*]}{dt} = -k_{M^*}[M^*] - k_d[M][M^*] \quad (1.3.22)$$

$$\frac{d[MM^*]}{dt} = -k_{MM^*}[MM^*] + k_d[M][M^*] \quad (1.3.23)$$

Solving equation 1.3.22 and 1.3.23 by using Laplace transform gives the following solutions

$$[M^*] = [M^*]_0 e^{-(k_d[M] + k_{M^*})t} \quad (1.3.24)$$

$$[MM^*] = \frac{k_d[M][M^*]_0}{k_d[M] + k_{M^*} - k_{MM^*}} [e^{-k_{MM^*}t} - e^{-(k_d[M] + k_{M^*})t}] \quad (1.3.25)$$

From the above equations it is evident that the decay constant of the monomer emission is the growth constant of excimer emission.

Using the expressions of $[M^*]$ and $[MM^*]$, we can write the time-dependent emission intensities of monomer and excimer as⁴¹

$$I_{M^*}(t) = k_r^{M^*} [M^*]_0 e^{-(k_d[M] + k_{M^*})t} \quad (1.3.26)$$

$$I_{MM^*}(t) = k_r^{MM^*} \frac{k_d[M][M^*]_0}{k_d[M] + k_{M^*} - k_{MM^*}} [e^{-k_{MM^*}t} - e^{-(k_d[M] + k_{M^*})t}] \quad (1.3.27)$$

The time-dependent ratio of the excimer and monomer intensity is given by

$$\frac{I_{MM^*}(t)}{I_{M^*}(t)} = \frac{k_r^{MM^*} k_d[M]}{k_r^{M^*} (k_d[M] + k_{M^*} - k_{MM^*})} [e^{(k_d[M] + k_{M^*} - k_{MM^*})t} - 1] \quad (1.3.28)$$

Hence the time-dependent ratio of the excimer and monomer intensity will increase single exponentially.

The steady state emission intensities of monomer and excimer emissions can be written as

$$I_{M^*}^{SS} = k_r^{M^*} [M^*]_0 \int_0^\infty e^{-(k_d[M] + k_{M^*})t} dt = \frac{k_r^{M^*} [M^*]_0}{(k_d[M] + k_{M^*})} \quad (1.3.29)$$

$$\begin{aligned} I_{MM^*}^{SS} &= k_r^{MM^*} \frac{k_d[M][M^*]_0}{k_d[M] + k_{M^*} - k_{MM^*}} \left[\int_0^\infty (e^{-k_{MM^*}t} - e^{-(k_d[M] + k_{M^*})t}) dt \right] \\ &= \frac{k_r^{MM^*} k_d[M][M^*]_0}{k_{MM^*} (k_d[M] + k_{M^*})} \end{aligned} \quad (1.3.30)$$

Therefore, the efficiency of excimer formation can be formulated as

$$\frac{I_{MM^*}^{SS}}{I_{M^*}^{SS}} = \frac{k_r^{MM^*} k_d[M]}{k_r^{M^*} k_{MM^*}} \quad (1.3.31)$$

Equation 1.3.31 suggests that increasing concentration of monomer proportionally increases the excimer efficiency. Pyrene is the most classic example of excimer emission.^{1,2,36-39} Monomeric pyrenes possess vibrationally structured emission around $\sim 380 \text{ nm}$. This monomeric emission intensifies with increasing concentration of pyrene up to pyrene concentration $\sim 10^{-5} M$. Beyond that point, any increase in concentration leads to formation and gradual intensification of a new broadband emission around $\sim 480 \text{ nm}$ with weakening of the vibrationally structured monomer emission. Therefore, the efficiency of excimer formation increases.

1.4. Intersystem Crossing (ISC): Spin Orbit Coupling (SOC) and Heavy Atom Effect (HAE)

Transition between states of different spin multiplicity is forbidden, which makes intersystem crossing (ISC) a spin-forbidden process. This is only valid until the states under consideration are of *pure spin*. Spin orbit coupling is a perturbation that makes spin angular momentum ($\vec{S}$) time dependent. Due to the spin-orbit coupling, individual conservation of the spin angular momentum and the orbital angular momentum ($\vec{L}$) is no longer valid. $\vec{L}$ and $\vec{S}$ are coupled and the total angular momentum remains conserved.⁴²

Electron is a negatively charged particle with intrinsic spin. It can be considered as a magnetic dipole with magnetic moment μ_e . If $\vec{S}$ is its spin angular momentum and γ is the gyromagnetic ratio, $\vec{\mu_e}$ can be expressed as

$$\vec{\mu_e} = \gamma \hbar \vec{S} \quad (1.4.1)$$

Where,

$$\gamma = -g_e \frac{\mu_B}{\hbar} \quad (1.4.2)$$

In equation 1.4.2, g_e is the electron g-factor and has an approximate value of 2, and μ_B is the Bohr magneton and is given by,

$$\mu_B = \frac{|e|\hbar}{2m_e} \quad (1.4.3)$$

Combining equation 1.4.1 & 1.4.2, we can write

$$\vec{\mu}_e = -g_e \mu_B \vec{S} \quad (1.4.4)$$

Point to note from equation 1.4.4 is that spin angular momentum vector ($\vec{S}$) and the magnetic moment vector ($\vec{\mu}_e$) of the electron are opposite to one another.

If the electron, which is a magnetic dipole, finds itself in a magnetic field ($\vec{B}$), they will interact. The $\vec{B}$ will apply torque ($\vec{\tau}$) on the magnetic dipole.

$$\vec{\tau} = \vec{\mu}_e \times \vec{B} \quad (1.4.5)$$

Using the form of $\vec{\mu}_e$ described in equation 1.4.4, we get

$$\vec{\tau} = -g_e \mu_B \vec{S} \times \vec{B} \quad (1.4.6)$$

Multiplying $\hbar$ in denominator and numerator, we obtain

$$\vec{\tau} = -g_e \frac{\mu_B}{\hbar} \hbar \vec{S} \times \vec{B} = g_e \frac{\mu_B}{\hbar} \vec{B} \times \hbar \vec{S} = \vec{\omega}_L \times \hbar \vec{S} \quad (1.4.7)$$

We have represented the vector $\left(g_e \frac{\mu_B}{\hbar} \vec{B}\right)$ as $\vec{\omega}_L$.

Torque is the change in the angular momentum. Therefore,

$$\vec{\tau} = \frac{d(\hbar \vec{S})}{dt} \quad (1.4.8)$$

And

$$\frac{d\vec{S}}{dt} = \vec{\omega}_L \times \vec{S} \quad (1.4.9)$$

This implies that $\frac{d\vec{S}}{dt}$ is perpendicular to $\vec{S}$. It can also be shown that the magnitude of $\vec{S}$ cannot change.

$$\vec{S} \cdot \frac{d\vec{S}}{dt} = \frac{d}{dt} \left(\frac{1}{2} \vec{S} \cdot \vec{S} \right) = \vec{S} \cdot (\vec{\omega}_L \times \vec{S}) = 0 \quad (1.4.10)$$

As $\vec{S}$ and $(\vec{\omega}_L \times \vec{S})$ are perpendicular to each other, their dot product is 0.

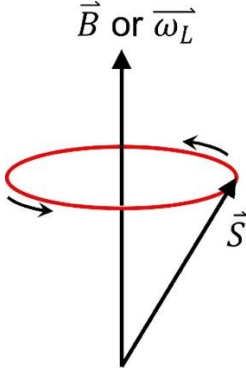


Figure 1.4.1. Larmor precession of an electron having spin angular momentum $\vec{S}$ because of the torque exerted on it by the magnetic field $\vec{B}$. Larmor precession frequency is represented by $\vec{\omega}_L$.

In conclusion, exposing an electron having magnetic moment $\vec{\mu}_e$ and spin angular momentum $\vec{S}$ to a magnetic field $\vec{B}$ will exert a torque on the electron. However, the magnitude of $\vec{S}$ cannot change. Consequently, the spin angular momentum $\vec{S}$ will start to precess around the vector $\vec{B}$ or $\vec{\omega}_L$. This is called Larmor precession and $\vec{\omega}_L$ represents Larmor precession frequency. In figure 1.4.1 we have depicted it.

We should remember that for energy calculation for the electron-magnetic field interaction we should consider the magnetic field at the site of the electron ($\vec{B}'$). The energy Hamiltonian ($\hat{H}$) is given by the following dot product.

$$\hat{H} = -\vec{\mu}_e \cdot \vec{B}' \quad (1.4.11)$$

Using the form of $\vec{\mu}_e$ described earlier one can modify equation 1.4.11 as

$$\hat{H} = -(-g_e \mu_B \vec{S}) \cdot \vec{B}' = \left(g_e \frac{\mu_B}{\hbar} \vec{B}'\right) \cdot \hbar \vec{S} = \vec{\omega}_L \cdot \hbar \vec{S} \quad (1.4.12)$$

The above expression only considers the site of the electron. Whereas all H-like atoms consist of a nucleus and an electron rotating around it. In this frame the interaction energy is different and is given by,

$$\hat{H} = (\vec{\omega}_L + \vec{\omega}_T) \cdot \hbar \vec{S} \quad (1.4.13)$$

Where, $\vec{\omega}_T$ is the Thomas precession vector and it equals to $-\frac{1}{2}\vec{\omega}_L$. Thus, equation 1.4.13 modifies to

$$\hat{H} = \frac{1}{2}\vec{\omega}_L \cdot \hbar \vec{S} \quad (1.4.14)$$

This $\frac{1}{2}$ is the famous Thomas factor.

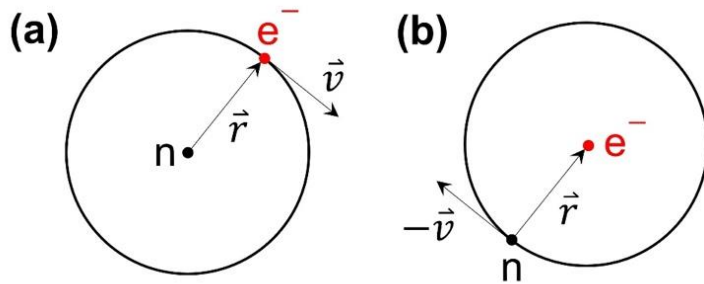


Figure 1.4.2. Two different frame of representation for a H-like atom, (a) where the nucleus (n) is stationary and the electron (e^-) is rotating around it with a velocity $\vec{v}$ and (b) where the electron (e^-) is stationary and the nucleus (n) is rotating around it with a velocity $-\vec{v}$. In both the cases the distance from the nucleus to the electron is $\vec{r}$.

We need to find $\vec{B}'$ to determine the energy. Let us consider a H-like atom, where an electron is rotating around the nucleus (figure 1.4.2a). The distance from nucleus to electron is $\vec{r}$ and the velocity of the electron is $\vec{v}$. The same system can also be modelled as if the electron is sitting in the center and the positively charged nucleus is rotating around the electron with velocity $-\vec{v}$ (figure 1.4.2b). The distance from nucleus to electron is $\vec{r}$. We should remember that, this relative circular motion of the positively charged nucleus creates the magnetic field ($\vec{B}'$). We can express the $\vec{B}'$ using Biot-Savart law.²⁰

$$d\vec{B}' = \frac{\mu_0}{4\pi} I \frac{d\vec{l} \times \vec{r}}{r^3} \quad (1.4.15)$$

Where, μ_0 is the magnetic constant and I is the current generated due to the positive nucleus and is given by,

$$I = Z|e|f = Z|e|\frac{1}{T} \quad (1.4.16)$$

Where, Z is the atomic number, f is the frequency and T is the time-period. $d\vec{l}$ can be written as,

$$d\vec{l} = \left(\frac{d\vec{l}}{dt}\right) dt = (-\vec{v})dt \quad (1.4.17)$$

Combining all the forms equation 1.4.15 changes to

$$d\vec{B}' = \frac{\mu_0}{4\pi} \frac{Z|e|}{T} dt \frac{-\vec{v} \times \vec{r}}{r^3} \quad (1.4.18)$$

The vector $\frac{-\vec{v} \times \vec{r}}{r^3}$ goes inside the page. Integration on equation 1.4.18 followed by some algebraic simplifications results in

$$\begin{aligned} \vec{B}' &= \frac{\mu_0}{4\pi} \frac{Z|e|}{T} T \frac{-\vec{v} \times \vec{r}}{r^3} \\ \Rightarrow \vec{B}' &= \frac{\mu_0}{4\pi} Z|e| \frac{-\vec{v} \times \vec{r}}{r^3} \\ \Rightarrow \vec{B}' &= \frac{\mu_0}{4\pi} Z|e| \frac{-\vec{v} \times \vec{r}}{r^3} \frac{\epsilon_0}{\epsilon_0} \\ \Rightarrow \vec{B}' &= -\mu_0 \epsilon_0 \vec{v} \times \left(\frac{Z|e|}{4\pi \epsilon_0} \frac{\vec{r}}{r^3} \right) \end{aligned} \quad (1.4.19)$$

The term $\left(\frac{Z|e|}{4\pi \epsilon_0} \frac{\vec{r}}{r^3} \right)$ is nothing but the electric field ($\vec{E}$) of the nucleus on the electron.

And $\mu_0 \epsilon_0 = \frac{1}{c^2}$.

Therefore,

$$\vec{B}' = -\frac{\vec{v} \times \vec{E}}{c^2} \quad (1.4.20)$$

And

$$\vec{\omega}_L = g_e \frac{\mu_B}{\hbar} \left(-\frac{\vec{v} \times \vec{E}}{c^2} \right) \quad (1.4.21)$$

Using the expression of μ_B (equation 1.4.3) and putting $\left(\frac{Z|e|\hbar}{4\pi\epsilon_0} \frac{\vec{r}}{r^3}\right)$ in place of $\vec{E}$, we get

$$\vec{\omega}_L = g_e \frac{|e|\hbar}{2m_e} \left(-\frac{\vec{v}}{c^2}\right) \times \left(\frac{Z|e|\hbar}{4\pi\epsilon_0} \frac{\vec{r}}{r^3}\right) \quad (1.4.22)$$

The orbital angular momentum vector can be written as

$$\hbar\vec{L} = \vec{r} \times m_e \vec{v} = -m_e \vec{v} \times \vec{r} \quad (1.4.23)$$

Using this expression in equation 1.4.22 we get

$$\vec{\omega}_L = g_e \frac{|e|\hbar}{2m_e} \left(\frac{1}{c^2}\right) \left(\frac{Z|e|\hbar}{4\pi\epsilon_0} \frac{1}{r^3}\right) \left(\frac{\hbar\vec{L}}{m_e}\right) = g_e \frac{Z|e|^2\hbar^2}{8\pi\epsilon_0 m_e^2 c^2} \left(\frac{\vec{L}}{r^3}\right) \quad (1.4.24)$$

Using this form of $\vec{\omega}_L$, in equation 1.4.14 we obtain

$$\hat{H} = \frac{1}{2} g_e \frac{Z|e|^2\hbar^2}{8\pi\epsilon_0 m_e^2 c^2} \left(\frac{\vec{L}}{r^3}\right) \cdot \hbar\vec{S} = \frac{AZ}{r^3} \vec{L} \cdot \vec{S} \quad (1.4.25)$$

Where

$$A = \left(\frac{g_e}{2}\right) \frac{\hbar^2 |e|^2}{8\pi\epsilon_0 m_e^2 c^2} \quad (1.4.26)$$

This hamiltonian $\hat{H}$ is the spin-orbit coupling hamiltonian and usually represented as $\hat{H}_{SO}$. The expectation value of energy can be written as

$$\langle \hat{H}_{SO} \rangle = \left\langle \frac{AZ}{r^3} \right\rangle \langle \vec{L} \cdot \vec{S} \rangle = \zeta_{SO} \langle \vec{L} \cdot \vec{S} \rangle \quad (1.4.27)$$

In the above equation, ζ_{SO} is the spin-orbit coupling factor. Determination of $\langle \vec{L} \cdot \vec{S} \rangle$ is quite straight forward.

$$\vec{J}^2 = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) = \vec{L}^2 + \vec{S}^2 + 2\vec{L} \cdot \vec{S} \quad (1.4.28)$$

Rearrangement gives

$$\vec{L} \cdot \vec{S} = \frac{1}{2} [\vec{J}^2 - \vec{L}^2 - \vec{S}^2] \quad (1.4.29)$$

Hence,

$$\langle \vec{L} \cdot \vec{S} \rangle = \frac{1}{2} [\langle \vec{J}^2 \rangle - \langle \vec{L}^2 \rangle - \langle \vec{S}^2 \rangle] = \frac{1}{2} [J(J+1) - l(l+1) - s(s+1)] \quad (1.4.30)$$

For the determination of ζ_{SO} , we need to evaluate the following integral

$$\begin{aligned}\zeta_{SO} &= \left\langle \frac{AZ}{r^3} \right\rangle = \left\langle R(r)_{n,l} \left| \frac{AZ}{r^3} \right| R(r)_{n,l} \right\rangle \\ \Rightarrow \zeta_{SO} &= \int_0^\infty R(r)_{n,l}^2 \frac{AZ}{r^3} r^2 dr = AZ \int_0^\infty R(r)_{n,l}^2 r^{-3+2} dr\end{aligned}\quad (1.4.31)$$

Solution of integration of this form is given below.

$$\int_0^\infty r^{k+2} R(r)_{n,l}^2 dr = a_0^k Z^{-k} P_k(n, l) \quad (1.4.32)$$

In our case, $k = -3$. Therefore,^{1,2,42-44}

$$\zeta_{SO} = AZ a_0^{-3} Z^3 P_{-3}(n, l) = \frac{A}{a_0^3} \frac{Z^4}{n^3(l+1)(l+1/2)l} \quad (1.4.33)$$

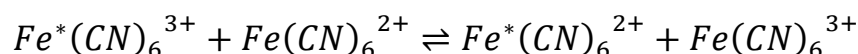
And

$$\langle \hat{H}_{SO} \rangle = \frac{A}{2a_0^3} \frac{Z^4}{n^3(l+1)(l+1/2)l} [j(j+1) - l(l+1) - s(s+1)] \quad (1.4.34)$$

If we estimate $\langle \hat{H}_{SO} \rangle$ for H-atom for $n = 2$ and $l = 1$, we will obtain value in the order of $10^{-5} eV$ which is negligibly small. Spin-orbit coupling is a very weak interaction. However, as $\zeta_{SO} \propto Z^4$, the strength of spin-orbit coupling is much higher in case of heavier atom. Introduction of heavy atoms externally or internally to a system has been a well-known technique to increase spin-orbit coupling and facilitate ISC. It is known as heavy atom effect.⁴³⁻⁵⁹

1.5. Photoinduced Electron Transfer (PET)

During the 1940s, radioactive isotopes were in use to track reaction mechanisms. Such studies revealed a simplest reaction.^{2,60-66}



In this reaction no bond has been broken or made, only an electron has been transferred from one centre to the other. This is a self-exchange reaction, where the energy of the reactants and products are same, and there is no driving force for this reaction. However, isotope labelling proves the transfer of electron. It is surprising

that, despite having no driving force for the reaction, the electron transfer takes place. Moreover, it was observed that smaller cations undergo slower exchange compared to the larger cations. Proper reasoning behind these kinds of observations remained mystery for a long time. Libby was the first to provide an explanation. According to him, an electron jump from reactant to product takes place first. This electron jump is a rapid process and the nuclear geometries of the reactants as well as the orientations of the surrounding solvent molecules cannot react to this sudden change, which is so called the Franck-Condon principle. Therefore, after the electron transfer, as the Fe^{3+} converts to Fe^{2+} , the solvent orientation and bond lengths around the Fe^{2+} remains as that of the Fe^{3+} and vice versa. This unfavourable environment creates a high energy state, which then relaxes to the stable conformations for the product. This required jump in energy is higher for smaller cations as smaller cations usually remains more solvated than larger ones. The problem with the Libby's mechanism is that it violates the law of conservation of energy.^{2,60-66}

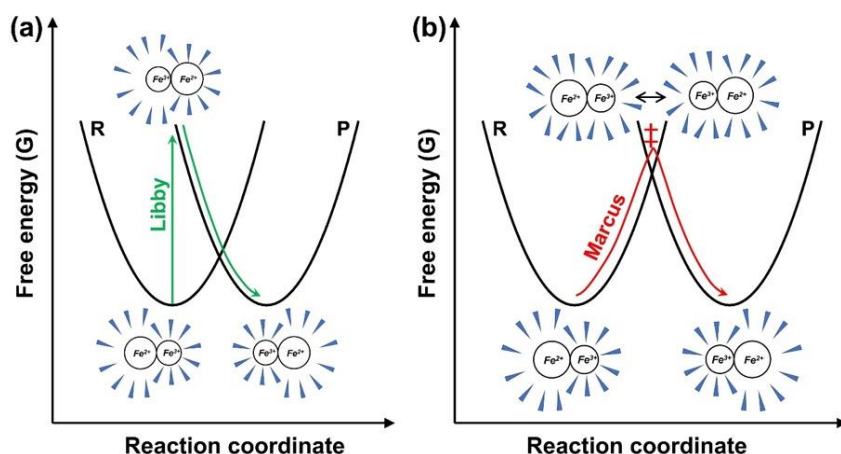


Figure 1.5.1. (a) Libby's mechanism of self-exchange reaction. (b) Marcus depiction of self-exchange reaction through a transition state formed by fluctuation along infinite nuclear and solvent coordinates.

It was Rudolph Marcus who first recognized this problem with Libby's theory and developed a new theory for outer sphere electron transfer reactions. Marcus asked a

simple question. "From where the energy comes for that sudden jump?". He realized that to hold the laws of energy conservation and still Franck-Condon principle be applicable, some other process must happen before and after the electron transfer. According to Marcus, those other processes are nothing but fluctuations along all possible nuclear coordinates and solvent coordinates. As a result, the reactant and the product energy fluctuate with the nuclear and solvent reorganization. This allows the reactant and product to reach an iso-energetic configuration and allows the electron transfer to proceed. In figure 1.5.1, we have depicted the process in a simple way. In the figure, energy of the reactants and the products with solvent fluctuations has been showed as parabolas (as in simple harmonic oscillator). Equilibrium solvent cages around the reactant and the product are different. Along the solvent fluctuation coordinate, there exists a solvent cage structure in which the energy of the reactant is exactly same as the energy of the product. It is this non-equilibrium state where electron transfer can take place without any jump in energy. This way the Frank-Condon like transfer will proceed without violating the energy conservation law. After the electron transfer the products can relax along the solvent and nuclear coordinates to reach the equilibrium configuration or they can simply separate.^{2,60-66}

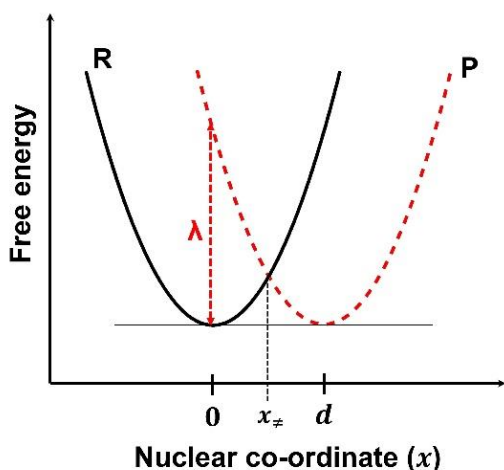


Figure 1.5.2. Parabolic representation of a self-exchange reaction. R and P represents the reactant and the product parabola respectively. λ is the energy of the product parabola (P) at the reactant geometry. It is known as the reorganization energy.

To develop his theory, Marcus described the potential energy profile of the reactant and the product to be parabolic in nature (as in simple harmonic oscillator).^{2,60-66} The equation for the reactant and product for a self-exchange reaction can be written as

$$G_R = \frac{1}{2} k x^2 \quad (1.5.1)$$

$$G_P = \frac{1}{2} k (x - d)^2 \quad (1.5.2)$$

The reorganization energy is the energy of the product at the equilibrium geometry of reactant ($x = 0$ in figure 1.5.2) when $\Delta G^0 = 0$. Therefore, λ can be expressed as,

$$\lambda = \frac{1}{2} k (0 - d)^2 = \frac{1}{2} k d^2 \quad (1.5.3)$$

At $x = x_\ddagger$, $G_R = G_P$

$$\therefore \frac{1}{2} k x_\ddagger^2 = \frac{1}{2} k (x_\ddagger - d)^2$$

$$\Rightarrow x_\ddagger^2 = (x_\ddagger^2 - 2d x_\ddagger + d^2)$$

$$\Rightarrow x_\ddagger = \frac{d}{2} \quad (1.5.4)$$

$\therefore \Delta G^\ddagger$ is the free energy of the reactant or the product parabola at $x = x_\ddagger$

$$\therefore \Delta G^\ddagger = \frac{1}{2} k x_\ddagger^2$$

$$\Delta G^\ddagger = \frac{1}{8} k d^2 = \frac{\lambda}{4} \quad (1.5.5)$$

Now let us add a driving force in the reaction making it more exergonic (negative ΔG^0) as shown in figure 1.5.3.

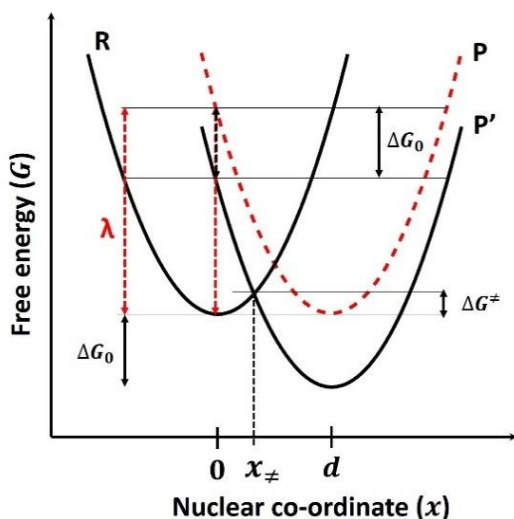


Figure 1.5.3. Parabolic representation of a reaction with negative ΔG^0 . R and P represents the reactant and the product parabola respectively. λ is the energy of the product parabola (P) at the reactant geometry. It is known as the reorganization energy. ΔG^0 is the change in free energy (G) from product to reactant. $\Delta G^\ddagger$ is the free energy change from the transition state geometry to the equilibrium reactant geometry. $x_\ddagger$ is the position of the transition state on the nuclear coordinate.

For this system,

$$G_R = \frac{1}{2} kx^2 \quad (1.5.6)$$

$$G_P' = \frac{1}{2} k(x - d)^2 + \Delta G^0 \quad (1.5.7)$$

at $x = x_\ddagger$, $G_R = G_P'$

$$\begin{aligned} \therefore \frac{1}{2} kx_\ddagger^2 &= \frac{1}{2} k(x_\ddagger - d)^2 + \Delta G^0 \\ \Rightarrow \frac{1}{2} kx_\ddagger^2 &= \frac{1}{2} k(x_\ddagger^2 - 2dx_\ddagger + d^2) + \Delta G^0 \\ \Rightarrow \frac{1}{2} kx_\ddagger^2 &= \frac{1}{2} kx_\ddagger^2 - kdx_\ddagger + \frac{1}{2} kd^2 + \Delta G^0 \\ \Rightarrow x_\ddagger &= \frac{(\Delta G^0 + \frac{1}{2} kd^2)}{kd} \end{aligned} \quad (1.5.8)$$

$\therefore \Delta G^\ddagger$ is the free energy of the reactant or the product parabola at $x = x_\ddagger$

$$\begin{aligned}
\therefore \Delta G^\ddagger &= \frac{1}{2} k x_\ddagger^2 \\
\Rightarrow \Delta G^\ddagger &= \frac{1}{2} k \frac{\left(\Delta G^0 + \frac{1}{2} k d^2\right)^2}{k^2 d^2} \\
\Rightarrow \Delta G^\ddagger &= \frac{\left(\Delta G^0 + \frac{1}{2} k d^2\right)^2}{2 k d^2} = \frac{\left(\Delta G^0 + \frac{1}{2} k d^2\right)^2}{4 \times \frac{1}{2} k d^2} \\
\Rightarrow \Delta G^\ddagger &= \frac{(\Delta G^0 + \lambda)^2}{4\lambda} \tag{1.5.9}
\end{aligned}$$

Equation 1.5.9 suggests that $\Delta G^\ddagger$ has a parabolic dependence with ΔG^0 . Initially, $\Delta G^\ddagger$ will decrease as the reaction becomes more exergonic (making ΔG^0 more negative). This is the normal region of ET ($-\Delta G^0 < \lambda$). By gradually making the reaction more exergonic, when we reach at the point where $-\Delta G^0 = \lambda$, $\Delta G^\ddagger$ becomes zero. After this point, any increase in the driving force for the reaction will start to gradually increase the $\Delta G^\ddagger$. This is called the inverted region ($-\Delta G^0 > \lambda$).^{2,60-66} In figure 1.5.4 we have displayed these three conditions using some parabolas.

Reorganization energy λ consist of the solvation and vibrational components.^{2,60-66}

$$\lambda = \lambda_s + \lambda_i \tag{1.5.10}$$

The solvent reorganization energy (λ_s) is expressed in terms of the electronic charge (e), the radii of the donor and acceptors (r_D & r_A), the donor-acceptor distance (r_{DA}), optical and static dielectric constant of the medium (ϵ_{op} & ϵ_s).^{2,60-66}

$$\lambda_s = e^2 \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{r_{DA}} \right) \left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s} \right) \tag{1.5.11}$$

On the other hand, nuclear reorganization energy depends on all the intramolecular normal modes of vibrations. It is given by,^{2,60-66}

$$\lambda_i = \sum_i \left(\frac{f_i^{D^* \dots A} f_i^{D^{\bullet+} \dots A^{\bullet-}}}{f_i^{D^* \dots A} + f_i^{D^{\bullet+} \dots A^{\bullet-}}} \right) \Delta q_i^2 \tag{1.5.12}$$

where Δq_i is the change in interatomic distances because of vibration and f_i s are the force constants of vibration.^{2,60-66}

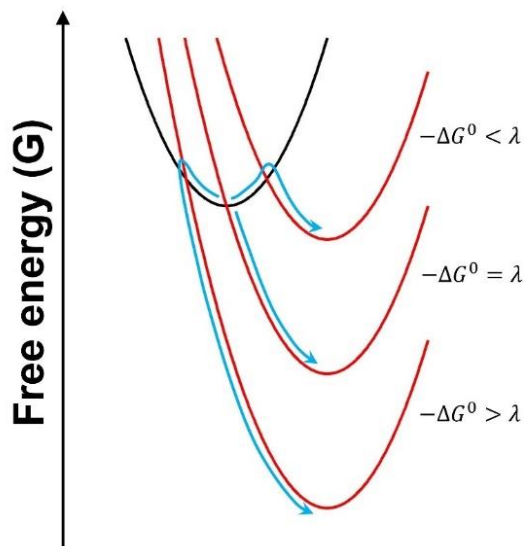


Figure 1.5.4. Parabolic representation of the normal region where $-\Delta G^0 < \lambda$, inverted region where $-\Delta G^0 > \lambda$, and the point where $-\Delta G^0 = \lambda$.

Combining the Marcus theory and the transition state theory, the rate constant of electron transfer (k_{et}) can be written as,^{2,60-66}

$$k_{et} = \frac{a}{\sqrt{\lambda}} \exp \left\{ -\frac{(\Delta G^0 + \lambda)^2}{b\lambda} \right\} \quad (1.5.13)$$

Where $a = \frac{4\pi^2}{h} \frac{V_{el}^2}{\sqrt{4\pi k_B T}}$ and $b = 4k_B T$

V_{el} is electronic coupling matrix element. Hence one should obtain a bell-shaped dependence on measuring k_{et} with varying ΔG^0 .^{2,60-66}

Most common technique to vary the free energy change of the ET reaction is to change the donor or the acceptor molecules.⁶⁷⁻⁸⁸ An important point to note is that, though we change the ΔG^0 of the reaction, we do not change the positions of the reactant or the product parabolas. Therefore, while varying ΔG^0 we should avoid significant change in the molecular structure of the donor or the acceptor molecules.

Another way to change the ΔG^0 is to simply change the temperature. This temperature variation technique has been recently cultivated.^{89,90}

At $-\Delta G^0 = \lambda$, k_{et} becomes k_{et}^{max} ,

$$k_{et}^{max} = \frac{a}{\sqrt{\lambda}} \quad (1.5.14)$$

Let us consider at $\Delta G^0 = x$, $k_{et} = \frac{k_{et}^{max}}{2}$

Thus, we can write,

$$\begin{aligned} \frac{a}{2\sqrt{\lambda}} &= \frac{a}{\sqrt{\lambda}} \exp\left\{-\frac{(x + \lambda)^2}{b\lambda}\right\} \\ \Rightarrow \frac{1}{2} &= \exp\left\{-\frac{(x + \lambda)^2}{b\lambda}\right\} \\ \Rightarrow \ln 2 &= \frac{(x + \lambda)^2}{b\lambda} \\ \Rightarrow x^2 + 2\lambda x + \lambda^2 - b\lambda \ln 2 &= 0 \\ \Rightarrow x &= -\lambda \pm \sqrt{b\lambda \ln 2} \end{aligned} \quad (1.5.15)$$

Hence,⁸⁸

$$FWHM = 2\sqrt{b\lambda \ln 2} = 4\sqrt{k_B T \lambda \ln 2} \quad (1.5.16)$$

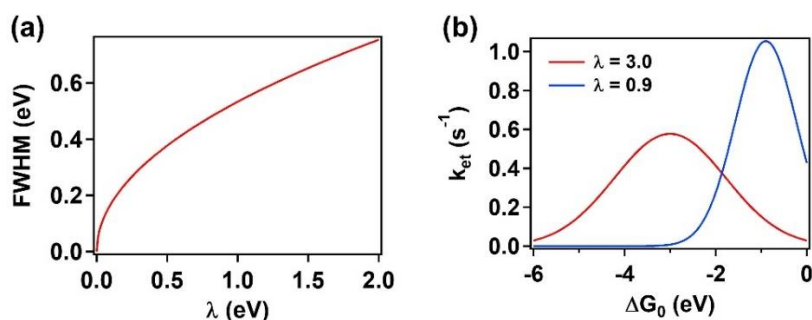


Figure 1.5.5. (a) λ -dependence of the FWHM of Marcus bell-shaped plot. (b) k_{et} vs ΔG^0 plot for two representatives λ values (for simplicity, a and b has been taken as unity).

The λ -dependence of the FWHM of Marcus bell-shaped plot is depicted in figure 1.5.5a. In figure 1.5.5b, I have displayed k_{et} vs ΔG^0 plot for two representative λ values. The graph is a clear representation of how the Marcus plot broadens for higher λ values. Consequently, for systems with high λ values, it becomes harder to achieve experimental points at the Marcus inverted region. For bulk mediums, there are significant contributions from the solvent coordinates in the overall reorganization energy. Because of that, the experimental observation of Marcus inversion in bulk solvents is still unknown. Whereas, as the involvement of solvent reorganization in the confined mediums are much less, there has been numerous reports of observation of Marcus inversion inside these mediums.⁶⁷⁻⁸⁸

Free energy released in an electron transfer reaction can be formulated using the ideas of ionization potential and electron affinity. In any ET reaction one electron leaves the donor orbital and ends up in an empty orbital of acceptor. Ionization potential is the energy required to remove an electron from an isolated gaseous molecule and electron affinity is the energy released when an electron resides in a vacant orbital of an isolated gaseous molecule. Therefore, the net free energy change (ΔG) for transfer of an electron from an isolated gaseous donor molecule to an isolated gaseous acceptor molecule can be written as^{2-4,60,91}

$$\Delta G = IP_D - EA_A \quad (1.5.17)$$

In the above equation, IP_D is the ionization potential for the isolated gaseous donor molecule and EA_A is the electron affinity of the isolated gaseous acceptor molecule.

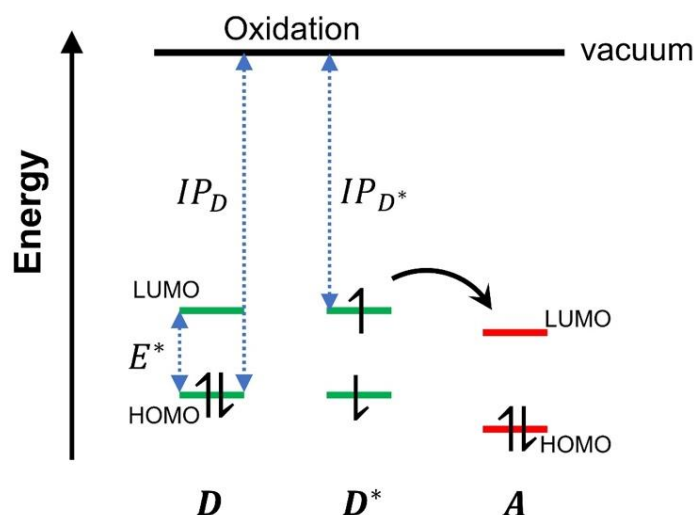


Figure 1.5.6. Energetics of a photoinduced electron transfer (PET) reaction. IP_D is the ionization potential energy for the donor molecule in its ground electronic state. E^* is its electronic excitation energy which excites one electron from the HOMO to the LUMO. Therefore, the required ionization potential energy decreases by the amount E^* . The ionization potential energy for the electronically excited donor molecule is IP_D^* . As a result, the free energy change for an electron transfer from donor to acceptor also changes accordingly.

Now let us consider the case of photoinduced electron transfer (PET). In figure 1.5.6, we have pictorially described the effect of photoexcitation on the energetics of electron transfer process. Photon promotes an electron of donor from its HOMO to LUMO. Hence the ionization potential energy (IP_D^*) for this promoted electron should be lesser than IP_D by the amount of energy same as the excitation energy. Thus IP_D^* can be written as^{-2-4,60,91}

$$IP_D^* = IP_D - E^* \quad (1.5.18)$$

As the acceptor is in its ground electronic state, electronic affinity should remain same. Finally, the ΔG for the PET reaction between an isolated gaseous acceptor and an isolated gaseous photoexcited donor can be formulated as^{-2-4,60,91}

$$\Delta G = IP_D - EA_A - E^* \quad (1.5.19)$$

Moreover, there must be some other factors that are needed to be considered to get the complete energetics of PET reaction in a solvent. Electron transfer reaction between two neutral molecules will give rise to a radical cation and a radical anion.

Therefore, the columbic attraction between them must be considered. Also, the solvation energy for these ion pair should be added. Taking care of all these factors, equation 1.5.19 can be modified to^{2-4,60,91}

$$\Delta G = IP_D - EA_A - E^* - \frac{e^2}{2} \left[\frac{1}{r_D} + \frac{1}{r_A} \right] \left(1 - \frac{1}{\varepsilon} \right) - \frac{e^2}{\varepsilon d} \quad (1.5.20)$$

In the above equation, e is electron's charge, ε is the dielectric constant of the medium where PET takes place, r_D & r_A are the radii of the donor and acceptor radical ions respectively and d is the distance between donor and acceptor radical ions.^{2-4,60,91}

IP_D and EA_A can be written in terms of redox potentials of the molecules as^{2-4,60,91}

$$IP_D = E(D^{\bullet+}/D) - \frac{e^2}{2r_D} \left(1 - \frac{1}{\varepsilon} \right) \quad (1.5.21)$$

$$EA_A = E(A/A^{\bullet-}) + \frac{e^2}{2r_A} \left(1 - \frac{1}{\varepsilon} \right) \quad (1.5.22)$$

Combining equation 1.5.20, 1.5.21 & 1.5.22, we get^{2-4,60,91}

$$\Delta G = E(D^{\bullet+}/D) - E(A/A^{\bullet-}) - E^* - \frac{e^2}{\varepsilon d} \quad (1.5.23)$$

This is known as the Rehm-Weller equation.^{2-4,60,91} Redox potentials of the donor and acceptor molecules are experimentally measurable. Using those experimentally obtained values in equation 1.5.23 we determine the free energy change of a PET reaction. Point to note here is that the equation 1.5.23 is specified for single step PET between neutral donor-acceptor pairs. For other systems, equation 1.5.23 is needed to be modified accordingly.^{2-4,60,91}

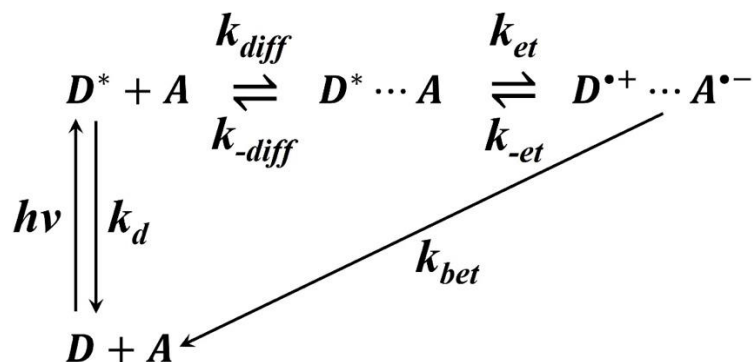


Figure 1.5.7. Schematic representation of a bimolecular photoinduced electron transfer (PET) reaction. D and A are the donor and acceptor. D^* is the photoexcited donor. $D^* \cdots A$ represents the encounter complex. $D^{\bullet+} \cdots A^{\bullet-}$ is the contact ion pair. ν is the frequency of excitation. The diffusion rate constants are denoted as k_{diff} and k_{-diff} . k_{et} and k_{-et} are the unimolecular electron transfer rate constant and unimolecular reverse electron transfer rate constant respectively. k_{bet} is the rate constant for back electron transfer.

A bimolecular PET process in solution has been schematically described in figure 1.5.7. In the figure the donor (D) has been excited by photon of frequency ν . The excited donor (D^*) can deexcite to the ground state by radiative transition or fluorescence. The rate constant of the radiative transition is k_d . Another possibility is that while the donor is in the excited state, D^* and the acceptor (A) can come closer by diffusion and form an encounter complex ($D^* \cdots A$). k_{diff} and k_{-diff} are the diffusional rate constants. In this encounter complex electron transfer reaction can take place and because of that contact ion pair ($D^{\bullet+} \cdots A^{\bullet-}$) will be formed. The rate constant of unimolecular electron transfer and unimolecular reverse electron transfer are k_{et} and k_{-et} . This contact ion pair will then reach the original ground state by back electron transfer process whose rate constant is k_{bet} . Therefore, this electron transfer channel of deexcitation acts as a quenching mechanism for the usual fluorescence from D^* . Because of that fluorescence quenching turned into the most common tool to study PET. Formation of encounter complex is crucial for electron transfer. For ET to happen orbital overlap between donor and acceptor is necessary.^{2,60-66} Both the donor and the acceptor molecules diffuse in the solution in completely random manner. The ‘random walk’ of these molecules lead to several collision or

encounter between two molecules.^{2,60-66} Some of which are between a donor and an acceptor. These encounters between molecules have a lifetime. ET must occur within that lifetime. ET within that lifetime creates contact ion pair (CIP). [PM29, 31-36] When the solvent is polar then CIP separates to form solvent separated ion pair (SSIP).^{2,60-66} To derive a relation between the different rate constants associated with the whole PET process, we have to solve the kinetic model based on the figure 1.5.7.

The rate of change in $[D^*]$ can be written as

$$\frac{d[D^*]}{dt} = -k_d[D^*] - k_{diff}[D^*][A] + k_{-diff}[D^* \cdots A] \quad (1.5.24)$$

On the other hand, from the Stern-Volmer equation, we get

$$\frac{d[D^*]}{dt} = -(k_d + k_q[A])[D^*] \quad (1.5.25)$$

The rate of change in $[D^* \cdots A]$ and $[D^{\bullet+} \cdots A^{\bullet-}]$ are given by

$$\frac{d[D^* \cdots A]}{dt} = k_{diff}[D^*][A] - k_{-diff}[D^* \cdots A] - k_{et}[D^* \cdots A] + k_{-et}[D^{\bullet+} \cdots A^{\bullet-}] \quad (1.5.26)$$

$$\frac{d[D^{\bullet+} \cdots A^{\bullet-}]}{dt} = k_{et}[D^* \cdots A] - k_{-et}[D^{\bullet+} \cdots A^{\bullet-}] - k_{bet}[D^{\bullet+} \cdots A^{\bullet-}] \quad (1.5.27)$$

Steady state approximation on $[D^* \cdots A]$ and $[D^{\bullet+} \cdots A^{\bullet-}]$ gives

$$[D^{\bullet+} \cdots A^{\bullet-}] = \frac{k_{et}[D^* \cdots A]}{k_{-et} + k_{bet}} \quad (1.5.28)$$

$$[D^* \cdots A] = \frac{k_{diff}\left(1 + \frac{k_{bet}}{k_{-et}}\right)}{k_{-diff}\left(1 + \frac{k_{bet}}{k_{-et}}\right) + \frac{k_{et}k_{bet}}{k_{-et}}}[D^*][A] \quad (1.5.29)$$

Mixing equation 1.5.24 and 1.5.25 and using the above showed forms of $[D^{\bullet+} \cdots A^{\bullet-}]$ and $[D^* \cdots A]$, we get by some mathematical simplification

$$k_q = \frac{k_{diff}}{1 + \frac{k_{-diff} + \frac{k_{-diff}k_{-et}}{k_{et}} + \frac{k_{-diff}k_{bet}}{k_{et}}}} \quad (1.5.30)$$

As for an exothermic PET reaction $k_{et} \gg k_{-et}$, we can further modify equation 1.5.30 into

$$k_q = \frac{k_{diff}}{1 + \frac{k_{-diff}}{k_{et}}} \quad (1.5.31)$$

$$\Rightarrow \frac{1}{k_q} = \frac{1}{k_{diff}} + \frac{1}{Kk_{et}} \quad (1.5.32)$$

In the above equation, K is the diffusional equilibrium constant $\left(= \frac{k_{diff}}{k_{-diff}} \right)$.

Equation 1.5.32 indicates that when $k_{et} \ll k_{diff}$ i.e., ET is the rate determining step, $\frac{1}{k_q} = \frac{1}{Kk_{et}}$ and quenching experiment is sufficient to determine the rate constant of ET. But for the cases where diffusion is the rate determining step ($k_{et} \gg k_{diff}$), $\frac{1}{k_q} = \frac{1}{k_{diff}}$. For these diffusion-limited cases, quenching study is unable to obtain correct k_{et} .^{91,92} This problem was first encountered by Rehm and Weller.^{91,92}

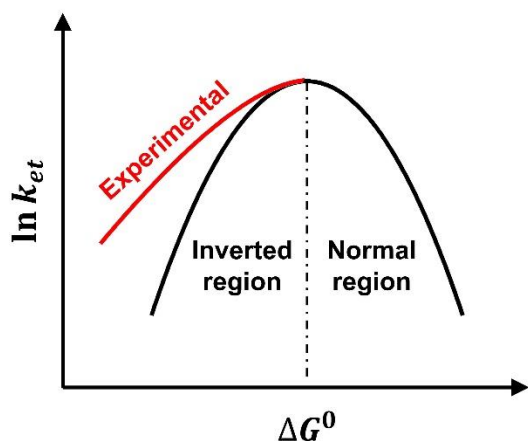


Figure 1.5.8. Experimentally observed deviation from ideality in the inverted region of Marcus plot. Black curve is the ideal. Red curve is the deviation.

This involvement of diffusion made the experimental observation of Marcus inversion challenging. This difficulty was first overcome by Miller et al. in 1984. They coupled the donor and the acceptor via steroid bridge between them and

nullified the diffusion.^{67,68} Following this pioneering work by Miller, numerous other groups have reported about the observation of Marcus inversion for PET in various mediums throughout the last three decades.⁶⁷⁻⁸⁸ According to the equation 1.5.13, the obtained plot of k_{et} vs ΔG^0 should be nicely symmetric on both sides. However, experimental results in many reports suggest otherwise. It is evident that the inverted region of the experimentally obtained Marcus plot deviates from the theoretical prediction. It seems that somehow the theory underestimates k_{et} in the inverted region (figure 1.5.8).⁶⁷⁻⁸⁸

Few explanations behind this observation are present. For PET in the inverted region, the reaction is more exergonic. As a result, the high frequency vibrational modes of the product get involved in the PET process. The observed deviation is probably the result of that.⁶⁷⁻⁸⁸

Solvent reorganization energy (λ_s) is dependent on the donor-acceptor separation distance (r_{DA}) as described in equation 1.5.11. V_{el} is also a function of r_{DA} .⁶⁷⁻⁸⁸

$$V_{el,r}^2 = V_{el,0}^2 \exp(-\beta(r_{DA} - \sigma)) \quad (1.5.33)$$

σ is the contact radius between the donor and acceptor. It has been reported that for more exergonic reaction, r_{DA} decreases. This affects the λ_s and V_{el} values in case of the PET in inverted region. Consequently, the Marcus plot deviates in the inverted region.⁶⁷⁻⁸⁸

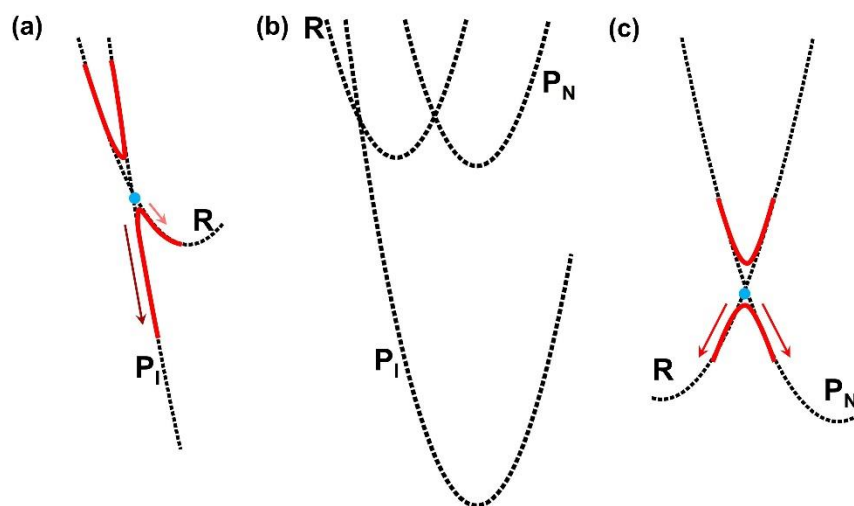


Figure 1.5.9. (b) Inverted and normal mechanism of PET has been depicted by one reactant (R) and two product (P_I and P_N) surfaces. Crossing between R and P_I corresponds to the inverted mechanism. Whereas, crossing between R and P_N corresponds to the normal mechanism. (a & c) Expanded view around the transition geometry for a non-adiabatic PET reaction in between reactant and product surfaces in inverted region (a) and in the normal region (c) respectively. The difference in slope between the two crossing surfaces is greater in the inverted region compared to the normal region.

Apart from these justifications, there are two other factors that can also contribute to the deviation from ideality in the Marcus inverted region. The probability of transition (P_t) between two surfaces are given by,^{1,2}

$$P_t \sim e^{\left(-\frac{\Delta E^2}{v\Delta s}\right)} \quad (1.5.34)$$

In the above equation, ΔE is the energy separation in the transition geometry, v is the velocity of nuclei approaching the transition geometry and Δs is the difference in the slope between the two surfaces. As Δs increases, P_t also increases. In figure 1.5.9b, I have depicted non-adiabatic PET reaction by one reactant (R) and two product (P_I and P_N) surfaces. The crossing between R and P_I gives the inverted mechanism and the crossing between R and P_N gives the normal mechanism of PET. In figure 1.5.9a & c, I have shown the expanded view at the transition geometry for the non-adiabatic PET reactions in inverted and normal region respectively. For a system sitting on the transition geometry in normal region, the slopes towards the R and P_N side are very much similar (see figure 1.5.9c). Whereas in case of the inverted

region, the slope towards the P_I surface is much steeper compared to the R surface (see figure 1.5.9a). As a result, in the inverted region, one should observe higher k_{et} compared to the normal region for same $\Delta G^\ddagger$. This can be one contributing factor behind the asymmetric Marcus plots.

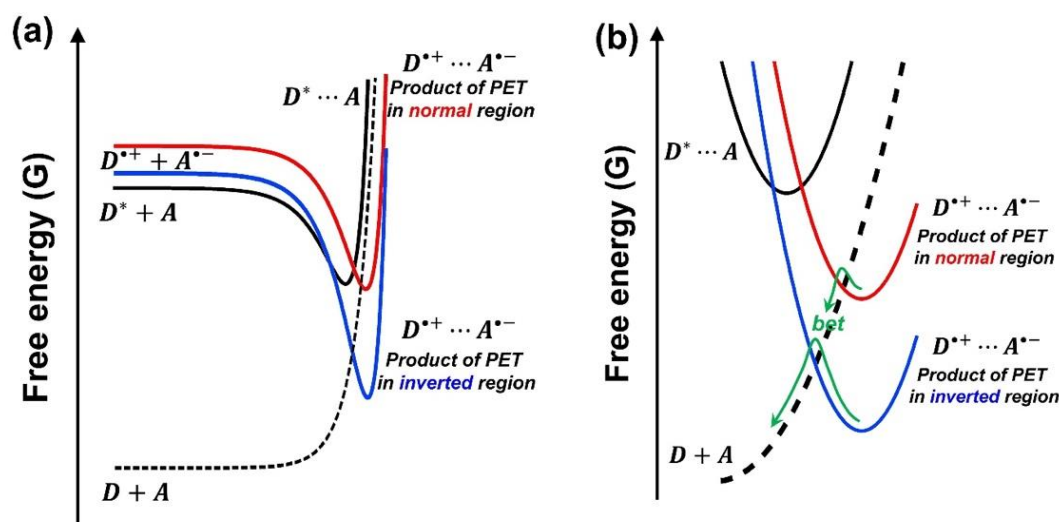


Figure 1.5.10. (a) Free energy surface representation of bimolecular PET reaction. It shows that the crossing between $D^* \cdots A$ and $D^{*+} + A^{*-}$ for the inverted mechanism happens at the left side of $D^* \cdots A$ well which has slower slope compared to the right side where the crossing happens in normal mechanism of PET. (b) Simplified zoomed in version of (a) that shows that for the contact ion pair (CIP; $D^{*+} \cdots A^{*-}$) formed due to PET in the inverted region, the back electron transfer (bet) is more difficult.

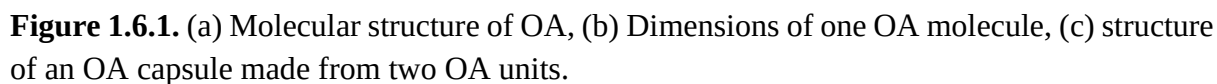
In the formulation of Marcus theory, R and P potentials are taken as parabolas, as if they represent simple harmonic oscillators. However, the overall picture for a bimolecular PET reaction can be somewhat different. The processes involved in a bimolecular PET reaction has been already shown in the figure 1.5.7. Keeping the processes described in the figure 1.5.7 in mind, the overall energy surface for a bimolecular PET reaction has been depicted in the figure 1.5.10a. In figure 1.5.10a, the left side indicates solvent separated donor and acceptor moieties. As we approach to the right the distance between the donor and acceptor moieties decreases, which indicates to the diffusion process. When the donor and acceptors in the electronic ground state ($D + A$) approach each other, due to absence of any stabilizing factor,

the energy will increase after a certain distance is reached (black dotted curve in figure 1.5.10a). On the other hand, when the photoexcited donor (D^*) and acceptor (A) diffuse to one another, after a certain point, encounter complex ($D^* \cdots A$) will form, and the energy will decrease to create a well (black solid curve in figure 1.5.10a). The minima of this well represents the equilibrium distance between the D^* and A in $D^* \cdots A$. Any further approach of D^* and A towards one another will destabilize the complex and energy will increase rapidly. One can correlate this model with the exciton model that describes excimer or exciplex formation. In this encounter complex electron transfer takes place and the contact ion pair ($D^{\bullet+} \cdots A^{\bullet-}$) generates. The energy surface for $D^{\bullet+} \cdots A^{\bullet-}$ (red and blue solid curve in figure 1.5.10a) should look like that of the $D^* \cdots A$. However, the equilibrium distance between $D^{\bullet+}$ and $A^{\bullet-}$ in $D^{\bullet+} \cdots A^{\bullet-}$ should be smaller than that of $D^* \cdots A$ due to the attraction between $D^{\bullet+}$ and $A^{\bullet-}$. Consequently, the well for $D^{\bullet+} \cdots A^{\bullet-}$ should be shifted towards the right side of the $D^* \cdots A$ well. Because of the same reason, separation of $D^{\bullet+} \cdots A^{\bullet-}$, will be much more difficult and will require more energy. For that reason, $D^{\bullet+} \cdots A^{\bullet-}$ will have a steeper and deeper well compared to $D^* \cdots A$. Upon separation of $D^{\bullet+} \cdots A^{\bullet-}$, two separate radical ions ($D^{\bullet+}$ and $A^{\bullet-}$) will generate and system will be energetically unstable. That is why near the solvent separated side of the curve $D^{\bullet+} + A^{\bullet-}$ have the highest energy. In figure 1.5.10a, two different $D^{\bullet+} + A^{\bullet-}$ wells have been displayed. The red and blue curve represents the $D^{\bullet+} + A^{\bullet-}$ produced by PET in the normal region (less exergonic) and the inverted region (highly exergonic). An important feature is that the surface crossing between $D^* \cdots A$ and $D^{\bullet+} + A^{\bullet-}$ for the inverted mechanism of PET happens at the left side of $D^* \cdots A$ well which has slower slope compared to the right side where the crossing happens in normal mechanism of PET. As a result, in the inverted region the $\Delta G^\ddagger$ value increases much slowly with increasing the driving force compared to what is expected theoretically. The observation of higher k_{et} values leading to the deviation from ideality in the inverted region of the Marcus plot can be attributed to this.

The significance of the existence of the Marcus inverted region lies in the fact that for PET reactions, occurring in inverted regions, the back electron transfer (or the charge recombination) becomes slower. Figure 1.5.10b which is a simplified zoomed in version of figure 1.5.10a, highlights the fact. There are two key observations to make from the figure 1.5.10b- (i) CIP formed by PET in the inverted region is lower in energy than the other and (ii) For the CIP formed by PET in the inverted region the back electron transfer (or the charge recombination) requires higher activation energy. These observations obviously indicate to the fact that CIP formed by PET in the inverted region will be stabler and have a longer lifetime than the CIP formed by PET in the normal region. This indicates that the inverted mechanism of PET can be crucial for enhancing solar energy efficiency in photovoltaics as well as in artificial photosynthesis.^{93,94}

1.6. Effect of Confinement: An Introduction to Octa Acid

Polarity and viscosity around a photoexcited molecule dictate its relaxation pathways.¹⁻⁴ For example, the extent of solvent relaxation usually increases with increasing solvent polarity for positive solvatochromic dyes.¹⁻⁴ On the other hand, for molecular rotors like thioflavin-T, the rate of non-radiative relaxation via twisting of either dimethylamino or dimethylanilino group decreases with increasing viscosity of the medium.⁹⁵⁻¹⁰⁹ Polarity and viscosity inside a confined medium differ a lot from the bulk. As a result, excited state dynamics for molecules trapped in confined environment gets affected.³⁵ Solvation dynamics in bulk water is ultrafast in nature and consist of three different time components. The origin of these three different components are the translation, vibration, and libration of the water molecules.^{31-33,35,110,111} However, inside confined medium like micelles or reverse micelles, these motions are restricted, and it reflects on the solvation dynamics in these mediums. From the studies by Sarkar et al. and Datta et al. on coumarin-480 and 4-aminophthalimide (4-AP) in triton-X, CTAB and SDS micelles, we know that inside the stern layer of aqueous micelles, the solvation time is in the order of few



hundreds of picoseconds.^{35,112,113} Similarly, inside the aqueous pool of a reverse micelle, the average solvent relaxation time is in the order of nanoseconds.^{35,114-121} Depending on the size of the pool the solvent relaxation can be mono- or bi-exponential.^{35,114-121} Other than micelles and reverse micelles, cavitands like γ -cyclodextrin (γ -CD) are among the other commonly studied confined medium.³⁵ In case of γ -CD, there are two components in solvation dynamics.^{35,122} Though one component is as fast as in the bulk water, the other component is much slower.^{35,122} Other than solvation dynamics there has been extensive studies on TICT, excited state proton transfer, photodimerization, etc. in such confined media.³⁵ Numerous studies of different excited state phenomena in different confined media have developed our knowledge on how certain changes in environment would affect certain excited state processes. Such a knowledge allowed us to use various excited state phenomena as a tool to sense the environmental properties of an unknown medium. As for example, thioflavin-T or any other molecular rotors can be used as a viscosity sensor or even a pressure sensor.⁹⁵⁻¹⁰⁹ This method of mapping unknown medium becomes extremely important when we consider that till today the cell

medium is an unknown environment which can be explored using photo-excited phenomena. Hence, the studies of different excited state processes inside any kind of confined system are relevant.

Octa acid (OA) is an organic cavitand that was first synthesized by Gibb in 2004.^{123,124} OA has a bucket like shape. It has two openings. One opening is 11.4 Å and the other is 5.5 Å. The height of the cavitand is 13.7 Å. We should note that these are all outer dimensions. Inside this molecular structure there is a cavity. The dimensions of this inner cavity are as follows. The larger of the openings has a diameter 9.1 Å. The depth of the cavity is approximately 6 Å.^{123,124} In figure 1.6.1, we have depicted the structure and dimensions of OA. The cavitand is synthesized such that the inner wall of the cavity is completely non-polar. Whereas eight carboxylic acid groups protrude from the outer wall of the cavitand. Because of these eight carboxylic acid groups, the molecule was named Octa acid.^{123,124} Earlier studies on this cavitand have established some crucial properties of OA. Because of the presence of eight acid groups, OA is soluble in aqueous buffer of pH 7.4.¹²⁴⁻¹²⁶ OA has an ability to form host-guest complex in aqueous buffer solution in presence of guest organic molecules. Depending on the properties of the guest molecules it can form 1:1 or 1:2 or 2:2 complexes.¹²⁴⁻¹²⁶ Unless the organic guest molecule has any ionic or hydrophilic moiety e.g., carboxylic acid group, two OA molecules come together to encapsulate one or two of the guest molecules to form 1:2 or 2:2 host-guest complex in aqueous medium. Preference between 1:2 and 2:2 complex depends on the size, shape, and concentration of the guest molecule.¹²⁴⁻¹²⁶ Naphthalene as well as anthracene can form both 1:2 and 2:2 complexes with OA as their size and shape permit that. However, tetracene or pyrene are too large to form the 2:2 complexes.¹²⁴ Usually, hydrophobic organic molecules are very poorly soluble in water. Consequently, they form turbid solution in water. Addition of OA in this turbid solution, gradually clarifies the turbidity. After addition of sufficient amount of OA, a clear solution appears. The stoichiometry of the complex is usually confirmed by ¹H-NMR titration.¹²⁴⁻¹²⁶

OA only absorbs the UV light of wavelength below 300 nm.¹²⁴ Because of that, it does not interfere any photophysical or photochemical studies of the encapsulated organic guest molecules which absorb in the visible region of the electromagnetic spectrum. From the work done by Jayraj et al., we know that capsular structure made by two OAs and the guest can partially open and close. However, this partial opening and closing of the capsule happens in μs timescale.^{124,127} For that reason, we can expect that during the excited state lifetime of the encapsulated guest molecule, the capsule remains closed, provided the excited state lifetime of the guest is in the order of few nanoseconds. This provides us the necessary condition to study different excited state processes inside the OA cavity.

Coumarin-1 shows a weak emission band around ~ 470 nm in aqueous medium.^{124,126} However, gradual addition of OA blueshifts the emission band until it reaches around ~ 410 nm. Other than the blueshift, the emission band also intensifies significantly. Coumarin-1 is a positive solvatochromic dye and the fluorescence quantum yield of coumarin-1 increases with decreasing solvent polarity. Hence, the observation suggests that the interior of the OA cavity is non-polar. Similar studies with other eight guest molecules by Porel et al. further solidify the statement.^{124,126} Hence OA generates a unique situation where a fluorophore remains soluble in aqueous medium, still the environment just around it is purely non-polar. It made me curious about one question: do the encapsulated fluorophore feel any relaxation due to the solvation or not? My first work which has been presented in chapter 3 in details, is engineered around this question.¹²⁸

Pyrene is well-known to show excimer emission in bulk solution.^{1,2} On the other hand, anthracene usually photodimerize upon photoexcitation.¹²⁹⁻¹³¹ There is one report of observation of anthracene excimer in rigid glass system by Chandross et al.¹³² Another report claimed to have observed anthracene excimer in chloroform.¹³³ However, the report was later found to be erroneous. In 2005, Kaanumalle et al. have observed excimer emission of anthracene in solution phase for the first time.¹³¹ This broad excimer emission was observed when anthracene formed 2:2 complexes with

OA. Though in general, observation of excimer emission is a well-known phenomenon, to the best of our knowledge there is no reports on excimer formation dynamics. I believe that being a diffusion-controlled process it is not possible to observe excimer formation dynamics in pure solution. Such is not the case when two anthracene are trapped inside the OA cavity to form the AN:OA 2:2 complex. In that system the role of diffusion will be nullified. This led me to the idea to study the AN:OA 2:2 complex to unravel the excimer formation dynamics. This work has been discussed elaborately in chapter 4.¹³⁴

Recently, Mohan Raj et al. have demonstrated that OA cavity possess the ability to stabilize triplets.¹³⁵ In this work they have established that populating Xe in the OA cavity containing a pyrene molecule, triggers pyrene phosphorescence. Heavy atom effect is a phenomenon which is known from 1949.⁴⁹ However, significant difference between the rate constant of ISC expected using heavy atom effect theory and the experimental rate constant of ISC, raised suspicion in my mind whether there are some other hidden factors that can control the ISC or not. To address this fundamental problem, I believed that the triplet stabilizing ability of the OA cavity can be proven crucial. In chapter 5, I have presented the detailed work on this matter.¹³⁶

Porel et al. were the first to observe that that photo-induced electron transfer from encapsulated coumarin derivatives to an acceptor present outside does take place across the molecular wall of OA capsule.¹³⁷⁻¹³⁹ They have used coumarin-1, coumarin-480 & coumarin-153 as donors and methyl viologen & TiO₂ as the acceptors. However, they have not mentioned any time constants associated, which was later addressed by Chuang et al.¹⁴⁰ There has been yet another observation of PET across the molecular wall of OA between azulene and methyl viologen by the Ramamurthy group.¹⁴¹ Despite of these observations, the mechanism of this kind of PET is yet to be cleared. One big question that lurks over this problem is the role of the OA molecular wall on the electron transfer. Moreover, is there any electronic coupling between the donor and acceptor molecules despite being separated by a

rigid molecular wall? I felt that these questions need some attention, and my last work has been based on this.¹⁴²

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Chapter 2

Experimental Methods

This chapter covers the details of the experimental methods used in this thesis. I have explicitly written the detailed instrumentation and data analysis procedure for time correlated single photon counting, femtosecond transient absorption spectroscopy and fluorescence up-conversion spectroscopy used in my research works. Besides a brief description of density functional theory has also been provided. I have also described the procedure of complexation between Octa acid as host and hydrophobic probe molecules as guests.

2.1. Steady State Measurements

Steady state absorption spectra were recorded in Shimadzu UV-2450 and JASCO V-670 spectrophotometer. Both the instruments are equipped with deuterium and halogen lamp as light source and photomultiplier tube as detector. Steady state emission spectra were recorded in Fluoromax-4, Horiba Jobin-Yvon spectrofluorimeter equipped with a 150W xenon arc lamp as excitation source and a photomultiplier tube (190nm-850nm) as detector.

2.2. Time Correlated Single Photon Counting (TCSPC) Method

2.2.1. Basic Principle

The basic idea behind measurement of fluorescence lifetime is to excite the sample using a delta function pulse and measure the gradual decrease in the fluorescence intensity as time progress. However, there are some problems associated with the measurements. Primarily, the time scale of fluorescence decays of most organic samples are very small i.e. in nanosecond time domain. So to measure fluorescence lifetime directly we need a detector with very fast response which is difficult. Secondly, to characterize a sample, we not only need to measure its fluorescence lifetime but also the complete shape of the decay i.e. the familiar exponential waveform of fluorescence lifetime to resolve any multi exponential decays present in the sample. Now the response of the detector is the measurement of a single photon. So in order to resolve a nanosecond order lifetime component, we would need a picosecond order response from the detector. Even with a very fast photodiode and GHz oscilloscope this is impossible to achieve and the weak emission from the sample after passing through all the optics may fail to create an electric signal. So an analog measurement can never be able to achieve a complete waveform of fluorescence decay of a sample. The solution is provided by time correlated single photon counting method (TCSPC), first introduced by Bollinger and Thomas in 1961, where time of arrival of photon at the detector is measured with respect to the reference signal i.e. the excitation pulse.^{1,2} This process is

repeated for several cycles until a histogram of the waveform is born. TCSPC can detect a very low level of signal because of its statistical method. In TCSPC measurements a high repetition rate laser source is used and the principle is that detection of a single photon within the pulse period is an unlikely event and detection of two photons is extremely unlikely. So only the first photon detected within two consecutive excitation of the sample is considered. The excitation pulse acts as the start signal and the first detected photon acts as the stop signal. The time difference between the start and stop signal is measure and stored. If the single photon detection criterion is followed, then there can be several cycles where no photon will be detected which is fine because the occurrence of no photon per cycle or single photon per cycle is completely random and measurement over many repeating cycles would statistically always generate the distribution. Whenever a photon is detected in a cycle, a count 1 is recorded in the memory and the time of its arrival is noted. The essential part of this type of data recording is the time to amplitude converter (TAC). The excitation pulse sends a synchronization signal (the “start” signal) to the TAC and the capacitor within it starts charging. When the emission photon or the “stop” signal is acquired, the charging of the capacitor stops. The voltage within the capacitor increases linearly in this time window and thus a voltage ramp is generated. An analog to digital converter named multichannel analyzer (MCA) stores the magnitude of this voltage in a designated channel according to the time. Over many repetitions, the complete histogram is stored in MCA. Adhering to the one photon detection per cycle principle, the experimental stop rate should be kept below 2% of the start rate. This ratio is important when the “dead time” of the electronics is considered. Dead time is the minimum time taken by the electronics to detect two successive photons. So if the “stop” rate is high, then chances are multiple photons can come in a pulse cycle and the first emitted photon will not be the first detected photon as it may fall within the dead time of electronics. This will results in a situation called “pulse pile-up” which is actually over-representation of certain points in the histogram.^{2,3}

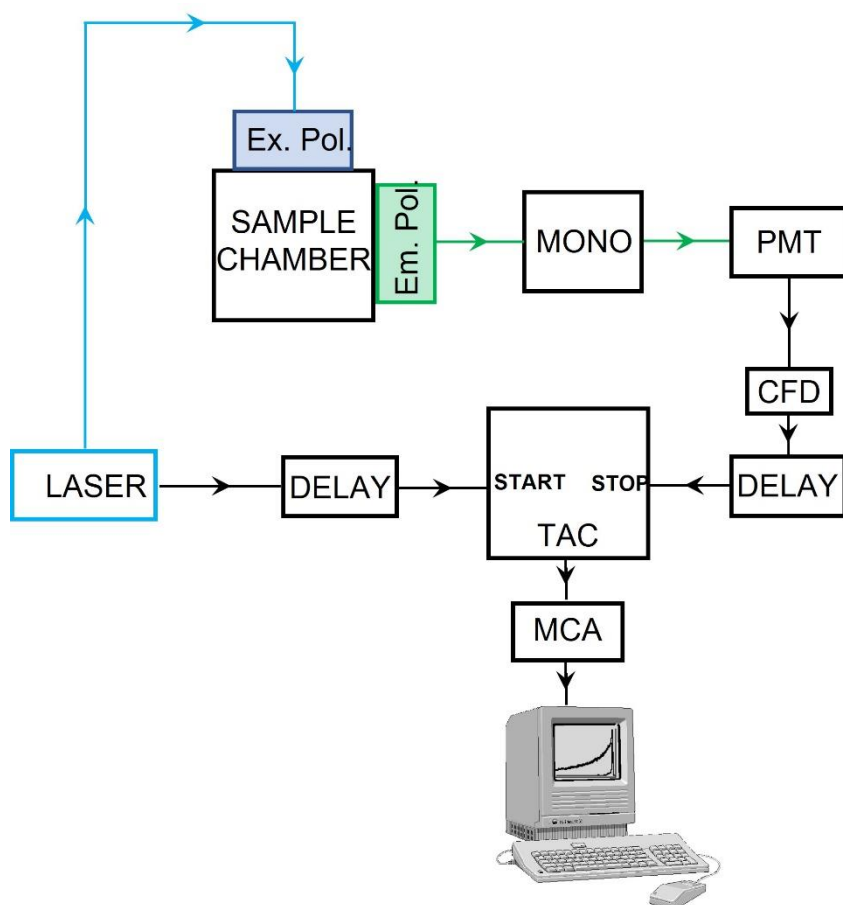


Figure 2.2.1.1. Schematic diagram of a standard TCSPC setup along with typical IRF and data

The detector used in modern TCSPC setup is multichannel plate photomultiplier tubes (MCP PMT). The advantage of using MCP PMT over single electron response detectors or simple PMT lies in the transit time spread (TTS) of the detector which seriously affects the time resolution of the instrument. Once a photoelectron is generated at the cathode of a PMT, it is amplified in the dynodes. As this process of multiplication generates a group of electrons having a range of velocities and individually they can take different paths to reach the anode, a distribution of transit times are generated which is the TTS. TTS is less for MCP PMT compared to PMT and as TTS determines the instrument response, the use of MCP PMT is preferred. The rise and fall time of the electronics used in the TCSPC

setup causes a time jitter in the measurement. Moreover random amplification optical signal by detector can cause a amplitude jitter in the electric signal. If a simple discriminator is used to send signal at TAC, then it can be triggered if the leading edge of the electric pulse crosses a certain threshold value. Therefore a constant fraction discriminator (CFD) is used in TCSPC. Basically, a CFD sends a signal at TAC at constant fraction of a pulse and therefore the height difference induced time jitters are avoided. The instrument response function (IRF) of a TCSPC instrument recorded by measuring the signal from a scattering process is influenced by laser pulse width, TTS and any other time jitters in the instrument. A schematic diagram depicting all the components of a TCSPC setup has been shown in figure 2.2.1.1.

In my experiments, I have used the TCSPC instrument LifeSpec II from Edinburgh Instruments, U.K. This instrument is equipped with thermoelectrically cooled Hamamatsu R3809-50 MCP PMT with intrinsic detector response <25 ps. The excitation sources are picosecond pulse diode lasers (EPL-series) from the same company. For my experiments, I have used 375nm diode laser with 80 ps pulse width. The IRF of this instrument measured by scattering from Ludox suspension was 120 ps. All the data were acquired at Magic Angle polarization to avoid any contribution from the rotational diffusion of the molecules. The data obtained from the instrument was analyzed in FAST and DAS software respectively. Here a brief overview of the fitting procedure has been presented.

2.2.2. Data Analysis

The data analysis procedure is not straight forward because the excitation pulse is not a delta function i.e. it has a finite width in time domain and the IRF of the instrument has a finite width. These factors affect the data and the measured fluorescence decay actually becomes a convolution of the IRF and the actual fluorescence intensity decay.

$$I(t) = \int_0^t P(t)F(t - t')dt' \quad (2.2.2.1)$$

Now using this convolution to fit the data is not straightforward as the problem itself is ill-posed. The convolutions requires exact form of IRF or prompt to be known, the theoretical model for fluorescence to be known and experimental random noise to be minimized. Therefore most of the commercial software like FAST or DAS uses iterative method or specifically non-linear least square method to extract fluorescence lifetime. First of all, the pure fluorescence intensity decay is estimated by a sum of lifetime components multiplied by their weighted amplitudes as follows.³⁻⁷

$$F(t) = \sum_{i=1}^n a_i e^{-\frac{t}{\tau_i}} \quad (2.2.2.2)$$

$$\sum_{i=1}^n a_i = 1 \quad (2.2.2.3)$$

Here, τ_i are the lifetime components and a_i are the amplitudes. The IRF profile is recorded using a scatter as stated before but it is measure at the excitation wavelength not at the emission wavelength which is intrinsically wrong. Nevertheless, measurement of IRF using the same number of channels is required for the reconvolution. As this reconvolution is done in a quantized manner i.e. per channel basis, a sum is used instead of integration in equation 2.2.2.1. The IRF is assumed to be a series of δ -functions with different amplitudes in different channels. The measured data is expressed as³⁻⁷

$$I(t) = \sum_{t_i=0}^t P(t)F(t - t_i)\Delta t \quad (2.2.2.4)$$

In the above equation, Δt is the time/channel. Two more parameters are needed in the final fitting equation. There can slight mismatch of time zero position of IRF and intensity decay data which is accommodated by a shift parameter(Δ). A noise factor (A) is needed to for the fitting. So, all together the final form is

$$D(t) = A + I(t + \Delta) \quad (2.2.2.5)$$

The consistency of the assumed model is tested by the “goodness of the fit”.³⁻⁷

$$\chi^2 = \sum_{j=1}^n \frac{[Y(j)-D(j)]^2}{\sigma_j^2} \quad (2.2.2.6)$$

In the above equation, $Y(j)$ is the fitted data, $D(j)$ is the experimental data and σ_j^2 is the standard deviation. However, χ^2 is not the best choice for large number of datapoints. Instead, a quantity χ^2_R is defined as

$$\chi_R^2 = \frac{\chi^2}{n-p} \quad (2.2.2.7)$$

Here, n is the number of data points and p is the number of parameters. For TCSPC measurements, n is much larger than p . The value of χ^2 is estimated with different choice of fitting parameters and multiexponential model and the fitting is accepted comparing the value of χ^2 for different sets. However, this iterative method suffers from an intrinsic problem of choice of model based on intuition and as many different models can satisfy the fitting criteria, prior knowledge of the system is extremely important for TCSPC fitting.

2. 3. Femtosecond Fluorescence Up-Conversion Spectroscopy

2.3.1. Basic Principle

Fluorescence up-conversion spectroscopy is based on the principle of cross-correlation between the emission from an electronically excited molecule and a gate beam. Such optical gating of fluorescence was first described by Halliday and Topp in 1977.⁸ The employment of femtosecond lasers has enabled this technique to measure fluorescence intensity decays from sub-picosecond to nanosecond time domain.⁹⁻¹² In this technique, the second harmonic of a femtosecond oscillator (a mode-locked Ti:Sapphire laser operating at frequency (ω_1) in this case) is used to excite the sample electronically.

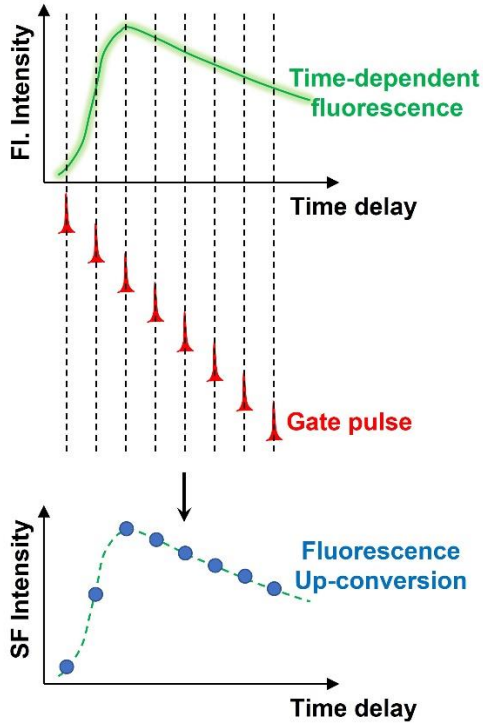


Figure 2.3.1.1. Schematic principle of fluorescence up-conversion spectroscopy

As depicted in figure 2.3.1.1, the arrival of the excitation pulse at the sample marks time zero ($t=0$) and results in the emission of incoherent fluorescent light (ω_2) from the excited molecules. It is mixed with the gate pulse which is basically the residual fundamental gate light arriving at time $t = \tau$ in a non-linear crystal (β -barium borate crystal, potassium dideuterium phosphate crystal etc) and thus the sum frequency (ω_3) of those two signals is generated.

$$\omega_3 = \omega_1 + \omega_2 \quad (2.3.1.1)$$

The time of arrival of gate pulse is controlled by a mechanical delay stage. It can be shown that at any time, the intensity of the sum frequency light (I_{sum}) is proportional to the cross correlation function of that of the fluorescence (I_{fl}) and gate beam (I_G).⁹

$$I_{sum} \propto \int_{-\infty}^{+\infty} I_{fl}(t) I_G(t - \tau) dt \quad (2.3.1.2)$$

The sum frequency light is only generated when the gate pulse is present in the crystal and thus we can achieve time resolution comparable to laser pulse width.

2.3.2. Instrumental setup

Schematic optical layout of the instrument (FOG 100, CDP systems, Moscow, Russia) along with the external laser source has been shown in figure 2.3.2.1. The output of a mode-locked Ti:Sapphire laser (Mai-Tai HP, Spectra Physics, USA) operating at a repetition rate of 80 MHz with average power ~ 2.5 W and ~ 100 fs pulse width was used as the fundamental frequency radiation (ω_1). The light was focused onto a β -barium borate crystal (BBO, 0.2 mm thickness) to generate the second harmonic ($2\omega_1$) of the fundamental light which was used for sample excitation. The second harmonic mixed with fundamental light was collimated using lens L_2 onto the dichroic mirror/dichroic beamsplitter (DM_1) which splits the input beam into excitation and gate beams. The reflected excitation beams passed through a Berek polarizer (B) which was used to adjust the polarization of the excitation light. I have used neutral density filters (ND filters, F) before the polarizer to control the intensity of the excitation light and cut-off filters to remove residual fundamental light. Then the light is reflected from another beam splitter (BS_1) and focused on the rotating sample cell S using lens L_3 . The fluorescence emission from the sample (ω_2) was collected by lens L_4 and passed through a cut-off filter F_2 to remove excitation ($2\omega_1$) light. The gate beam was directed with mirrors M_3 and M_4 to a gold coated retro-reflector (RR) mounted on a mechanical delay line controlled by the software. Both the emission and the gate pulse were collected by lens L_5 and focused on a second non-linear BBO crystal (0.2mm or 0.5mm thick) where the sum frequency of the two incident beams are generated i.e. $\omega_3 = \omega_1 + \omega_2$. For the experiments described in this thesis, the fluorescence are in visible region and the gate pulse in near IR region and therefore the sum frequency obtained was in the UV region. The emission and the gate beam were prevented to reach the detector by means of iris and by using appropriate cut-off filters (F_3). Lens L_7 was used to focus the sum frequency light to the input slit of the monochromator. The sum frequency signal was selected by the monochromator and detected by a photomultiplier tube (PMT) coupled with a photon counting device. Data acquisition, monochromator and optical delay line is controlled by LUMEX software (CDP Corp).

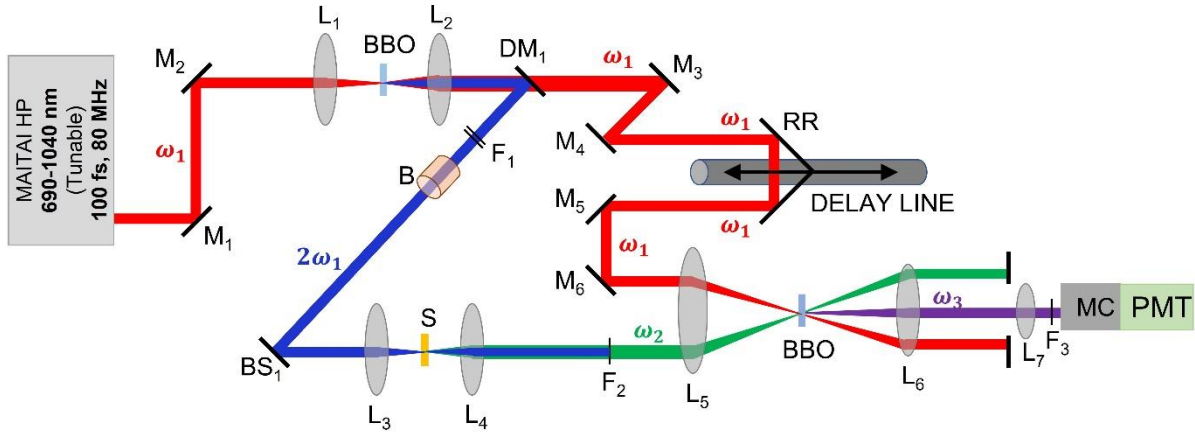


Figure 2.3.2.1 Schematic optical diagram of femtosecond fluorescence up-conversion

2.3.3. Principle of Second Harmonic and Sum Frequency Generation

Fluorescence up-conversion spectroscopy involves generation of sum frequency of fluorescence from sample and the gate beam. It also involves generation of second harmonic light of the fundamental beam for excitation purpose. Both the phenomena are a part of non-linear optical phenomenon which is discussed in this section. At normal condition i.e. in presence of low intensity light, the response of the medium of propagation to the light is linear. This is to say that the optical phenomenon in this situation can be explained with a linear refractive index of the medium. However, when an intense high power laser light is present the response of the medium deviates from linearity. The electric field associated with high intensity radiation can alter the refractive index of medium which is the origin of non-linear effect.¹³⁻¹⁵ The response of a medium to the electric field of propagating electromagnetic radiation can be described as the Taylor expansion of the dielectric polarization density (dipole moment per unit volume) or simply induced polarization (P_k) as a function of electric field (E_i) at time t .

$$P_k(t) = \epsilon_0 \left(\chi_{ik}^{(1)} E_i(t) + \chi_{ijk}^{(2)} E_i(t) E_j(t) + \chi_{ijkl}^{(3)} E_i(t) E_j(t) E_l(t) + \dots \right) \quad (2.3.3.1)$$

In the above equation, ϵ_0 is the permittivity of vacuum and $\chi^{(n)}$ is the n -th order optical susceptibility of the medium and it is a $(n + 1)$ order tensor. In right hand

side of equation 2.3.3.1, the first term corresponds to linear response whereas the higher order terms correspond to higher order (nonlinear) response of the medium. For simplicity, P_k and E_i are considered to be scalar quantities for a non-linear optical process occurring in a specific direction. Both second harmonic and sum frequency generation is a second order non-linear phenomenon and so, I will refer only the second order polarization as ¹³⁻¹⁵

$$P^{(2)}(t) = \epsilon_0 \chi^{(2)} E^2(t) \quad (2.3.3.2)$$

Now let us consider the second order response to a monochromatic input field of frequency ω is given by

$$E(t) = \mathcal{E} \exp(-i\omega t) + \mathcal{E}^* \exp(i\omega t) \quad (2.3.3.3)$$

In the above equation, $\mathcal{E}$ is the field amplitude. Plugging equation 2.3.3.3 to equation 2.3.3.2 we get the second order response of the medium as

$$P^{(2)}(t) = 2\epsilon_0 \mathcal{E} \mathcal{E}^* + \left(\epsilon_0 \chi^{(2)} \mathcal{E}^2 \exp(-i2\omega t) + \epsilon_0 \chi^{(2)} \mathcal{E}^{*2} \exp(i2\omega t) \right) \quad (2.3.3.4)$$

The first term in equation 2.3.3.4 defines a constant static field which is known as optical rectification and the second term defines an output of frequency twice of the input field which is the second harmonic generation.¹³⁻¹⁵ It is important to point out that the even order terms in equation 2.3.3.1 will vanish if the crystal has inversion symmetry and therefore second harmonic generation can occurs only in specific non-linear optical (NLO) crystals. One more important thing in non-linear processes such as frequency doubling is phase matching among the interacting waves to ensure that amplitude contribution of the output wave from different part of the NLO crystal are in phase at the end of crystal. In second harmonic generation, we are creating light of twice frequency whose wave vector $k_{2\omega}$ is given by

$$k_{2\omega} = \frac{2\omega}{c} n_{2\omega} \quad (2.3.3.5)$$

In the above equation, c is the speed of light and $n_{2\omega}$ is the refractive index for the second harmonic light. Similarly, the wave vector for input light is given by

$$k_{\omega} = \frac{\omega}{c} n_{\omega} \quad (2.3.3.6)$$

In frequency doubling in crystal, phase matching satisfies when $k_{2\omega} = k_{\omega}$ i.e. $n_{2\omega} = n_{\omega}$ but dispersion inhibits this from occurring. So birefringent crystals are used where the refractive index for light of different polarization are different and phase matching condition is satisfied by using extraordinary polarization for ω and ordinary polarization for 2ω so that $n_o(2\omega) = n_e(\omega)$. Moreover, the intensity of the sum frequency signal generated in a NLO crystal of thickness is given by

$$I_{sig}(\lambda) \propto \left(\frac{L}{\lambda}\right)^2 \text{sinc}^2\left(\frac{\Delta k L}{2}\right) \quad (2.3.3.7)$$

$$\Delta k(\lambda) = \frac{4\pi}{\lambda} \left(n_{\lambda} - n_{\frac{\lambda}{2}}\right) \quad (2.3.3.8)$$

Therefore, phase matching only works for a light of particular wavelength. However, femtosecond laser pulses consists of large bandwidth and the frequency doubling of the signal will be regulated by the FWHM of the $\text{sinc}^2\left(\frac{\Delta k L}{2}\right)$ function. In our case, as described in previous section we use a BBO crystal of thickness ~ 0.2 mm and as BBO is a negative birefringent crystal, the phase matching condition will be satisfied only when the input radiation is ordinary polarized and second harmonic light is extraordinary polarized.

Now, BBO crystal was also used in the setup I used to generate the sum frequency signal of sample emitted fluorescence and gate light. In case of sum frequency generation (SFG) the two incident radiation have two different colours of light or two different frequencies.¹³⁻¹⁵

$$E(t) = \mathcal{E}_1 \exp(-i\omega_1 t) + \mathcal{E}_2 \exp(-i\omega_2 t) + c.c. \quad (2.3.3.9)$$

Here, $c.c.$ denotes complex conjugate. Replacing equation 2.3.3.9 into equation 2.3.3.2 gives us

$$P^{(2)}(t) = 2\epsilon_0(\mathcal{E}_1 \mathcal{E}_1^* + \mathcal{E}_2 \mathcal{E}_2^*) + \epsilon_0 \chi^{(2)} [\mathcal{E}_1^2 \exp(-2i\omega_1 t) + \mathcal{E}_2^2 \exp(-2i\omega_2 t) + 2\mathcal{E}_1 \mathcal{E}_2 \exp(-2i(\omega_1 + \omega_2)t) + 2\mathcal{E}_1 \mathcal{E}_2^* \exp(-2i(\omega_1 - \omega_2)t) + c.c.] \quad (2.3.3.10)$$

So in this case we will generate the sum frequency $(\omega_1 + \omega_2)$, the difference frequency $(\omega_1 - \omega_2)$ and the optical rectification. Phase matching also applies to this case and based on the phase matching condition either the sum frequency light

or the difference frequency light will be emitted with significantly more intensity than the other. For SFG, the phase matching condition is¹⁰⁻¹⁵

$$k_3 = k_1 + k_2 \quad (2.3.3.11)$$

In the above equation, k_3 represents the wave vector of the sum frequency light and k_1 and k_2 represents the same for input beams. Now, in a crystal the refractive index seen by one polarization of light can be adjusted by changing the angle. For simplicity, if I consider a uniaxial crystal i.e. $n_x = n_y = n_o$ and $n_z = n_e$ considering z-axis as the optical axis, we can write the phase matching condition as given below.¹⁰⁻¹⁵

$$\frac{1}{n_e^2(\theta)} = \frac{\cos^2 \theta}{n_o^2(\theta)} + \frac{\sin^2 \theta}{n_e^2(\theta)} \quad (2.3.3.12)$$

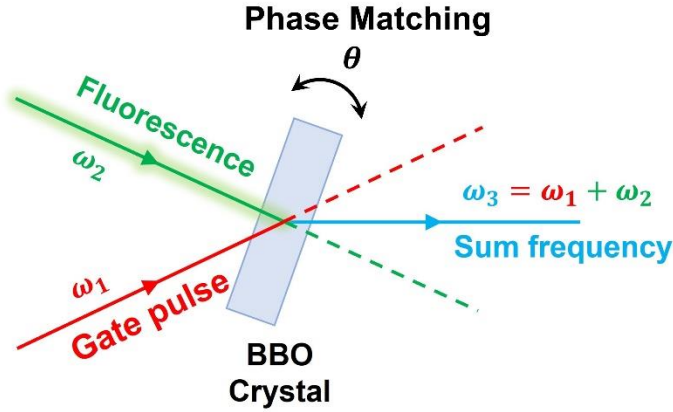


Figure 2.3.3.1 Schematic diagram depicting sum frequency generation in a BBO crystal

It should be pointed out that there are broadly two kinds of phase matching e.g. Type 1 where the output wave has different polarization than the input waves and Type 2 where one of the input waves has different polarization than the other two. In the setup I used, the fluorescence from the sample was collected from the sample using a lens and leaking excitation light was cut-off through filter. Then the gate beam and the fluorescence beam were focused onto the BBO crystal through another lens. As I collected fluorescence intensity decay of various samples at various wavelengths, data acquisition at a particular wavelength required rotating the BBO crystal at the suitable phase matching angle where intensity of the sum frequency signal generated from the gate light and that specific wavelength of fluorescence light was maximum.

However it should be mentioned that in most of the fluorescence up-conversion systems only type 1 phase matching is used. To collect the fluorescence intensity decays at magic angle polarization, the pump beam was rotated with respect to the gate beam at a certain angle with the help of a Berek compensator. Berek compensator consists of a uniaxial crystal which when tilted at a certain angle makes the axis in the plane of incidence extraordinary and depending on the tilting, a light of certain wavelength can be rotated at any angle.

2.3.4. Data Analysis

When we measure the fluorescence intensity decay of a fluorophore having a long lifetime, we can assume that the excitation pulse is an δ -function i.e. it has no width in time domain. However, in femtosecond fluorescence up-conversion spectroscopy we deal with lifetime components in sub-picosecond time domain and the above assumption becomes invalid as no optical pulse has zero width. Moreover, the laser pulse passes through several dispersive optics which inherently broadens the pulse. NLO crystals also impose dispersion and therefore the overall instrument response function has a finite non-negligible width. In my case, I measured the instrument response function (IRF) before each experiment using the Raman signal of water which is shifted about 3300 cm^{-1} compared to the excitation light.^{10-12,16} Raman scattering process is known to have zero-time delays and so when the sum frequency of water Raman and gate beam was generated the temporal profile of the pulses were preserved. The intensity of the water Raman signal at different time delays will be in accordance with the cross-correlation function described by equation 2.3.1.2. Thus replacing the sample cell with a water cell and measuring the decay at specific wavelength, I ended up with an IRF which can be perfectly modelled by a Gaussian function having a FWHM of about 250 fs.

$$G(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} \quad (2.3.4.1)$$

In the above equation, σ is the width parameter of the Gaussian and μ is the x-axis position of the function. The FWHM (H) of the above function is given by

$$H = 2\sigma\sqrt{2\ln 2} \approx 2.3548\sigma \quad (2.3.4.2)$$

For all practical purposes, we consider the excitation occurring at zero time. So, for data analysis, I have used the Gaussian function with $\mu = 0$. Now, in any time dependent fluorescence lifetime measurement using a pulsed light, the decay curve is altered by the finite width of the pulse. Especially, when we want to extract very short lifetime components, it is absolutely necessary to extract the exact intensity decay from the acquired data. The procedure to filter the data from any undesired signal is known as deconvolution. Fluorescence intensity decays obtained from femtosecond fluorescence up-conversion measurements were a convolution of IRF and actual intensity decay of the sample. To extract the lifetime components, I fitted individual decays using a convolution function of IRF and a sum of exponential functions. Briefly, I am presenting the convolution of a Gaussian (IRF) given and a single exponential function which can be extended to multiple exponentials. Setting $\mu = 0$ in equation 2.3.4.1

$$G(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-x^2/2\sigma^2} \quad (2.3.4.3)$$

$$S(x) = \exp\left(-\frac{x}{\tau}\right) \quad (2.3.4.4)$$

In equation 2.3.4.4, τ is the lifetime. Now the convolution is defined as

$$\begin{aligned} I(t) = G(x) * S(x) &= \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp\left(-\frac{x}{\tau}\right) \exp\left(-\frac{(t-x)^2}{2\sigma^2}\right) dx = \\ &= \frac{1}{\sigma\sqrt{2\pi}} \int_0^\infty \exp\left(-\frac{\left(x^2 + t^2 + \frac{2\sigma^2 x}{\tau} - 2tx\right)}{2\sigma^2}\right) dx \end{aligned} \quad (2.3.4.5)$$

Now using the transformation,

$$z = \frac{\left(x - \left(t - \frac{\sigma^2}{\tau}\right)\right)}{\sigma\sqrt{2}} \quad (2.3.4.6)$$

$$\frac{(x^2+t^2+\frac{2\sigma^2x}{\tau}-2tx)}{2\sigma^2} = z^2 + \frac{1}{\tau}\left[t - \frac{\sigma^2}{2\tau}\right] \quad (2.3.4.7)$$

Using equation 2.3.4.6 and 2.3.4.7 in equation 2.3.4.5 we get,

$$I(t) = \frac{1}{\sqrt{\pi}} \exp\left(-\frac{1}{\tau}\left(t - \frac{\sigma^2}{2\tau}\right)\right) \int_{-\left(\frac{t-\frac{\sigma^2}{\tau}}{\sigma\sqrt{2}}\right)}^{\infty} \exp(-z^2) dz \quad (2.3.4.8)$$

Now the error function are introduced as

$$\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-z^2) dz \quad (2.3.4.9)$$

Here, it should be noted that error function is an odd function which means $\text{erf}(x) = -\text{erf}(-x)$. Now introducing the error function in equation 2.3.4.9 gives

$$I(t) = \frac{1}{\sqrt{\pi}} \exp\left(\frac{\sigma^2}{2\tau^2} - \frac{t}{\tau}\right) \left(1 - \text{erf}\left(\frac{\sigma^2-t\tau}{\sqrt{2}\sigma\tau}\right)\right) \quad (2.3.4.10)$$

The above equation has been used to fit the fluorescence intensity decay data. Equation 2.3.4.10 depicts only the convolution of single exponential with Gaussian. However, while fitting the data, in most of the cases I needed more than one exponential function to fit the data. Convolution is a linear operation which follows distributive and additive property. So in case of multiexponential fitting, equation 2.3.4.10 was expanded as a summation of several lifetime exponential convoluted with same Gaussian having proper weightage coefficients. Therefore, in this thesis, when fitting with multiexponential function is mentioned it actually means the convoluted function. All the fitting of the up-conversion data were done using IGOR Pro (WaveMetrics, Inc.) software.

2.4. Time Resolved Emission Spectra

Fluorescence intensity decay with time at particular wavelength recorded from TCSPC or fluorescence up-conversion spectroscopy provides information about the excited state processes. However, another powerful tool to observe fate of photoexcited molecule is to study its time resolve emission spectra (TRES).

Basically the steady state emission spectra of a molecule is a time average of all the TRES and investigation of TRES can provide very valuable important information about the excited state processes such as charge transfer, excited state reactions etc.^{6,17-21} Moreover it can also elucidate the interaction of excited state molecules with surrounding solvents.⁶ Recording of TRES at different times was done in the past but they were distorted by the instrument response.¹⁷⁻²¹ Besides recording of TRES directly requires detection of a large number of wavelengths simultaneously. Fortunately, TRES can be prepared from the time resolved fluorescence decays recorded at various wavelengths over the entire range of emission spectra.^{6,17-21} TRES can be expressed mathematically as (see chapter 1 for details)

$$I(\lambda, t) = \frac{I_{ss}(\lambda)}{\sum_i a_i \tau_i} \sum_{i=0}^n a_i e^{-t/\tau_i} \quad (2.4.1)$$

According to equation 2.4.1, we can record fluorescence intensity decay at a particular wavelength and knowing its steady state intensity can construct the time dependent intensity behavior. This procedure was applied to several wavelengths to obtain multiple points and then each of the TRES was fitted by a lognormal function described by Maroncelli and Fleming.^{18,19}

$$L(\nu) = g_0 \exp \left\{ -\ln 2 \left(\frac{\ln \left(1 + \frac{2b(\nu - \nu_p)}{\Delta} \right)}{b} \right)^2 \right\} \quad (2.37)$$

In the above equation, g_0 , b , ν_p , Δ are peak height, asymmetry parameter, peak frequency, width parameter. The width parameter is related to full width half maxima (Γ) as follows^{18,19}

$$\Gamma = \Delta \left(\frac{\sinh(b)}{b} \right) \quad (2.38)$$

The fitting has been done IGOR Pro software and different fitting parameters obtained were used to understand different excited state processes which will be discussed in their appropriate sections.

2.5. Femtosecond Broadband Transient Absorption Spectroscopy

2.5.1. Basic Principle

Femtosecond molecular dynamics is studied by several techniques out of which pump-probe techniques are very popular and broadband transient absorption spectroscopy is one of them. Generally, in pump probe experiments, a non-stationary molecular state is prepared by an ultrashort laser pulse which is called the pump and the time evolution of that newly prepared state is monitored using another suitable time delayed laser pulse known as the probe.²²⁻²⁵ In transient absorption spectroscopy, we use resonant excitation i.e. the excited electronic state population is prepared by the pump pulse and the population decay is not instantaneous unlike Raman spectra.²²⁻²⁵ The study of the dynamics of the excited state will depend on the choice of the probe pulse. The probe can be monochromatic or broadband in UV-Visible or IR region and they can be used to explore different photophysical properties of the molecule.²²⁻²⁵ Moreover, observation of the action of pump depends on either the change in characteristic (like intensity) of the probe or the events created by the probe itself after the action of the pump.²²⁻²⁵ We observe the first case in transient absorption spectroscopy.

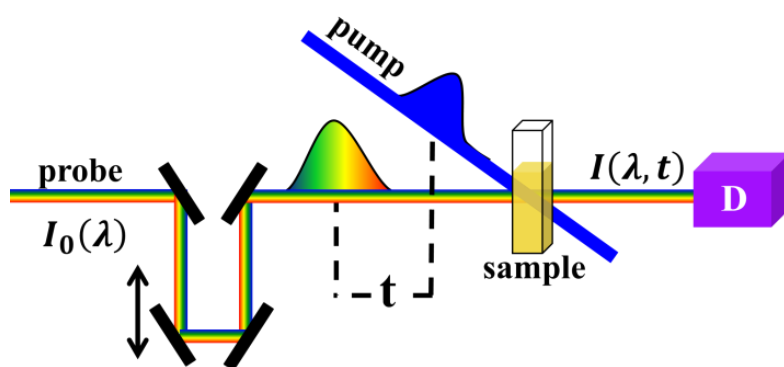


Figure 2.5.1.1. Schematic representation of transient absorption spectroscopy experiment

In our lab setup, I used either 400nm or 266 nm light as pump light which excites a fraction of molecules in the electronic excited state. A visible (450nm-750nm) white light continuum (WLC) probe is passed through the sample at various delay times controlled by a mechanical delay stage and the change in intensity of the probe light

is monitored by the detector while the pump is dumped. In figure 2.5.1.1 a schematic diagram is shown to explain the operation. The intensity of the probe is kept very low compared to the pump to avoid any multistep or multiphoton processes exerted by the probe itself. The detection is done simultaneously over the range of probe spectrum at a particular time and the process is repeated over multiple time delays which is basically the time gated detection.²²⁻²⁵ Since this is an absorption spectroscopy, Lambert-Beer law can be applied on the probe light.

$$I(\lambda, t) = I_0(\lambda) \times 10^{-\varepsilon(\lambda)N(t)l} \quad (2.5.1.1)$$

In equation 2.5.1.1, $I_0(\lambda)$ and $I(\lambda, t)$ are the intensity of the probe light before and after passing the sample at delay time t respectively as illustrated in figure 2.5.1.1. It should be specified that the time zero is labeled to the particular position of the delay where pump and probe pulses reach the sample simultaneously. $\varepsilon(\lambda)$ is the molar extinction coefficient at wavelength λ , $N(t)$ is the population of a state after t time of the pump excitation and l is the path length of the sample. So according to figure 2.5.1.1 and equation 2.5.1.1, the absorbance $A(\lambda, t)$ is given by

$$A(\lambda, t) = \log \frac{I_0(\lambda)}{I(\lambda, t)} = \varepsilon(\lambda)N(t)l \quad (2.5.1.2)$$

Now the quantity that is observed in transient absorption technique is the change in absorbance with and without the action of pump which is mathematically expressed as follows.

$$\Delta A(\lambda, t) = A(\lambda, t) - A(\lambda) \quad (2.5.1.3)$$

$$\Delta A(\lambda, t) = \log \frac{I_0(\lambda)}{I(\lambda, t)} - \log \frac{I_0(\lambda)}{I(\lambda)} = \log \frac{I(\lambda)}{I(\lambda, t)} \quad (2.5.1.4)$$

Equation 2.5.1.4 implies a situation where the measurement of probe intensity with and without illumination of the sample by pump will give us the observable quantity.

So we can simply write

$$\Delta A(\lambda, t) = \log \frac{I^{probe}}{I^{probe}_{pump}} \quad (2.5.1.5)$$

It should be pointed out that in equation 2.5.1.5; the quantity I^{probe} is actually measured blocking the pump light completely with the use of a chopper. The population created or depleted by pump light will decay or grow with time i.e. as

$N(t)$ changes with time, $\Delta A(\lambda, t)$ also changes with time and that provides us the photophysical dynamics of the system. Furthermore, as the observable $\Delta A(\lambda, t)$ does not contain any $I_0(\lambda)$ term, the intensity of probe before the sample need not to be measured which means a single beam spectrophotometer will work just fine. However, to subtract the noise in the probe light, a dual beam spectrophotometer is often used. Now this particular pump probe technique being an absorption spectroscopy can track both radiative and non-radiative processes depending on the spectrum of the probe.²²⁻²⁵ Four major processes can be observed in transient absorption spectroscopy which are depicted in figure 2.5.1.2 and described below.

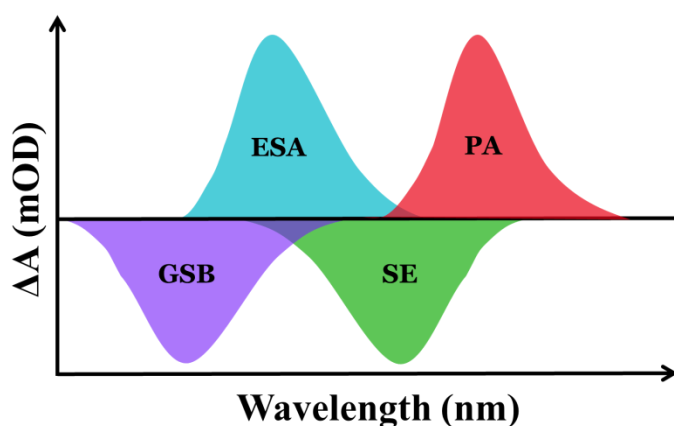


Figure 2.5.1.2. Contribution of different photophysical processes in transient absorption spectra

Ground state bleaching - The pump pulse excites a portion of molecules from ground state to excited state and the population in ground state decreases. Therefore, the amount of probe light absorbed by the ground state molecule become less after the pump excitation compared to the absorption without pump excitation i.e. $I^{probe} < I_{pump}^{probe}$. So a negative ΔA spectrum is observed which reduces with increment in time delay between the pump and the probe due to deactivation of molecules from excited to ground electronic state. This particular signal is known as ground state bleaching (GSB).

Stimulated Emission:- Electronically excited molecules undergoes spontaneous emission (fluorescence) and deactivate to ground state. However, if a resonating

photon from external radiation passes through the excitation volume, it can stimulate the emission process from excited to ground state which is known as stimulated emission. The stimulated emitted photon has the same direction as the stimulating radiation photon. So if some or all frequencies present in the probe pulse resonate with the excited and ground state of the sample (including vibrational levels), probe can stimulate emission from the sample excited by the pump. Moreover, the emitted photons will travel with the probe and reach the detector which in turn will see an increase in intensity of the probe at certain wavelengths after the action of pump. Therefore $I^{probe} < I_{pump}^{probe}$ will be satisfied and a negative spectrum will be observed in transient absorption. This is known as stimulated emission (SE) signal which resembles the spontaneous emission spectra of the molecule. SE signal remains Stokes shifted compared the GSB signal but there can be significant overlap at early times. SE also decreases with time exactly as the excited state population decreases due to different radiative and non-radiative molecular processes under the assumption that the intensity of the probe light is so small that it does not change the population of the excited state significantly.

Excited State Absorption:- The applicability of transient absorption signal lies in the distinction of recognizing transitions which are not possible to observe using fluorescence techniques. One of them is the observation of excited state absorption (ESA) signal. The pump beam creates a particular electronic excited state in the sample. Now, some of the wavelengths of light present in probe light can be in resonance with the energy gap between the populated excited state and other higher energy states and thus is absorbed by the excited state molecules. This particular transition is not possible without the pump and therefore, in this case, $I^{probe} > I_{pump}^{probe}$ and we can observe a positive signal in the spectra.

Product Absorption:- Product absorption (PA) signal is another feature in transient absorption spectroscopy which is difficult to observe using fluorescence techniques. Once excited, the molecule can undergo several transformations and excited state reactions like photoinduced electron and proton transfer etc. and the new transient

species thus generated can absorb the probe light which results in a positive spectral signature in the transient absorption spectroscopy as $I^{probe} > I_{pump}^{probe}$.

The observation of these four phenomena makes transient absorption spectroscopy an immensely powerful technique but the limitations are put by several factor and among them the spectral spread of the probe and instrument response can restrict observation of one or more processes described above.

2.5.2. Instrumental Setup

The femtosecond broadband transient absorption spectrometer in our lab is a commercially one (Femto-Frame-II, IB Photonics, Bulgaria) which I have used for all my studies. The optical layout of the system has been shown in figure 2.5.2.1. The 800 nm output of a Ti:Sapphire regenerative amplifier (SpitfirePro XP, Spectra-Physics, USA) pumped by a 20-W Q-switched Nd:YLF laser (Empower, Spectra-Physics, USA) and seeded by a Ti-Sapphire femtosecond oscillator (MaiTai SP, Spectra-Physics, USA) was used as the fundamental light for transient absorption experiments. The repetition rate and the pulse width of the output was 1kHz and ~80 fs measured using a commercial autocorrelator. This fundamental beam was split into two parts at beamsplitter BS₁. One part was used to generate the pump light and the other was used for the probe. The pump light was generated inside a JANOS tripler supplied by the same company. The 800 nm light was focused onto a BBO crystal where the second harmonic 400nm light was produced. The second harmonic and the residual 800 nm light passed through a waveplate and collinearly fell onto a second BBO crystal where the third harmonic 266 nm light was generated according to the principles described in section 2.3.3. These three lights were separated using a set of dichroic mirrors and the 400 nm or the 266nm light was used for excitation light by using mirror M₆ or M₇. The other part of the fundamental beam after reflecting through mirror M₅ was passed through a retroreflector (RR) mounted on a mechanical delay stage using mirrors M_{B1}, M_{B2} & M_{B3}. This delay stage was used to generate maximum 2ns time delay between the pump and the probe. A very small part of the 800 nm light was split in BS₂ and allowed to fall on a photodidode PD

which controlled the chopper. The rest of the fundamental beam passed through a linear neutral density filter (ND₁), an iris and focused on a 0.3 mm sapphire crystal by lens L₄.

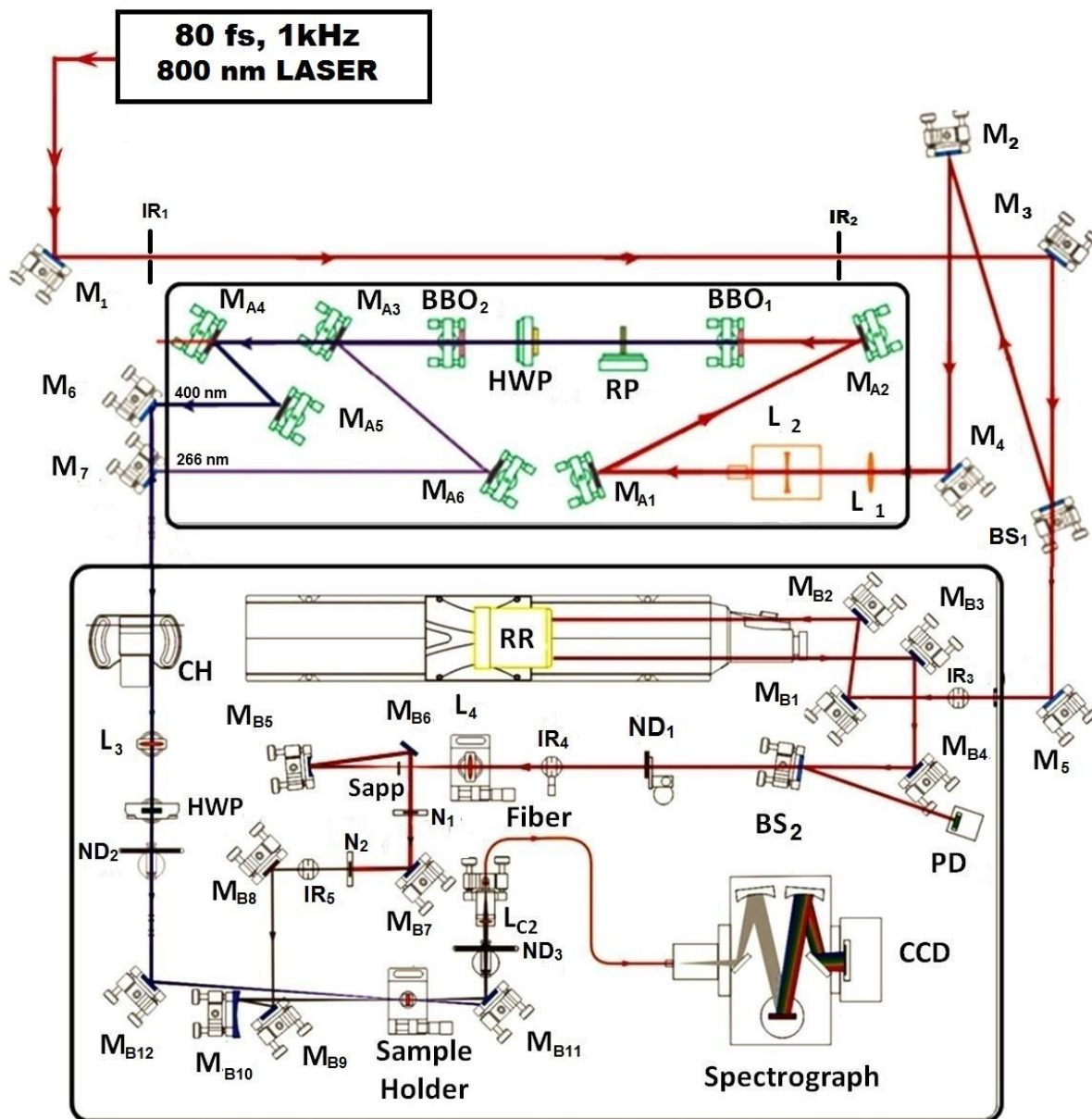


Figure 2.5.2.1. Optical layout of the femtosecond broadband transient absorption spectrometer

Thus the white light continuum (WLC) probe spanning across 450nm-750nm was generated in the sapphire crystal (Sapp). However, the character/shape of the probe light largely depends on the power and beam shape controlled by the ND filter and the iris. The WLC then collected by a parabolic mirror M_{B5} and directed through the two Notch filters (N₁ and N₂) to cutoff residual fundamental radiation of 800nm

using mirror M_{B6} and M_{B7} . Then the probe light is focused on the sample using another parabolic mirror M_{B10} . Meanwhile the pump light is directed through chopper and its polarization is adjusted compared to the probe using a half wave plate. A rotating ND filter (ND_2) controls the power of the pump and using lens L_3 and mirror M_{B12} the pump beam is focused into the same spot in the sample cuvette as the probe beam. A typical focal spot size is 100-200 μ m. The function of the chopper is to cut-off the pump light for certain time to allow measurement without pump as explained in the previous section. The polarization control is required to record data without interference from anisotropy of the system. The probe beam after passing through the sample is focused on the 200 μ m optical fiber cable by means of mirror M_{B11} . Another ND filter (ND_3) controls the amount of probe light that reaches the detector. The detector is a CCD spectrograph which detects the probe light scattered by a pair of diffraction gratings. The pump beam have slight inclination compared to the probe beam and therefore cannot reach the detector. The zero time is adjusted by observing the signal of a known sample (C152 in ethanol in my case) varying the delay time. The whole setup is controlled by software based on LABVIEW platform. The pump power is kept ~ 10 -15 μ W during measurements. Steady state absorption spectra were taken before and after the measurements to ensure no photo degradation of the sample.

2.5.3. Instrument Response Function (IRF) and Chirp

In broadband transient absorption spectroscopy, the instrument response function (IRF) is given by the cross correlation of the pump and the probe light.²⁶⁻²⁸ Generally pulses travelling through transmitting optics broadens them but in this pump probe technique several other factors like presence of instantaneous signals or artifacts, group velocity dispersion etc. do affect the data and IRF acquisition. The use of high power pulses in transient absorption spectroscopy gives rise to several kinds of artifacts in the data and two photon absorption (TPA) is one of them. The sample under study can absorb two photons from the pump and spectrally broad probe pulse simultaneously which will result in the change in absorbance of the probe light

resulting in an unwanted signal.^{24,27,28} Stimulated Raman amplification can also occur if the pump and the probe are very close in frequency.^{27,28} However, in my case the spectral separation of the excitation from the probe let this effect diminish. Moreover, the timescale of SRA is in the range of instrument response i.e. very short lived. Cross-phase modulation occurs when the intense pump light modifies the refractive index of the medium which in turn changes the spectra of the probe light. Cross phase modulation affects the spectra at time zero mostly.^{27,28} All three artifacts have a linear correspondence with the intensity of the pump pulse. So using less intense pump pulse, higher optical density of the sample and less chirped WLC probe light, these artifacts can be avoided in the acquired data. However, the IRF measurement can get seriously affected by them. The IRF of the transient absorption setup was measured by replacing the sample solution in the cuvette with pure solvents. The femtosecond pump pulse induces instantaneous effects in solvents which can be applied to measure the IRF. For instance, pump pulse can induce non-resonant coherent signal from pure solvent like stimulated Raman scattering, impulsive Raman scattering or off-resonant transient birefringence etc. which give the pump-probe cross correlation of the system.^{25,27-30} Two factors are to be considered for IRF and data analysis. The first one is the group velocity dispersion and subsequent chirp present in the data. Group velocity dispersion (GVD) is a well-known optical process where light of different frequencies travel at different velocity in a medium other than vacuum. The probe light has a broad spectrum. Naturally, the red end of the probe light travels faster than the blue end and as the probe light passes through transmitting optics, the light gets spread in time. Moreover, inside sample solution, the probe light travels faster than the pump light as the pump has a shorter wavelength than the probe. GVD in optics and sample cell induces chirp in the measured data i.e. the overlap of the pump and probe at different wavelengths happens at different times. In other words the time zero is shifted along the probe spectrum which does not affect the actual dynamics of the sample but it needs to be known to compare the sample dynamics at different wavelengths or to fit the data globally. However, the chirp can be easily estimated from the time zero position of

the pure solvent response at different wavelengths.^{25,27-30} Along with GVD, cross phase modulation induced by the pump light on a linearly chirped probe light modulates the Gaussian shaped IRF and distorts it.²⁷⁻³⁰ Therefore, once the solvent response is measured, it is fitted at different wavelengths with a Gaussian and its first and second derivative to account for the shape. The time position obtained from such fitting at several wavelengths are then used to estimate the chirp in the data. The chirp is usually corrected by fitting with a polynomial and designating a position in the spectrum where time zero is to be set. In figure 2.5.3.1, I have shown the IRF obtained at multiple wavelengths in acetonitrile, methanol and chloroform along with the fitting. The width of the Gaussian fit obtained was 50-60 fs depending on the wavelength. Using the relation between the width parameter and the FWHM of Gaussian given in equation 2.3.4.2, the estimated IRF is 120-140 fs. From the figure, it is quite clear that the center of IRF is shifted to longer times at longer wavelengths of the probe.

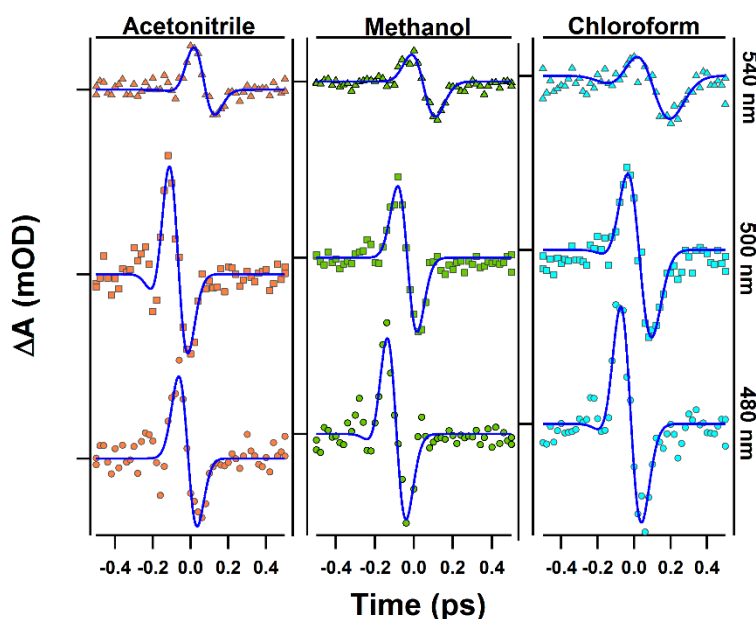


Figure 2.5.3.1. The IRF of transient absorption setup recorded in acetonitrile, methanol and chloroform using 400nm pump. The solid blue lines indicate fitting.

2.5.4. Data Analysis

Broadband transient absorption spectroscopy generates a massive amount of data which is simultaneously or “globally” analysed. The dataset itself is a two way data

or in other words it contains two independent experimental variable; time and wavelength. So a model based global analysis procedure is necessary. I have used an open source java-based software GLOTARAN for analysis of transient absorption data. The operational details of this software have been discussed in ref 31 and 32. A very brief idea of the procedure employed is discussed here. First of all, while analyzing transient absorption data it is assumed that the data has homogeneity i.e. a set of parameters can describe the data and the overall dynamics can be assigned to individual member or reaction pair of the system. The data has contribution from all the photophysical processes described in previous section at different times and wavelengths. The experiment essentially an absorption spectroscopy and therefore Beer-Lambert's law can be applied. It is also considered that the whole dataset is the superposition of spectral properties weighted by their concentration.

$$\psi(t, \lambda) = \sum_{l=1}^{n_{comp}} c_l(t) \varepsilon_l(\lambda) \quad (2.5.4.1)$$

In the above formalism, $c_l(t)$ is the concentration of the l -th component at time t and $\varepsilon_l(\lambda)$ is the extinction coefficient of the same component at wavelength λ . A typical global analysis procedure can resolve upto 10 such components. Prior knowledge of the system is used to assume the minimum number of components necessary to fit the data. Now the overall data can be fitted by two methods. Either we can fit the data with knowledge of $c_l(t)$ which is known as the kinetic model or we can fit the data using the knowledge of $\varepsilon_l(\lambda)$ which is known as the spectral model. In our case we have a prior understanding of the concentration profiles which are exponentially variable with time. Therefore the idea is to fit $\psi(t, \lambda)$ with sufficient number of exponential components convoluted with the IRF function. IRF is modeled with Gaussian function and the convolution of exponential with Gaussian has already been described in section 2.3.4. Now the experimental data is in the form of a $m \times n$ matrix where measurements are done over m wavelengths for n times. One of the ways to extract the number of independent components in such kind of data is singular value decomposition (SVD) which is defined as ^{31,32}

$$\psi(t, \lambda) = \sum_{n=1}^{n_{max}} u_n(t) w_n(\lambda) S V_n \quad (2.5.4.2)$$

So the minimum number of parameters needed for fitting was first estimated from SVD, then the sum of exponentials convoluted with Gaussian IRF was fitted into the whole dataset simultaneously. The dispersion was modeled with a polynomial function while fitting.

2.6. Density Functional Theory (DFT) Calculations

Prediction of photophysical behavior of a molecule requires knowledge of its electronic structure in ground and electronic excited state, energy gap between different levels, electron density in molecular orbitals etc. Additionally, the changes in electronic state energies brought about by distortions in molecular geometry often help photo-chemists understand molecular properties.³³⁻³⁷ For these purposes and many more, computational chemistry is essential. I have explicitly used density functional theory calculations for works done in this thesis. All the calculations were performed in Gaussian 09 software and results were viewed using Gaussview 05 software.³⁸ Density functional theory (DFT) is probably the most powerful tool for calculating electronic structure of a molecule.³³⁻³⁷ DFT was introduced in two groundbreaking papers in 1964 and 1965 and Walter Kohn received the Nobel Prize in chemistry in 1998.³⁹⁻⁴⁰ Ground state geometry and electronic structure calculations were all calculated using DFT but for excited state calculations time dependent potentials are needed which are incorporated in time dependent density functional theory (TDDFT). Here I am going to discuss their basic idea based on which the computations were performed without going into details.

For any quantum chemical calculation in ground state, the goal is to solve the time independent Schrödinger equation which under Born-Oppenheimer approximation can be written as

$$\hat{H}_{el} \psi_{el} = E_{el} \psi_{el} \quad (2.6.1)$$

In an N-electron M-nuclei system the electronic Hamiltonian is given by

$$\hat{H}_{el} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{r_{iA}} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{r_{ij}} \quad (2.6.2)$$

The problem is equation 2.6.2 cannot be solved without proper approximations and even then the wavefunction being a non-observable quantity cannot be truly measured. So it becomes increasingly difficult to construct increasingly accurate wavefunctions with so many degrees of freedom.³³⁻³⁷ In DFT, the state is defined by the density of the interacting electrons; not by their individual interaction which is valid for any fermions for that matter.³³⁻³⁷ Contrary to wavefunction, electron density is an observable and the information of all the coordinates are not required to calculate expectation value.³³⁻³⁷ Now, first Hohenberg-Kohn theorem stated that the electron density determines all ground state properties of the system.³³⁻³⁷ So total energy ($E[\rho]$) is a functional of electron density(ρ) in presence of an external potential ($v_{ext}(r)$) like electric field from nuclei.³³⁻³⁷

$$E[\rho] = F[\rho] + \int v_{ext}(r)\rho(r)dr \quad (2.6.3)$$

The second Hohenberg-Kohn theorem states that variational principle applies to $E[\rho]$ and it will reach minimum when ρ will be equilibrium electron density. Here $F[\rho]$ is universal functional i.e. it does not depend on external potential.³³⁻³⁷ The recipe for calculating the functional came from Kohn-Sham theorem which gave the ground state electronic energy as

$$E[\rho] = -\frac{1}{2}\sum_{i=1}^N\langle\psi_i|\nabla_i^2|\psi_i\rangle - \int \sum_{A=1}^M \frac{Z_A}{r_{Ai}}\rho(r)dr + \frac{1}{2}\int\int\frac{\rho(r_1)\rho(r_2)}{r_{12}}dr_1dr_2 + E_{xc} \quad (2.6.4)$$

In the above equation, the first term is the kinetic energy of electrons, second term is electron nucleus attraction term, the third term is the electron-electron repulsion term and E_{xc} is exchange correlation energy which is unknown. So several approximated functional are used. The ground state electron density is defined by one orbital Kohn Sham wavefunctions.³³⁻³⁷

$$\rho(r) = \sum_{i=1}^N|\psi_i(r)|^2 \quad (2.6.5)$$

One of the approximations for exchange correlation is the local density functional (LDA). It assumes the inhomogenous density of solid or liquid can be calculated using homogenous electron gas. More sophisticated approximations are hybrid functional and among them the Becke, 3-parameter, Lee-Yang-Parr (B3LYP) is

probably the most popular in chemistry. Hybrid functional like B3LYP combines orbital dependent Hatree-Fock and an explicit density functional like LDA and generalized gradient approximation.³³⁻³⁷

Another important point for computations is the use of basis set which is a mathematical description of orbitals. In Gaussian calculations I have used split-valence basis sets like 6-31G, 6-311G etc. The idea proposed by Boys and explicitly developed by Pople is to replace Slater type orbitals with Gaussian orbitals.^{33-37,41,42} However, calculations with Gaussian orbitals do not match that of Slater type orbitals specially at shorter distance.^{33-37,41,42} One way out is to use a sum of multiple Gaussian orbitals and each of those Gaussian are called primitive Gaussian.^{33-37,41,42} Now the most used are the split-valence basis sets where a sum of Gaussian functions (6 in case of 6-31G) known as contracted Gaussian function is used to represent the inner shell atomic orbitals, and a larger number of contracted Gaussian to represent valence orbitals. Like in 6-31G, the compact valence orbital is represented by a contraction of 3 Gaussian and the extended valence orbital is represented by one Gaussian. The – indicates split-valence and G indicates Gaussian.^{41,42}

In photochemistry, we often need to calculate the vertical excitation energy to match the absorption spectra and to study the dynamics of a molecule in the excited state by performing a geometry scan. DFT does not include a way to calculate the excited state properties and therefore time dependent density functional theory (TDDFT) has been developed. In TDDFT, we calculate the response of system to an external perturbation like polarizability which is system response to an external electric field. The basic idea is to solve the time dependent many particle Schrodinger equation.

$$i \frac{\partial}{\partial t} \psi(r_1, r_2 \cdots r_N, t) = \hat{H}(t) \psi(r_1, r_2 \cdots r_N, t) \quad (2.6.6)$$

The problem is in time independent Schrodinger equation we solve for an eigenstate whereas in time dependent Schrodinger equation, we observe the time evolution of a state. The time dependent Hamiltonian $\hat{H}(t)$ consist of kinetic energy and electron

electron interaction term with the external potential term ($\hat{V}_{ext}(\{r\}, t)$) which is expressed as a sum of one body potentials.⁴³⁻⁴⁷

$$\hat{V}_{ext}(\{r\}, t) = \sum_{i=1}^N v_{ext}(r_i, t) \quad (2.6.7)$$

Now, the time evolution of the system is controlled by the external potential like illumination with light/radiation. Runge and Gross established that there is an one to correspondence between the time dependent potentials and densities i.e. if two different time dependent potentials act on same initial state of a system then they will generate two different time dependent densities.⁴³⁻⁴⁷ Another problem with TDDFT is variational principle cannot be applied to it as energy is not conserved here.⁴³⁻⁴⁷ So instead a quantity called quantum mechanical action (A_{xc}) is defined which can be used in place of energy. Runge and Gross also modified the Kohn-Sham equation to show that the exchange correlation functional (v_{xc}) is a derivative of action functional.⁴³⁻⁴⁷

$$v_{xc}(\rho) = \frac{\partial A_{xc}}{\partial \rho} \quad (2.6.8)$$

As the correct form of the functional in the ground state is not known, adiabatic local density approximation (ALDA) is applied and then the same functional which is applied in the ground state is used in the excited state. Next the problem of causality exists in TDDFT which states that the response functions must be zero before a certain time or before the time at which the external perturbation was turned on. The causality problem along with the boundary conditions were solved by van Leeuwen in 1998.⁴³⁻⁴⁷ In TDDFT, adiabatic approximations are made to the exchange correlations which works satisfactorily if the excited state does not differ much from the ground state. Now, photoabsorption cross section is related to imaginary part of dynamic polarizability which is estimated from the linear density response function of the system perturbed by a small external potential. Lastly, specific photoabsorption phenomenon such as double excitation, excitation to higher states or charge transfer states were calculated using TDDFT by several modifications made by researchers in the last decade.⁴³⁻⁴⁷

Solvent effects in DFT and TDDFT computation performed with Gaussian software can be incorporated through self-consistent reaction field method which places the solute in a cavity of reaction field.^{33-37,48} The most commonly used method and the one I have used in all the solvent dependent calculations is Polarizable Continuum Model (PCM). PCM model calculates the free energy of a molecule as a sum of electrostatic energy, dispersion-repulsion free energy and cavitation energy. The cavity is an Onsager cavity defined by van der Waals radius of atoms.⁴⁸ PCM model does not take into account any specific solvation like hydrogen bonding interaction. It only applies a dielectric continuum which behaves like the polarity of the solvent.

2.7. Cyclic Voltammetry Measurements

I used the Cyclic Voltammetry (CV) to measure the redox potential of some molecules which act as electron donors and acceptors in photoinduced electron transfer (PET) reaction. I performed the CV experiments at room temperature using a commercial electrochemical workstation (600B Series, CH Instruments, USA). A standard three-electrode cell, comprised of a glass carbon electrode as working electrode, platinum wire as auxiliary electrode and Ag/AgCl as reference electrode, was used. No correction was made for liquid junction potential. The CV of donor molecules was measured in acetonitrile solution containing 1.0 mM compound and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. The CV of acceptor molecules which are mainly viologen derivatives, were measured using 1.0 mM compound in a 2.0 mM OA solution containing 50 mM NaCl as supporting electrolyte. The $E_{1/2}$ values were taken as the average between the peak potential of the cathodic peak and the peak potential of the anodic peak.

2.8. Materials

Coumarin 152 (C152), coumarin 153 (C153), coumarin 152A (C152A), coumarin 1 (C1), coumarin 466 (C466) and coumarin 480 (C480) were purchased

from Exciton Inc. and used as received. Anthracene (AN) was purchased from Sigma-Aldrich and was recrystallized from ethanol before use. Deuterated anthracene from MSD Isotopes was used as received. Azulene (Az), guaiazulene (Gaz), pyrene (Py), methyl viologen dichloride dihydrate (MV^{2+}) and benzyl viologen dichloride (BzV^{2+}) was also from Sigma-Aldrich. Phenothiazine (PTZ) from TCI Chemicals were used as received. Naphthalene (Nap), 1-bromonaphthalene (1Br-Nap) and 2-bromonaphthalene (2Br-Nap) were purchased from Avra Synthesis Pvt. Ltd. and used after recrystallization. Spectroscopic grade methanol (MeOH), acetonitrile (ACN) and cyclohexane (CHX) bought from Fisher Scientific, India were used after distillation. Double distilled water was used throughout the study. Deuterated water from Sigma-Aldrich was used as received. The coumaryl esters were synthesized by following reported procedure.⁴⁹ 3-bromo-coumarin 1 (3Br-C1) and 3-iodo-coumarin 1 (3I-C1) were also synthesized. Their synthetic procedures and characterizations are presented in the following section. Octa acid (OA) was synthesized, purified and characterized following the published procedure.⁵⁰⁻⁵¹

2.9. Synthetic Procedures

I would like to express my gratitude to Prof. V. Ramamurthy and his group in University of Miami, USA for the synthesis of octa acid (OA), coumaryl esters, and the following halogen-substituted coumarins.

2.9.1. Synthesis of 3-bromo-7-(diethylamino)-4-methyl-2H-chromen-2-one (3Br-C1)

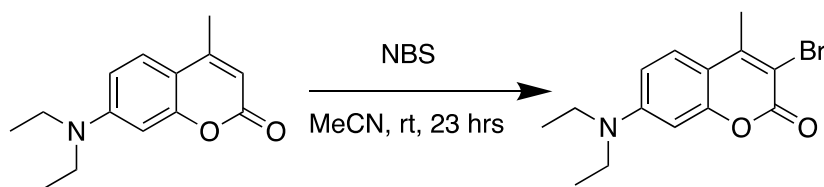


Figure 2.9.1.1. Synthesis of 3-bromo-7-(diethylamino)-4-methyl-2H-chromen-2-one.

7-(diethylamino)-4-methylcoumarin (1.00 gm, 4.32 mmol) and 20 ml of acetonitrile (ACN) were taken in a 50 ml RB and stirred few mins until clear solution was obtained followed by addition of N-bromosuccinamide (846 mg, 4.75 mmol, 1.1 equiv.). The reaction mixture was kept under stirring at room temperature for 24 hours. The mixture is then poured into water, extracted with ethyl acetate, washed with brine, and dried over Na₂SO₄. The organic layer was evaporated and purified by silica gel column chromatography (Hexane/Ethyl Acetate 4:1). The product was obtained as pure 3-bromo-7-(diethylamino)-4-methyl-2*H*-chromen-2-one as yellow solid (1.2 gm, 3.86 mmol, 89 %). ¹H-NMR (400 MHz, CDCl₃, δ; ppm) 7.42 (1H, d, J = 9.0 Hz), 6.62 (1H, dd, J₁ = 9.3 Hz, J₂ = 2.8 Hz), 6.49 (1H, d, J = 2.4 Hz), 3.41 (4H, q, J = 7.1 Hz), 2.53 (3H, s), 1.22 (6H, t, J = 7.1 Hz).

2.9.2 Synthesis of 3-iodo-7-(diethylamino)-4-methyl-2*H*-chromen-2-one (3I-C1)

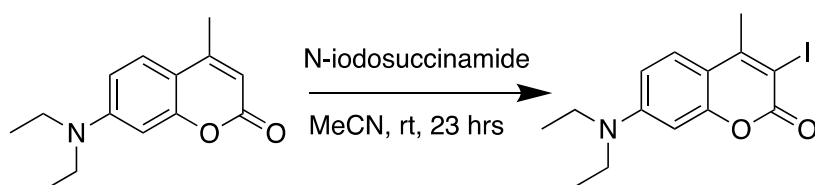


Figure 2.9.2.1. Synthesis of 3-iodo-7-(diethylamino)-4-methyl-2*H*-chromen-2-one. 7-(diethylamino)-4-methylcoumarin (1.00 gm, 4.32 mmol) and 10 ml of acetonitrile (ACN) were taken in a 50 ml RB and stirred few mins until clear solution was obtained followed by addition of N-iodosuccinamide (1.06 gm, 4.75 mmol, 1.1 equiv.). The reaction mixture was kept under stirring at room temperature for 4 hours. The solvent was evaporated and purified by silica gel column chromatography (Hexane/Ethyl Acetate 4:1). The product was obtained as pure 3-iodo-7-(diethylamino)-4-methyl-2*H*-chromen-2-one as yellow solid (980 mg, 2.74 mmol, 63 %). ¹H-NMR (400 MHz, CDCl₃, δ; ppm) 7.45 (1H, d, J = 9.1 Hz), 6.56 (1H, dd, J₁ = 9.1 Hz, J₂ = 2.4 Hz), 6.50 (1H, d, J = 2.2 Hz), 3.41 (4H, q, J = 7.1 Hz), 2.60 (3H, s), 1.22 (6H, t, J = 7.1 Hz).

References

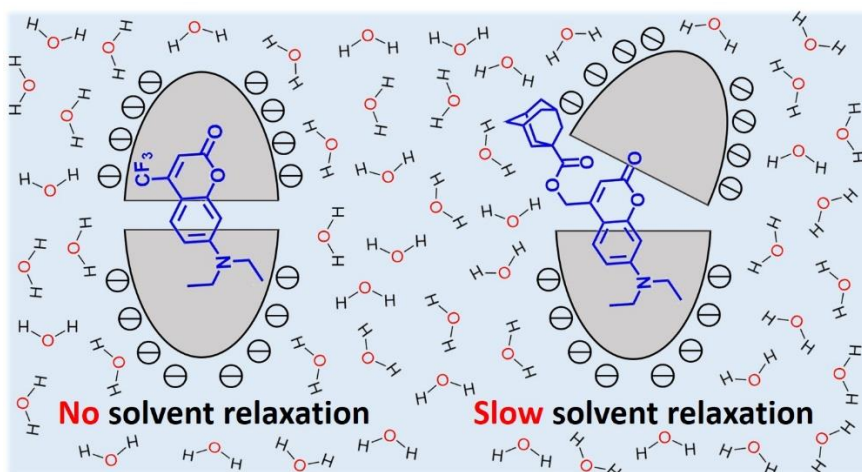
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Chapter 3

Ultrafast Solvation Dynamics Reveal that Octa Acid Capsule's Interior Dryness Depends on the Guest



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In this chapter, I have studied the solvation dynamics for six different photo-excited guest molecules trapped inside Octa Acid (OA) cavity. For smaller guest molecules the complexation with OA is firm and no water molecule can access the trapped guest during its lifetime. As a result, no solvent relaxation was observed. With increasing guest sizes, the guest-OA complex distorts and water molecules sip in. Consequently, solvation becomes faster with increasing guest size.

3.1. Introduction

During the last three decades, interest in understanding the physicochemical behavior and dynamics of molecules in confined spaces has grown steadily.^{1–4} In this context, various organic and inorganic well-defined hosts have been employed as reaction space.^{5–8} Our long-standing interest in exploring the photochemical and photophysical behavior of molecules in confined spaces^{9,10} led us to use a synthetic molecule, octa acid (OA, Figure 3.1.1), as the reaction medium.^{11–13} In the presence of a guest molecule, two molecules of OA are assembled to form a capsule with the host to guest ratio of 2:1 or 2:2 in aqueous solution under basic conditions.¹⁴ A variety of fluorescent as well as electron paramagnetic resonance active nitroxide probes revealed the interior of the capsule to be nonpolar and the micropolarity to be similar to that of benzene.^{15,16} Considering that the capsule is present in an aqueous medium, absence of water molecules within the capsule was unanticipated. Fluorescence probes revealed that during the measurement time, the capsule neither disassembled nor partially opened to expose the probe molecules to the aqueous exterior. On the other hand, phosphorescence quenching of a variety of encapsulated guest molecules by oxygen indicated that the capsule partially opened and closed in the time scale of 5 μ s.¹⁷ The disassembling–assembling of the OA capsule takes place in the time-scale of 2.7 s that is 5 orders of magnitude slower than the partial opening and closing.¹⁸ Thus, although in a nanosecond timescale, the capsule is intact, in a microsecond timescale, it partially opens and closes, and in a second time scale, it disassembles and assembles. The above conclusion is based on probes that are presumed to form a tight 2:1 capsule. Given that well-known hosts such as micelles, cyclodextrins, cucurbiturils, calixarenes, and related organometallic cavitands are permeable to water molecules, absence of water within the OA capsule is unique and provides an opportunity to conduct photochemical and photophysical studies under “dry” conditions even in an aqueous medium.

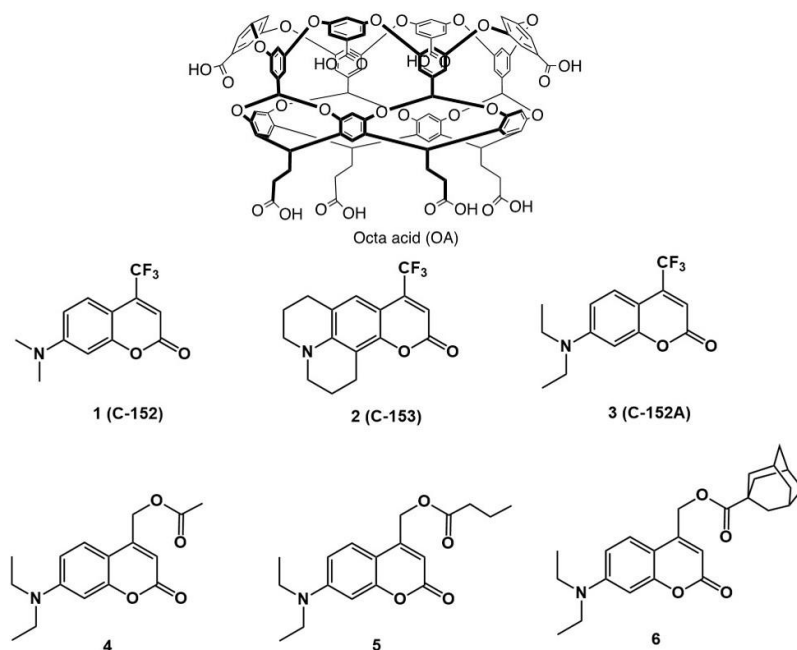


Figure 3.1.1. Structures of water-soluble octa acid cavitand, and guest molecules; **1** (Coumarin-152), **2** (Coumarin-153), **3** (Coumarin-152A) and coumaryl esters **4–6**. The coumaryl esters **4–6** were synthesized by Prof. Ramamurthy Group in University of Miami, USA.

In a recent study, we established the occurrence of energy, electron, and spin communication between two molecules, one present within and the other outside the capsule.^{19–27} The donors in this study were coumarin 152 (Figure 3.1.1) and others of similar size and structure. Although we postulated that the above communications occurred through the capsular wall, until now, we do not have firm evidence to support the claim that the donor molecule remained within the capsule unexposed to the outside during its excited state lifetime. In contrast to this, using coumarin-based phototriggers of the type 4–6, we succeeded in releasing an intermediate resulting from the excited state of the encapsulated guest.^{28–32} This suggested that within the time period of the excited state of the phototrigger, the capsule at least slightly opened to let an intermediate come out. These contrasting observations with smaller (1–3) and larger coumarins (4–6) prompted us to probe the ultrafast solvation dynamics^{33–37} of OA-encapsulated coumarin probes of different sizes to ascertain water accessibility to the interior of the capsule. The expectation was that if the

capsule remains completely closed during the excited state lifetime, there would not be any time-dependent solvation of the encapsulated guest by water molecules. On the other hand, if the capsule remains partially open during the excited state lifetime, the encapsulated guest would be solvated by water molecules and this could be monitored by ultrafast solvation dynamics experiments. Coumarins such as **1–3** are known to show solvent polarity-dependent emission maxima, emission quantum yields, and S1 lifetimes.³⁸ For example, excited **1** in cyclohexane emits fluorescence with a maximum of 395 nm and quantum yield of 0.49. On the other hand, in water, these are 456 nm and 0.055. This trend continues with a number of 7-amino-substituted coumarins.³⁸ This vast difference in emission characteristics between polar and nonpolar solvents has been exploited to monitor the solvent structure and its dynamics around coumarin molecules present in a variety of environments.^{39–49} As mentioned above, based on several photophysical probes, we have concluded that the interior of the OA capsule is dry and there are no water molecules. This suggested that the excited state guest molecules remain firmly locked within the capsule with no access to water molecules. However, with the change in the dipole moment of coumarins upon excitation, their exit from the capsule is a likely possibility. We believed that if the ground-state coumarin is present in a “dry” capsule, the photophysical characteristics would be similar to that of benzene. Upon excitation, if the capsule does not open and the guest stays within, the surroundings of the excited coumarin would be similar to that of the ground-state one. Under such conditions, there would be no change in emission characteristics if there are no water molecules near the excited probe.

This is expected to be the case when the capsule is compact. On the other hand, if the capsule structure is distorted, exposing the guest molecule to the surrounding water, the photophysical characteristics would change from that in benzene to that in water. With this expectation in mind, we performed ultrafast solvation dynamics experiments with the coumarins **1–3** listed in Figure 3.1.1. As mentioned above, the photobehavior of OA-encapsulated **4–6** is different from that of **1–3**. This suggested

that solvation dynamics around these is likely to be different from that around **1–3** in OA. This prompted us to pursue ultrafast solvation dynamics studies of OA-encapsulated **4–6**. An insight into the structure of OA complexes of **1–6** obtained through molecular modeling, including docking and molecular dynamics (MD) simulations, was exceptionally useful in understanding the different solvation dynamics obtained with the two groups of coumarins, smaller **1–3** and larger **4–6**. According to molecular modeling, guests **1–3** are present in a dry capsule, whereas **4–6** are present in a slightly distorted capsule in touch with one or more water molecules.

The complimentary experimental and theoretical approaches employed here have provided a unique understanding of the dynamics of OA-encapsulated excited coumarins, **1–6**, in ultrafast time domain. Results discussed here suggest that the OA capsules with smaller coumarins, **1–3**, as guests that are used as donors in electron-transfer experiments remain tight within the capsule during their lifetime and the ones with larger coumarins, **4–6**, as guests, which are used as phototriggers, keep the guests exposed to increasing number of water molecules during their lifetime.

3.2. Results

According to ^1H NMR study^a, six guests listed in figure 3.1.1 formed 2:1 host–guest complexes with OA in a phosphate or borate buffer. Hydrophobic feebly water-soluble **1–6** formed transparent solutions in the presence of OA at pH ~ 8.9 (borate buffer). Observed upfield shift of N-alkyl group confirmed the inclusion of the above guests within OA (Figure 3.2.1).^{13–15} The ^1H NMR spectra of **4** in the presence of OA are shown in Figure 3.2.2. Lack of changes in the spectra when more than half equivalent of the guest was added to the host in the buffer suggested the ratio of the host to the guest in the capsule to be 2:1 (see Figures 3.2.3 and 3.2.4 for **5** and **6**).

^a A 600 μL of 1 mM OA (in 10 mM $\text{Na}_2\text{B}_4\text{O}_7$ in D_2O , pH = 8.7) solution was placed in an NMR tube. Then 0.25 equivalent increments of guest solution (2.5 μL of a 60 mM solution in $\text{DMSO}-d_6$) were added. After shaking the NMR tube for 5 min, the ^1H NMR spectrum was recorded to confirm the complex formation. The complex formation was monitored by the upfield shift of the aliphatic proton peaks of the guest.

Furthermore, careful ^1H NMR titration experiments supported the above conclusion. Consistent with the capsule formation, the diffusion constants were measured to be closer to $1.35 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (Table 3.2.1 for **5** and **6**). It is known that the diffusion constants of free OA and 1:1 open cavitandplex are 1.88×10^{-6} and $\sim 1.7\text{--}1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.^{14,15} The reduced diffusion constant noted above for **4@OA**₂ is a clear indication of the formation of a capsular assembly rather than an open 1:1 cavitandplex.

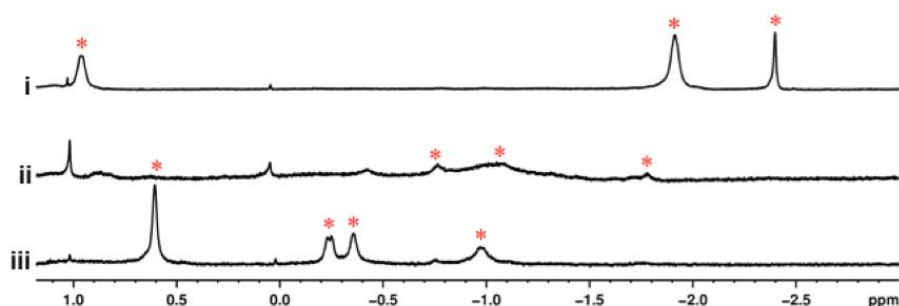


Figure 3.2.1. Selected guest region of the ^1H NMR spectra of complexes [guest@(OA)₂ (2:1)]; (i) **4**, (ii) **5** (iii) **6**. The red asterisk indicates the OA-bound guest aliphatic proton peaks. This experiment was performed by Prof. V Ramamurthy group in University of Miami, USA.

Table 3.2.1. Diffusion constant of OA and complexes. This experiment was performed by Prof. V Ramamurthy group in University of Miami.

Compound	Diffusion constant (cm^2/s)
Only OA	1.88×10^{-6}
4@OA ₂	1.35×10^{-6}
5@OA ₂	1.49×10^{-6}
6@OA ₂	1.52×10^{-6}

Furthermore, as expected for a 2:1 capsule (two OA and one guest molecules), the integrations of the NMR peaks of the host (H_f) and the guest, N-dimethyl protons of the solution, containing no free host or guest were 8:6 (a capsule will have 8 H_f protons). Upon addition of the guest to the OA buffer solution, there were NMR signals only because of the complexed guest which remained constant, independent

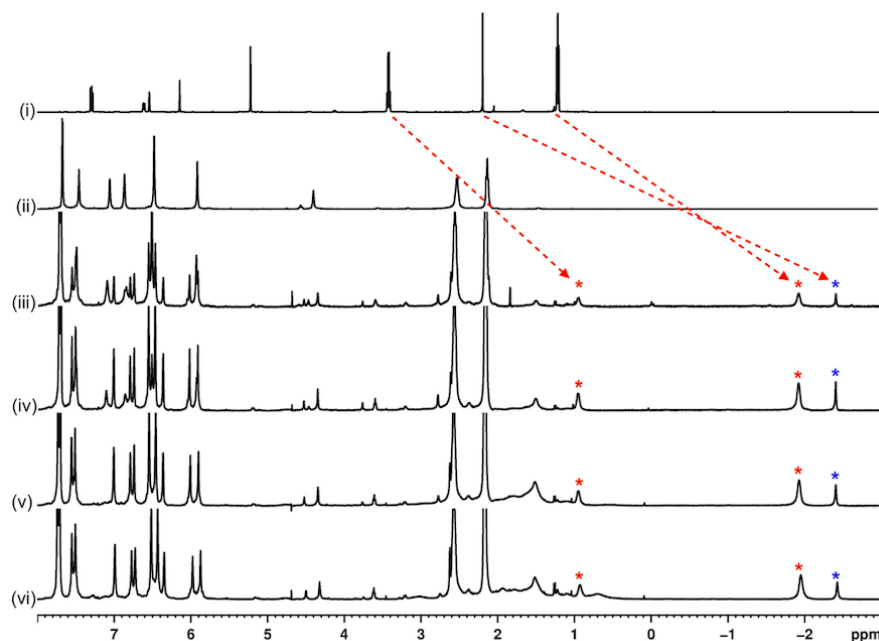


Figure 3.2.2. ^1H -NMR (500 MHz, 10 mM $\text{Na}_2\text{B}_4\text{O}_7$ buffer/ D_2O , pH = 8.7) spectra of (i) **4** in CDCl_3 ; (ii) **1**@OA ([OA] = 1 mM and [**1**] = 0.25 mM); (iii) **4**@OA ([OA] = 1 mM and [**1**] = 0.5 mM); (iv) **4**@OA ([OA] = 1 mM and [**1**] = 0.75 mM); (v) **1**@OA ([OA] = 1 mM and [**1**] = 1.0 mM); “*” indicates the OA bound guest proton peaks, “*” indicates the residual solvent peak (water) of D_2O . This experiment was performed by Prof. V Ramamurthy group in University of Miami.

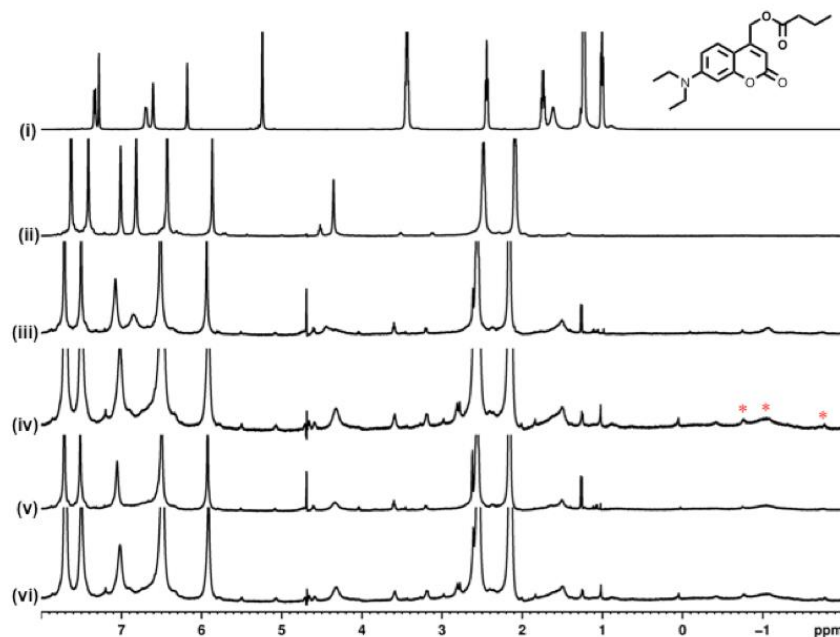


Figure 3.2.3. ^1H -NMR (500 MHz, 10 mM $\text{Na}_2\text{B}_4\text{O}_7$ buffer/ D_2O , pH = 8.7) spectra of (i) **2** in CDCl_3 ; (ii) OA ([OA] = 1 mM); (iii) **5**@OA ([OA] = 1 mM and [**5**] = 0.25 mM); (iv) **5**@OA

([OA] = 1 mM and [5] = 0.5 mM); (v) 5@OA ([OA] = 1 mM and [5] = 0.75 mM); (vi) 5@OA ([OA] = 1 mM and [5] = 1.0 mM); * indicates the OA bound guest proton peaks, ■ indicates the residual solvent peak (water) of D₂O. This experiment was performed by Prof. V Ramamurthy group in University of Miami.

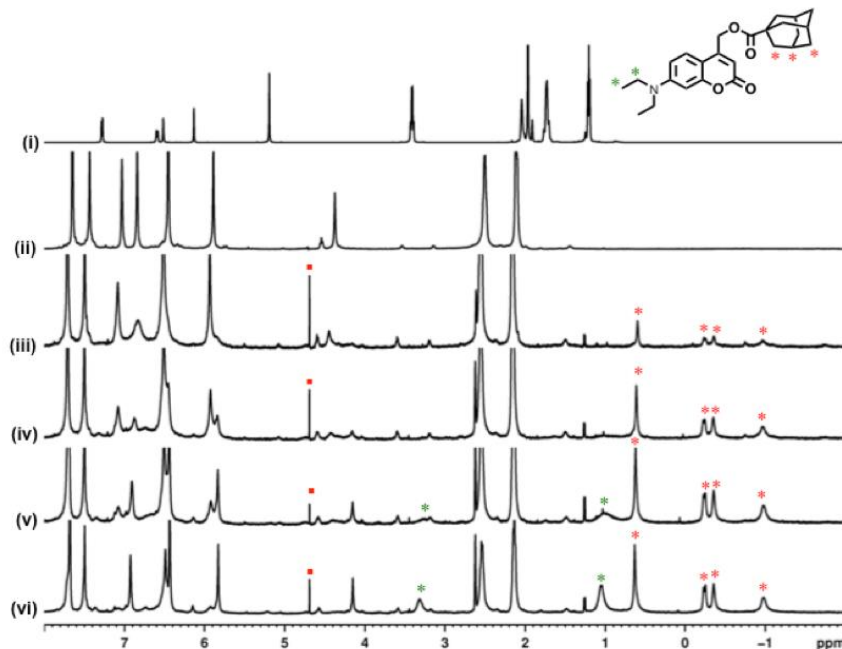


Figure 3.2.4. ¹H-NMR (500 MHz, 10 mM Na₂B₄O₇ buffer/D₂O, pH = 8.7) spectra of (i) **6** in CDCl₃; (ii) OA ([OA] = 1 mM); (iii) **6**@OA ([OA] = 1 mM and [**6**] = 0.25 mM); (iv) **6**@OA ([OA] = 1 mM and [**6**] = 0.5 mM); (v) **6**@OA ([OA] = 1 mM and [**6**] = 0.75 mM); (vi) **6**@OA ([OA] = 1 mM and [**6**] = 1.0 mM); * indicates the OA bound guest proton peaks, “*” indicates the NCH₂CH₃ peaks, ■ indicates the residual solvent peak (water) of D₂O. This experiment was performed by Prof. V Ramamurthy group in University of Miami.

of the amount of the guest present in solution, and only the intensity changed. No signals due to a free guest were seen. This suggested that there was no exchange between the complexed and uncomplexed guest molecules. In the absence of exchange, we could not generate a Job plot to obtain the host–guest ratio. Finally, till now, OA–guest complexes could not be crystallized. This prevented unequivocal confirmation of the host–guest ratio. Inclusion of guests within OA is also revealed by the changes in the emissions spectra upon gradual addition of OA to a buffer solution of **4** (Figure 3.2.5c). It is clear that the emission maximum of 506 nm in water steadily shifted to 451 nm upon addition of OA to the buffer solution of **4** (see

Figure 3.2.6 for **5** and **6**). The latter value is closer to that in benzene (Figure 3.2.5b). A similar observation was also made from the absorption spectra (Figure 3.2.5a). Considering that the polarity of the capsular interior has been inferred to be similar to that of benzene, the observed shift confirmed that upon addition of OA, the guest **4** is included within the OA capsule. Similar shift in the absorption and emission observed for other coumarins used in this study (Figure 3.2.7) confirmed their inclusion within the OA capsule.

Structures of the OA-encapsulated guest molecules **1–6** in water obtained from molecular modeling^b are provided in Figures 3.2.8 and 3.2.9. The difference in the structures between the two sets of molecules, especially in terms of water penetration into the capsule must be noted. In the case of **1–3**, the coumarins are in a dry hydrophobic environment with nearest water molecules being hydrogen bonded to the carboxylates projecting away from the capsule. On the other hand, **4–6** are in a less hydrophobic environment and are bonded to at least one water molecule. In these cases, the capsule is slightly ajar in the middle, the extent being dependent on the bulkiness and size of the guest. The trend is clear; **4** is hydrogen bonded to one molecule, **5** to two molecules, and **6** to at least six molecules of water.

^b The structure of OA was taken from our previous work⁵⁰ and the guest molecules were modeled using GaussView program. Gaussian09 program⁵¹ was used to optimize OA and guest molecules without any geometrical constraint at the B3LYP⁵²/6-31g(d)⁵³ level. Molecular docking was performed to investigate the binding of the guest molecule to the OA using the AutoDock Vina 1.5.6 program.⁵⁴ The size of the grid was chosen to cover the entire cavity of OA and the spacing was kept to 1.00 Å which is a standard value for AutoDock Vina. The docking procedure yielded 20 poses and the structures with the highest scoring function were used for the molecular dynamics (MD) simulations. The GROMACS4.5.6 program⁵⁵ utilizing the AMBER03 force field⁵⁶ was used to perform these simulations of the OA-guest complexes. Antechamber, an inbuilt tool in Amber, was used to calculate the Restrained Electrostatic Potential (RESP) charges and making topology files.⁵⁷ The starting structures were placed in a cubic box with dimensions of 60 × 60 × 60 Å and was filled with TIP3P water molecules.⁵⁸ To neutralize the system some of the water molecules were replaced by Na⁺ ions and the system was energy minimized for 3000 steps. They were used to study the OA-guest interactions through all-atom 100 ns MD simulations. The MD simulations were carried out with a constant number of particles (N), pressure (P), and temperature (T) (NPT ensemble). Electrostatic interactions were calculated using the Particle Mesh Ewald method⁵⁹, and a cutoff at 1.2 nm was used for both van der Waals and Coulombic interactions. The bond lengths and angles of the water molecules were constrained by SETTLE⁶⁰ algorithm and LINCS⁶¹ algorithm was used to constrain the bond lengths of the OA. The MD trajectories were computed for each model with a time step of 2 fs. Cluster analysis was performed to derive the most representative structures of the OA-guest complex. Yasara⁶², Chimera⁶³, and VMD⁶⁴ programs were used for the visualization and preparation of the structural diagrams presented in the current study.

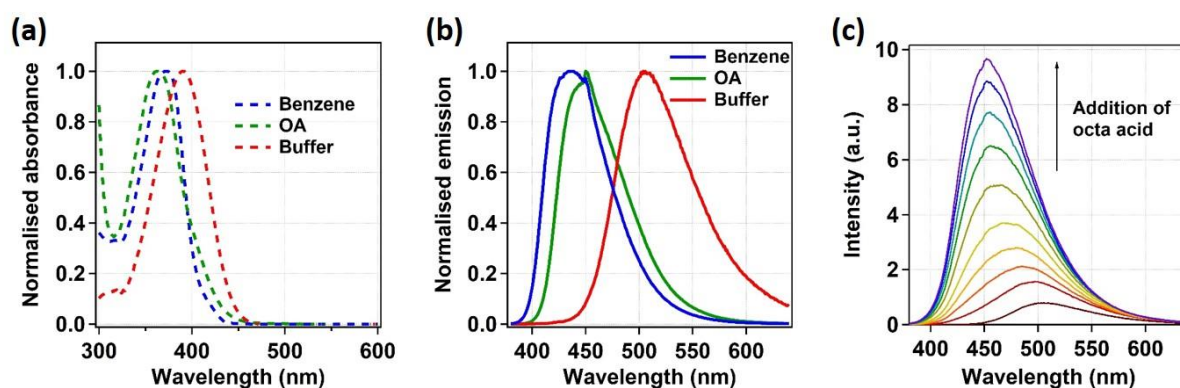


Figure 3.2.5. (a) Normalised absorption spectra and (b) normalized emission spectra of **4** in benzene (purple), **4**@(OA)₂ (green), **4** in buffer (red); ([**4**] = 2.5×10^{-5} M, [OA] = 5×10^{-5} M in phosphate buffer/H₂O, pH = 7.4) and (c) Fluorescence titration spectra ($\lambda_{\text{ex}} = 370$ nm) of **4** with addition of OA

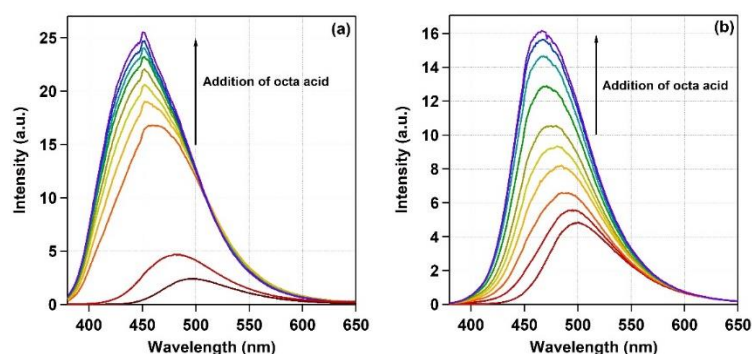


Figure 3.2.6. Fluorescence titration spectra ($\lambda_{\text{ex}} = 370$ nm) of coumaryl esters with addition of OA: (a) **5**; (b) **6**. With incremental addition of OA, the emission maxima shift to shorter wavelength.

Having confirmed by ¹H NMR that **1–6** formed 2:1 capsular assemblies with OA, we proceeded to perform ultrafast time-resolved experiments to probe the change of environment around the guest molecule. In this context, we have carried out both TCSPC and femtosecond fluorescence upconversion experiments to find the average solvation time for all six OA complexes. Results with **4–6** are presented first. We have presented the time-resolved emission spectra (TRES) and representative fluorescent transients measured by TCSPC and upconversion method at some selected wavelengths for **6**@(OA)₂ in Figure 3.10g-i. The same for **4**@(OA)₂ and **5**@(OA)₂ are shown in Figure 3.2.10a-f. TCSPC measurements revealed substantial

dynamic Stokes shift in case of **4**@OA₂. Because similar shift was not observed with **5**@OA₂ and **6**@OA₂ by TCSPC measurements, we undertook the femtosecond fluorescence upconversion study. TRES for all three cases were generated using the fitting parameters of the fluorescence transients. Combined results of upconversion and TCSPC identified the dynamic Stokes shift in these cases. Results of these are displayed in Figures 3.2.10c, f, i. The average solvation time for these three complexes was estimated from the solvent response function, $C(t)$. As shown in Figure 3.2.11, the plot of solvent response function with respect to time fitted into a triexponential function. Table 3.2.2 lists various parameters for **1**–**6** extracted from absorption, emission, and ultrafast time-resolved experiments.

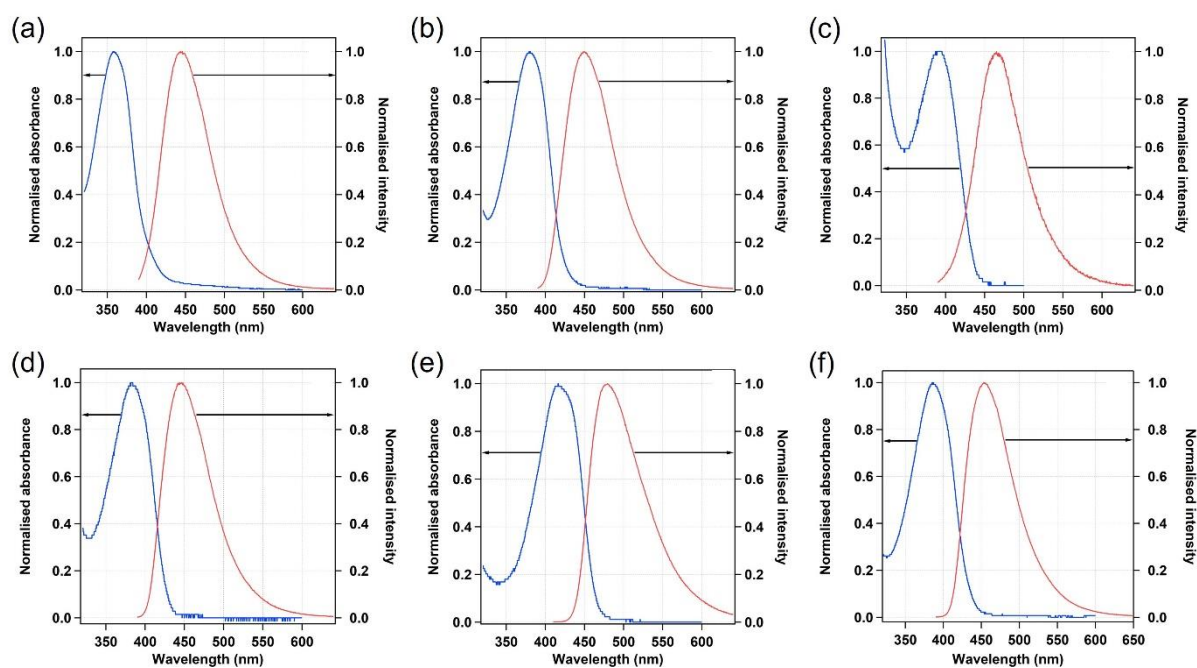


Figure 3.2.7. Steady state absorption and emission spectra of (a) **4**@OA₂, (b) **5**@OA₂, (c) **6**@OA₂, (d) **1**@OA₂, (e) **2**@OA₂ and (f) **3**@OA₂

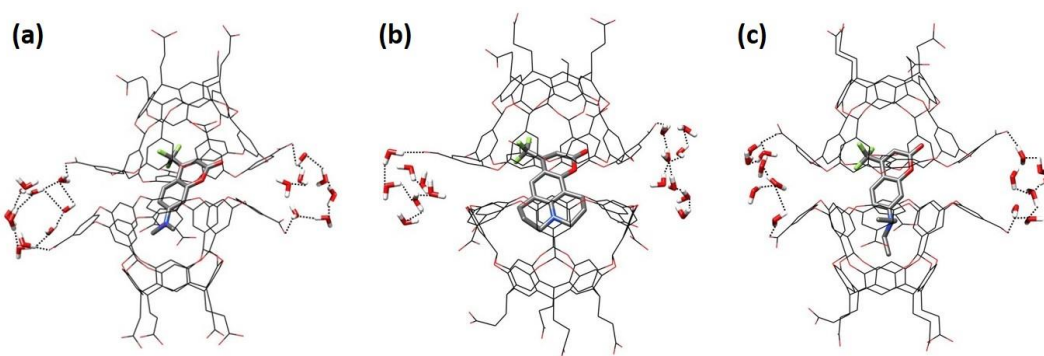


Figure 3.2.8. Molecular dynamics simulated structure for (a) **1@OA₂**, (b) **2@OA₂**, & (c) **3@OA₂** in water. This MD simulations were done by Prof. Rajeev Prabhakar group in University of Miami, USA.

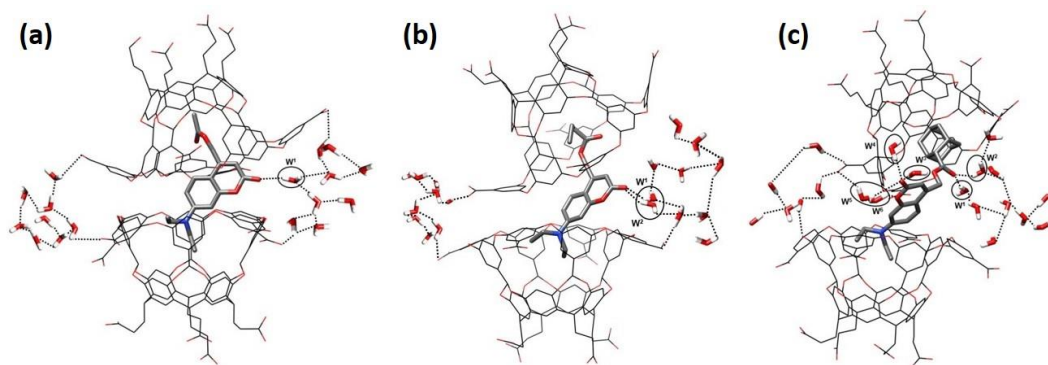


Figure 3.2.9. Molecular dynamics simulated structure for (a) **4@OA₂**, (b) **5@OA₂**, & (c) **6@OA₂** in water. This MD simulations were done by Prof. Rajeev Prabhakar group in University of Miami, USA.

Table 3.2.2. Solvation dynamics parameters for **1-6** encapsulated within OA cavity. (NA stands for not applicable.)

Host-guest complex	$\lambda_{max}^{abs}(\text{nm})$	$\lambda_{max}^{em}(\text{nm})$	$\lambda_{0\text{ ps}}^{em}(\text{nm})$	$\lambda_{3000\text{ ps}}^{em}(\text{nm})$	Observed shift (nm)	Average solvation time (ps)
1@OA₂	384	446	446	446	nil	NA
2@OA₂	416	480	478	480	nil	NA
3@OA₂	385	453	454	453	nil	NA
4@OA₂	359	446	422	446	25	440
5@OA₂	379	450	437	449	12	250
6@OA₂	389	465	454	465	11	144

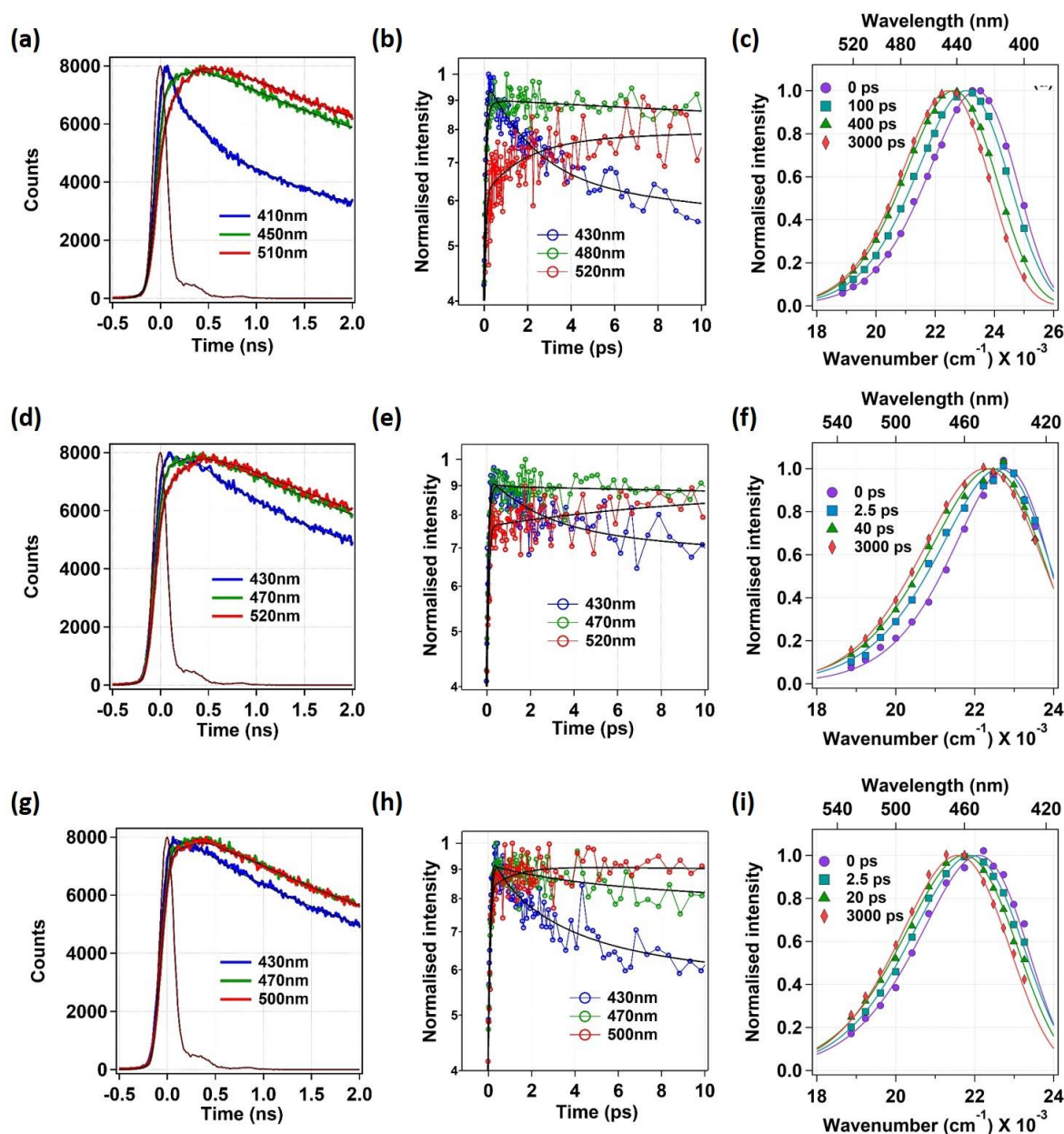


Figure 3.2.10. (a) Representative TCSPC decay profile at some selected wavelengths, (b) representative ultrafast fluorescence transients at some selected wavelengths and (c) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for **4@OA₂**, (d) Representative TCSPC decay profile at some selected wavelengths, (e) representative ultrafast fluorescence transients at some selected wavelengths and (f) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for **5@OA₂**, and (g) Representative TCSPC decay profile at some selected wavelengths, (h) representative ultrafast fluorescence transients at some selected wavelengths and (i) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for **6@OA₂**

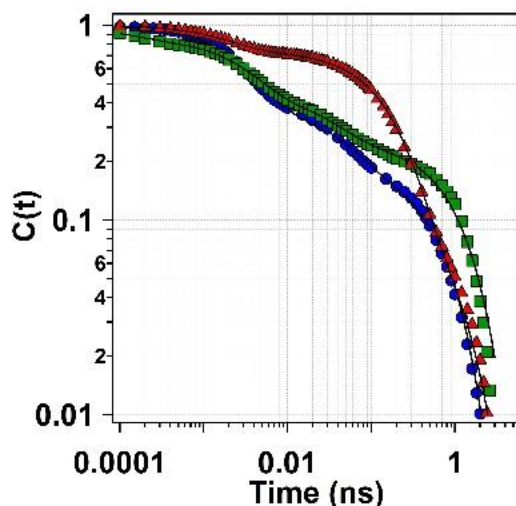


Figure 3.2.11. Variation of Solvent response function with time for **4@OA₂** (red triangle), **5@OA₂** (green square) and **6@OA₂** (purple circle)

This led us to examine the solvation dynamics of **1@OA₂**, **2@OA₂**, and **3@OA₂** that according to molecular modeling remain fully enclosed and away from water molecules. As anticipated, upconversion and TCSPC experiments did not reveal any change in emission spectra as a function of time. TRES and representative fluorescent transients measured by TCSPC and the upconversion method at some selected wavelengths for **3@OA₂** are depicted in Figures 3.2.12g-i, and Figures 3.2.12a-f display the same for **1@OA₂** and **2@OA₂**. The lack of variation of the emission spectra with time is consistent with the conclusion that there are no changes in the environment around enclosed **1–3** during their excited state lifetime.

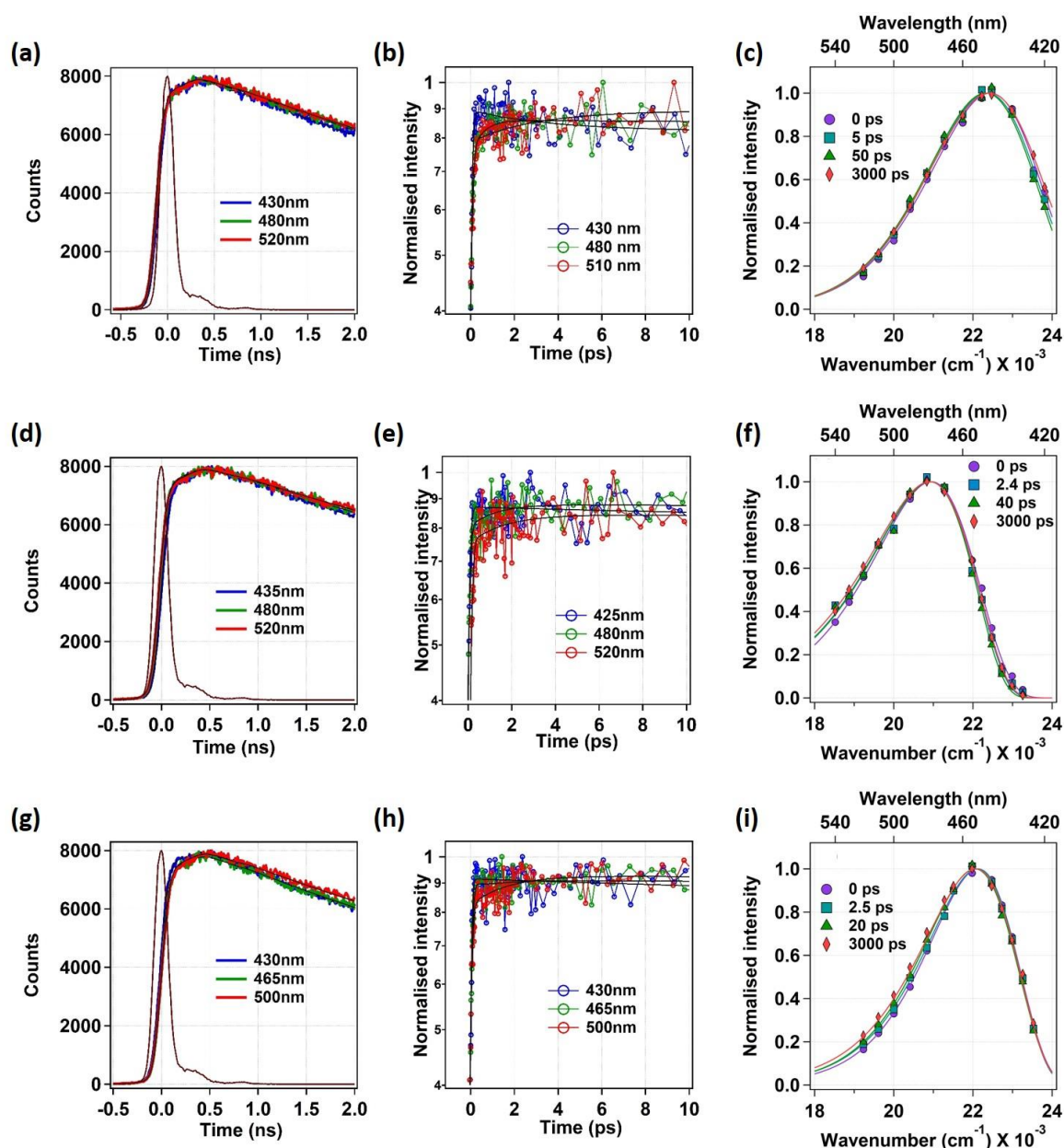


Figure 3.2.12. (a) Representative TCSPC decay profile at some selected wavelengths, (b) representative ultrafast fluorescence transients at some selected wavelengths and (c) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for **1@OA₂**, (d) Representative TCSPC decay profile at some selected wavelengths, (e) representative ultrafast fluorescence transients at some selected wavelengths and (f) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for **2@OA₂**, and (g) Representative TCSPC decay profile at some selected wavelengths, (h) representative ultrafast fluorescence transients at some selected wavelengths and (i) time-resolved emission spectra (TRES) constructed from the combination of femtosecond fluorescence up-conversion and TCSPC method for **3@OA₂**.

3.3. Discussion

As mentioned in the Introduction section, coumarins 1–3 were used as donors in our studies on electron transfer across the capsular wall of OA.^{19–21} To be able to accurately interpret the results, we needed to know whether there is any physical contact between the encapsulated donor and the acceptor present outside the capsule. This led us to obtain the structures of the OA complexes by MD simulation and ultrafast solvation dynamics. In this context, MD simulated structures presented in Figure 3.2.8 and the TCSPC decay profiles, ultrafast fluorescence profiles, and TRES displayed in Figure 3.2.12 are revealing. The structures for **1–3**@OA₂ generated by MD simulations in water share common features: the guest remains aligned vertically along the long axis of the capsule with the hydrophilic carbonyl group away from the median of the capsule. More importantly, there are no water molecules near the guest. The two halves of the capsule appear tightly closed pushing the water molecules to the periphery. This is the equilibrated ground-state structure from where light absorption occurs.

The most important question is whether there are changes following excitation, especially in terms of their immediate environment. Such changes could lead the excited guest to be in contact with the acceptor outside. Data presented in Figure 3.2.12 show that this is not the case. Particularly important spectra to note are the TRES shown in Figure 3.2.12. In none of the three molecules, during the initial 3000 ps time period, is there a shift in the spectra. The emission maxima for **1**, **2**, and **3** immediately upon excitation (0 ps) are 446, 478, and 454 nm. Even after 3000 ps, there is very little shift, 446, 480, and 453 nm, respectively (Table 3.2.2). Given that these coumarins are well known to display solvent polarity-dependent emission maxima, a lack of shift when confined in an OA capsule confirms that the environment around the three coumarins is the same during their excited state lifetime. Comparison of the behavior of **1–3** with **4–6** (discussed below) reinforces the conclusion that the coumarins **1–3** remain within the capsule and are not exposed to water or any other molecules all through their excited state lifetime.

As described in an earlier publication, molecules **4–6** upon excitation release acids (acetic acid, propionic acid, and adamantyl carboxylic acid, respectively) to the aqueous exterior.^{28–32} Excitation of **4–6** leads to α -cleavage leading to two radical intermediates, leaving one inside and extruding the other to the aqueous exterior. Obviously, for this to happen unlike the capsules of **1–3**, that of **4–6** will have to open up at some stage after excitation. If this occurs during the excited state lifetime of **4–6**, the ultrafast solvation dynamics of these molecules must be different from that of **1–3**.

A comparison of Figures 3.2.8 and 3.2.9 reveal that the MD simulated structures of these two sets of complexes are different. The capsules containing **4–6** are slightly distorted and even have a few water molecules seeping into them. The extent of distortion and how many molecules of water interact with the guest depend on the size of the guest. The largest adamantyl-substituted one has at least six molecules of water in contact with the encapsulated guest. Because the parent chromophore in **4–6** is the same, the absorption and emission characteristics are expected to be the same, provided the environment surrounding them is identical. However, the absorption and emission maxima listed in Table 3.2.2 show that this is not the case. Clearly, the microenvironments around **4–6** are not identical, a conclusion consistent with the results of the MD simulations.

We have been able to capture most of the dynamic shift for encapsulated **4** with TCSPC, whereas for **5** and **6**, the TCSPC measurement did not show any significant dynamic Stokes shift. This implies that for **4**, the solvent relaxation process is much slower compared to that in the cases of **5** and **6**. To capture the dynamic Stokes shift in the case of OAencapsulated **5** and **6**, we performed solvation dynamics study in the femtosecond fluorescence upconversion mode. The results obtained are shown in Figure 3.2.10. Important information about the dynamics is provided by the solvation time, which is slow for **4** (440 ps), medium for **5** (250 ps), and relatively fast for **6** (144 ps). The origin of the difference in solvation time, we believe, rests in the initial excited structure within OA that gets solvated and the number of nearby

water molecules. We believe that solvation must start from vertically excited, vibrationally relaxed structures of **4**, **5**, and **6**. Such structures must in reality be closer to the MD simulated ground-state structures shown in Figure 3.2.9. The difference between the two groups of molecules (**1–3** and **4–6**) becomes obvious upon perusal of Figures 3.2.10 and 3.2.12 and upon noting the emission maxima at 0 and 3000 ps time. In the case of **1–3**, the emission maxima are identical at 0 and 3000 ps and the TRES do not change with time (Figure 3.2.12). However, in the case of **4**, **5**, and **6**, there is a significant shift between 0 and 3000 ps: 25, 12, and 11 nm, respectively. The TRES shown in Figure 3.2.10 clearly recorded the shift with time. The above shift suggests that the guest molecules' environment is changing with time.

3.4. Conclusions

In this study, we have focused on bringing out the difference between the two groups of coumarin-based guest molecules. Our interest in these systems arises from their use as electron donors and as phototriggers. We have demonstrated through ultrafast solvation dynamics studies that small coumarins such as **1–3** remain enclosed within the OA capsule with no contact with water molecules during their excited state lifetimes. The second set of coumarins, **4–6** have traditionally been used as phototriggers. Upon inclusion within the OA capsule, these molecules remain in touch with a few molecules of water and upon excitation, there is some dynamics within the capsule which probably facilitates the release of a fragment of the molecule. A comparative ultrafast solvation dynamics investigation of the six molecules has brought out the extent of water inclusion and dynamics of the guest and nearby water molecules, depending on the size and structure of the guest molecules. Detailed understanding of the dynamics of water molecules near the capsule opening and the origin of slow solvation time is likely to provide a better understanding of water structure in confined spaces.

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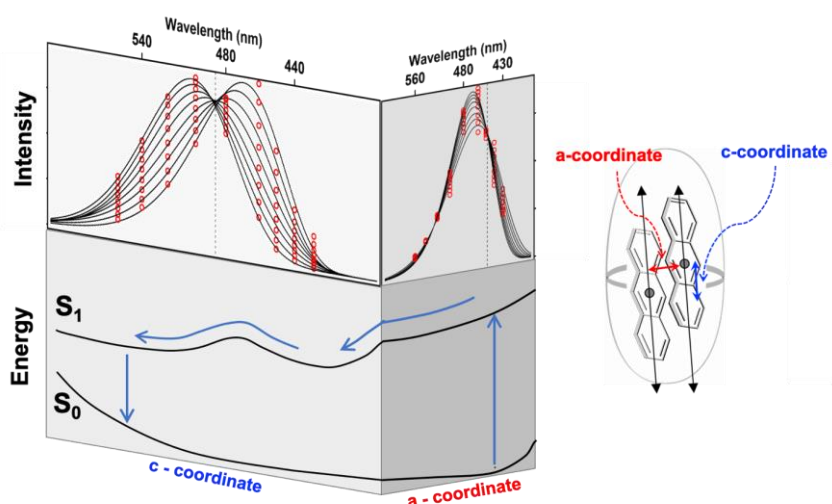
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Chapter 4

Dynamics of Anthracene Excimer Formation within a Water-soluble Nanocavity at Room Temperature



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This work presents the first ever observation of excimer formation dynamics. The observation has been made by successfully nullifying the role of diffusion. As the system, the 2:2 complex between anthracene and octa acid has been used. Time-resolved emission studies revealed two-step dynamics of excimer formation. Theoretical calculations supported the experimental observation.

4.1. Introduction

Anthracene (AN) and pyrene (PY) occupy a special place in the history of the photochemistry¹⁻² and photophysics of aromatic molecules.³⁻⁴ The concepts that currently prevail concerning the excited state chemistry of aromatic molecules could be traced back to these two molecules serving as exemplars in the development of concepts related to excimers and photodimerizations.^{1-2, 5-7} A century ago AN was established to photodimerize with a limiting quantum yield of one in solution at room temperature.¹⁻² On the other hand, PY is known not to photodimerize under any conditions. However, it shows a concentration and temperature dependent emission, in addition to fluorescence and phosphorescence, in solution at room temperature even at 10^{-4} M.³ The intense structureless broad emission with a lifetime of 90 ns initially recorded by Forster and Kasper⁸⁻⁹ is established to originate from excited dimer (excimer). In contrast, AN that photodimerizes from excited singlet state mainly fluoresce and phosphoresce in isotropic solution.³ Recognizing the anomaly between AN and PY, Chandross devised an ingenious method by which excimer emission from anthracene could be recorded at 77 K in an organic glass.¹⁰⁻¹² He generated ‘sandwich’ dimers (two AN molecules placed side by side with long and short axis parallel to each other) via photolytic decomposition of dianthracene (covalent dimer of AN; Figure 4.1.1), which upon excitation gave intense broad emission red shifted with respect to fluorescence. This was attributed to excimer and found to have a long lifetime ($\sim 185\text{--}225$ ns).¹³⁻¹⁶ Following this, Ferguson showed that excimer emission could be recorded in crystalline state as well as in KBr matrix by following the above procedure.¹⁷⁻²⁰ As expected, the excitation spectrum corresponded to the absorption spectrum of AN monomer. While the ‘sandwich’ dimer showed intense excimer emission at 77 K, upon warming the matrix the excimer emission disappeared and the dianthracene was formed with near unit quantum yield at room temperature.²¹ The above observations suggested that excimer is an intermediate en-route to photodimer.

Having recorded excimer emission from PY in solution at room temperature⁶ and knowing the location and shape of the excimer emission spectrum of AN from the work of Chandross and Ferguson,^{10, 19} several workers searched for AN excimer emission in solution at room temperature.²²⁻²⁷ Results have been mixed. An early report suggested the formation of AN excimer (λ_{max} : 520 nm) in glycerol solution at room temperature during triplet-triplet annihilation.²² Next two studies were unable to detect excimer emission but identified it through transient absorption in the IR region (half-life of 3 ns).²³⁻²⁴ Yang and co-workers' recorded emission from at 0.2 M of AN in chloroform at 305 K consisted of a structured (350-470 nm) and a broad (480-600 nm) emissions.²⁵ The broad emission with a lifetime of 1.45 ± 0.22 ns was attributed to excimer. A different group by measuring the rise time of the broad emission (710 ± 30 ps) supported the claim that the weak broad emission is indeed due to excimer.²⁶ Finally, liquid AN, formed by melting crystalline AN, was found to show excimer emission with a lifetime of 0.2 ns and rise time of 100 ps.²⁷ Based on above studies one can conclude that AN excimer emission in solution is very weak (if at all) and has a short lifetime (< 2 ns, compare with lifetime at 77 K > 200 ns).

It is clear from the above studies that to record AN excimer emission in solution three criteria need to be fulfilled: (a) two molecules of anthracene should be pre-organized to be closer, (b) the barrier for dimerization should be increased and (c) temperature of irradiation should be controlled so that the required energy is not available for the excimer to overcome the barrier to reach the dimer. In general, several approaches are employed to enhance excimer emission from aromatic molecules. In crystals of aromatic molecules excimer emission is enhanced by controlling the interplanar π - π distance²⁸⁻²⁹ between two molecules through pressure³⁰ and temperature.³¹⁻³² In solution this is achieved by covalently linking the two aromatic molecules that are involved in excimer formation.³³ While this strategy is effective, one should note that upon functionalization one is no longer dealing with the parent system. An approach that does not involve covalent

functionalization is supramolecular encapsulation where two molecules are brought closer through non-covalent weak interactions. Following the initial report of Forster and Selinger on 2-methyl naphthalene and PY in micelles,³⁴ the literature is replete with examples where excimer emission in various supramolecular assemblies is reported.³⁵⁻⁴⁰ Recognizing the potential of the supramolecular approach one of the current authors' group attempted to record the excimer emission from AN included in conventional organized media such as micelles and cyclodextrins with no success. However, one of the current authors in collaboration with Gibb's group recorded the excimer emission from AN in aqueous solution.⁴¹ This involved the inclusion of AN within the capsule of a synthetic host, octa acid (OA⁴²; Figure 4.1.1). The above publication included NMR characterization of 2:2 host-guest complex and recording steady state emission spectra.⁴¹

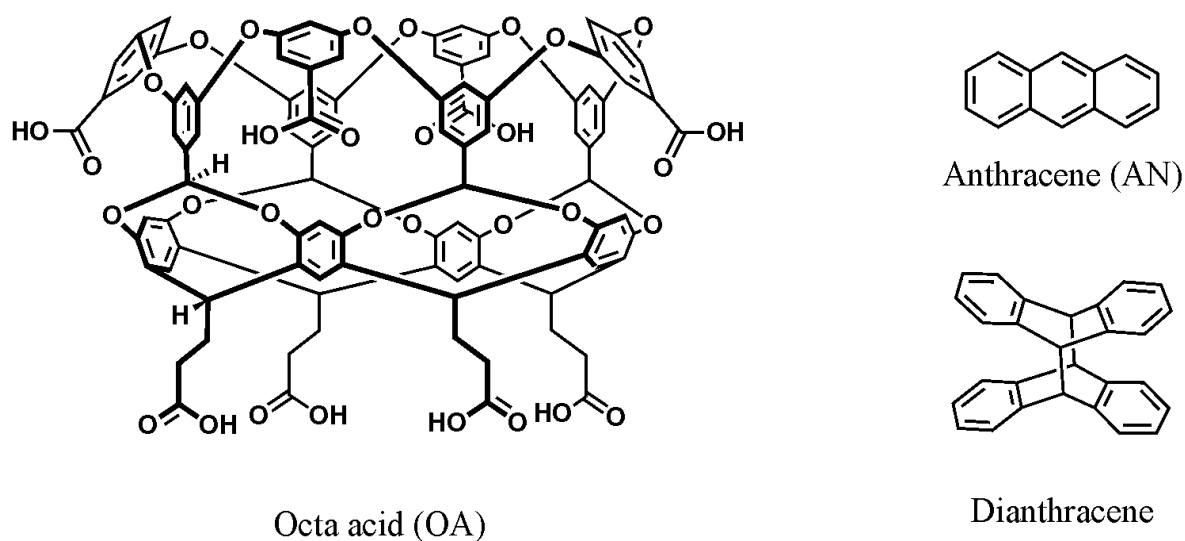


Figure 4.1.1. Structures of host OA, guest anthracene and the dianthracene from which anthracene sandwich dimer is generated.

The current study was undertaken to gain a comprehensive understanding of the dynamics of two AN molecules in the confined space of OA capsule. This study includes confirmation of host-guest complexation by NMR, probing the host-guest structure by molecular dynamics simulation, following the dynamics AN molecules in the excited state by ultrafast time resolved experiments and mapping of the excited

surface through quantum chemical calculations (QM/MM-TDDFT method). Results discussed below make a valuable addition to the fundamental understanding of the excited state dynamics of an exemplar molecule, AN, in a highly confined space. The OA capsule not only enhances the local concentration of AN but also increases the barrier for dimer formation forcing the molecule to show excimer emission. The study reveals that the pathway to excimer is much more tortuous within OA capsule than in an isotropic solution.

4.2. Results and Discussion

4.2.1. Host-Guest Complexation–NMR studies: AN, although only sparingly soluble ($\sim 10^{-6}$ M) gave a clear solution in presence of host OA at 10^{-3} M. Preliminary studies that noted the changes in the signals of both OA and AN hydrogens in the ^1H NMR spectrum established the inclusion of AN within OA.⁴¹ In order to probe the feasibility of forming different types of complexes the NMR spectra at various host-guest concentrations were recorded. (Figure 4.2.1.1). Due to AN's poor solubility in water reverse titration by addition of OA to AN could not be carried out. Figure 4.2.1.1 (i) and (v) display the signals due to OA and 2:2 complex, respectively. As can be seen, the signals due to both OA and AN are significantly altered in Figure 4.2.1.1 (v). Most important is the presence of signals of AN at $\delta \sim 2.95, 3.5, 5.65, 5.9$ and 6.3 ppm (marked in the spectra as # 1-5). Such a remarkable upfield shift from $> \delta 7$ ppm in CDCl_3 to δ between 2.95 and 6.3 in borate buffer due to diamagnetic shielding of the OA cavity confirms the inclusion of AN within OA.⁴¹ The above upfield shifted signals are indeed due to AN hydrogens was confirmed by including perdeuterated AN as the guest. As seen in Figure 4.2.1.1 (vi) while the OA signals remained, that due to AN hydrogens were not seen. Upon carefully examining the spectra displayed in Figure 4.2.1.1 (ii) to (v) one can conclude that AN forms a stable 1:1 stoichiometric complex in presence of one equivalent of OA. Further addition of AN does not result in any changes to the spectra displayed in Figure 4.2.1.1 (v) suggesting that the complex present in Figure 4.2.1.1 (v) does not

undergo further changes. However, at early stages of addition wherein excess OA is present with respect to AN, signals due to 1:2 complex (guest to host) are visible.

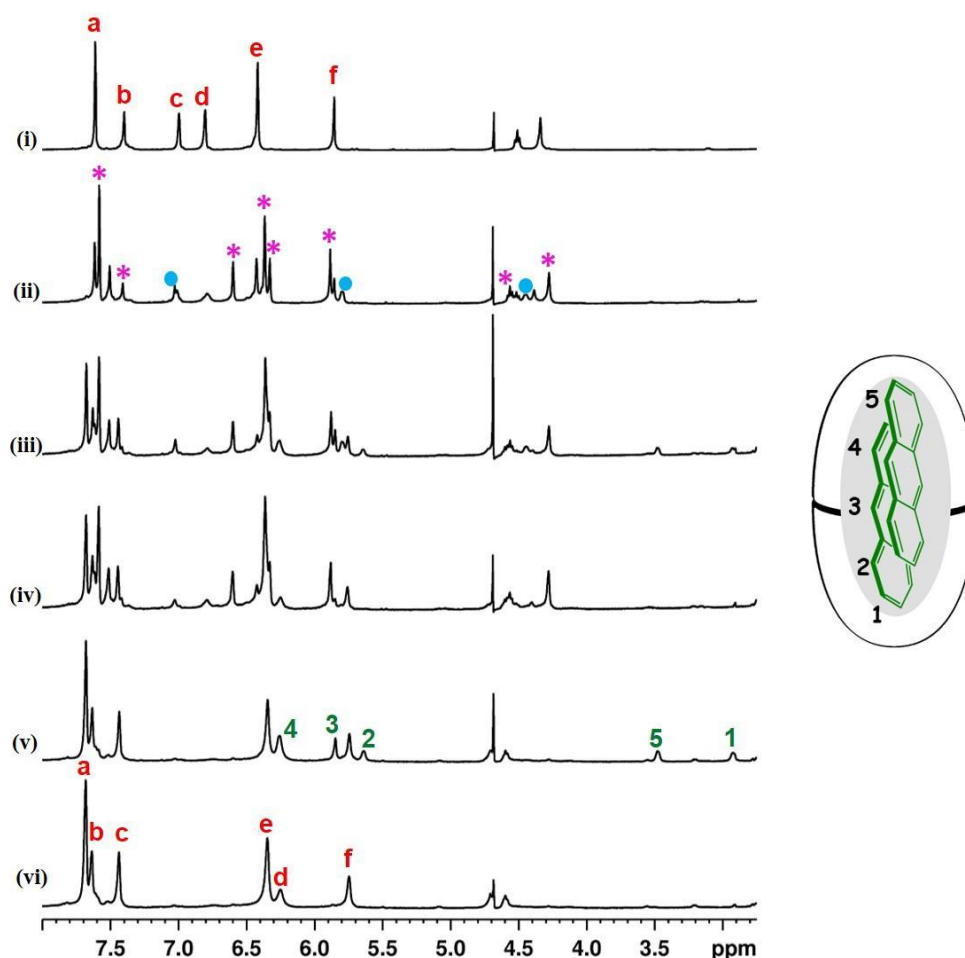


Figure 4.2.1.1. ^1H NMR spectra of AN in octa acid. (i) OA (1 mM in 10 mM buffered D_2O), (ii) OA : AN 10:2, (iii) OA : AN 10:6, (iv) OA : AN- d_{10} 10:6, (v) OA : AN 10:10 and (vi) OA : AN- d_{10} 10:10. (1-5 denotes the AN protons oriented inside OA as 2:2 complex as shown above, red stars denote OA protons of 2:1 complex and blue circles denote the AN protons of 2:1 complex. This experiment was performed by Prof. V. Ramamurthy group in University of Miami, USA.

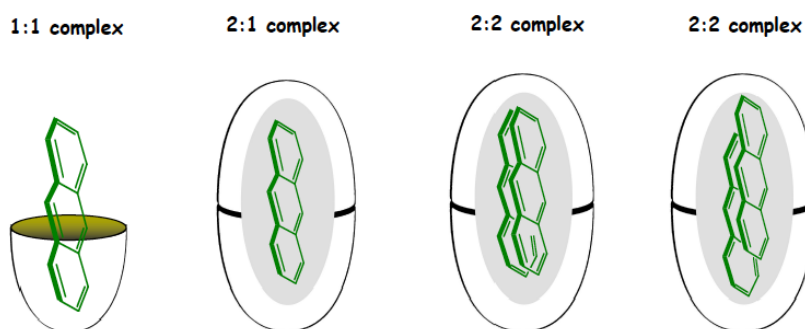


Figure 4.2.1.2. Cartoon representation of possible types of complexes of Anthracene with OA.

For example, in Figure 4.2.1.1 (ii) while the OA signals are significantly altered indicating the complex formation, the five signals due to AN (1:1 complex) are not seen. However, three upfield shifted signals could be identified between δ 4.5 and 7.2 ppm (marked in circles). These we interpret to be due to 1:2 complex (emission spectra discussed later provide clear evidence in favor of this). In Figure 4.2.1.1 (iii), upon further addition of AN to the solution mentioned in Figure 4.2.1.1 (ii), in addition to the above indicated three signals, five signals due to 1:1 complex appeared. Addition of more AN to Figure 4.2.1.1 (iii) results in spectra shown in Figure 4.2.1.1 (v) in which only the five signals due to AN are present. In this the three signals due to 1:2 complex were replaced by signals due to 1:1 complex. We interpret this series of changes in spectra in Figure 4.2.1.1 to the formation of 1:2 (guest to host) complex at early stages of addition of AN to OA (excess OA with respect to AN) and to its transformation to stable 1:1 complex when the solution contains equal amounts of OA and AN are present. Thus, based on ^1H NMR titration spectra we conclude: (a) AN is readily included within OA in borate buffer solution to yield a transparent solution. (b) Addition of AN to OA initially results in 1:2 guest to host complex and depending on the amount of AN present 1:2 and 1:1 complexes exist in equilibrium. (c) Even when more than one equivalent of AN is added, no higher order complexes are formed. A point to note is that 1:1 stoichiometric complex also means 2:2 host-guest complex. But 1:1 and 2:2 complexes represent different types of host to guest complex structures. The former is an open cavitandplex while the latter is a fully closed capsuleplex. Structures of various possible complexes are provided in Figure 4.2.1.2.

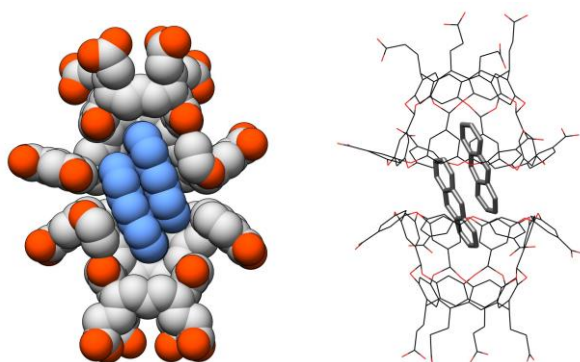
Based on the 1:1 stoichiometry inferred from 1-D NMR spectra three different structures for AN@OA complex could be visualized, 1:1 cavitandplex, 2:2 capsuleplex where two AN molecules are placed directly one above the other (symmetrical sandwich structure) and 2:2 capsuleplex where the two AN molecules

are placed one above the other but slightly slipped along the long axis (slipped sandwich structure, Figure 4.2.1.2). The cavitandplex where half of the AN amework is exposed to water is eliminated based on peak assignments using COSY spectra. In cavitandplex three upfield shifted signals and two with no shift would be expected. The fact that all five signals are upfield shifted rules out the 1:1 cavitandplex structure. Between the two possible 2:2 capsuleplex structures (symmetrical and slipped sandwich), presence of five signals in NMR favors the slipped one. Symmetrical sandwich structure would give rise to an NMR spectrum with only three signals. Slipped sandwich structure is also consistent with the NOESY correlations reported earlier.⁴¹

4.2.2. Host-Guest Complexation–Molecular Modeling: To confirm the proposed structure molecular dynamics (MD) simulations were performed as per the procedure outlined in the experimental section and the results are shown in Figure 4.2.2.1a. Based on NMR spectra and MD simulations we conclude that two molecules of AN are held within OA in a slipped sandwich arrangement. Most likely such an arrangement is favored by π - π stacking between two AN molecules (distance 3.26 Å; Figure 4.2.2.1b).^{28, 30-32} Inclusion of AN within OA is probably facilitated by π - π interaction between AN molecules and aromatic walls of the capsule (3.5 Å) and hydrophobic effect due to aqueous exterior. Perusal of Figure 4.2.2.1a also reveals the lack of free space around the AN molecule. This arrangement hints at the lack of free space around the two AN molecules for any type of reaction. Such a congested arrangement would forbid the photodimerization within the closed capsule. In fact, attempts to include the synthetic dianthracene (Figure 4.1.1), the product of photodimerization, within OA were not successful. Another point to note is that the proposed slipped sandwich structure is not the ideal geometry for excimer formation. Formation of excimer as in organic glass or crystal at 77° K would require the two AN molecules to move a total of ~ 1.9 Å along the

long axis (c-coordinate in Figure 4.2.2.1b) and closer to attain a symmetrical sandwich arrangement in the excited state.

(a)



(b)

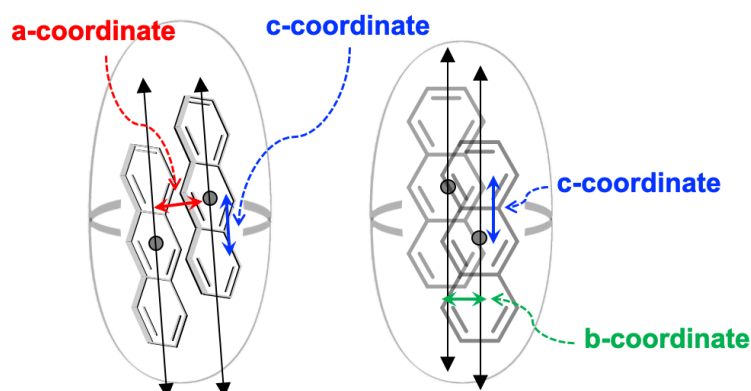


Figure 4.2.2.1. (a) Molecular dynamics (MD) equilibrated structure of the $\text{AN}_2@\text{OA}_2$ complex in space-filling and wire modes. The distance between two AN within the capsule is 3.26 Å. Distance between AN and OA wall is 3.5 Å. The MD simulation was done by Prof. Rajeev Prabhakar group in University of Miami, USA. (b) Two AN molecules are slipped along the c axis by 1.9 Å.

4.2.3. Host-guest Complexation Followed by Emission Spectroscopy: Having inferred from NMR and molecular dynamics calculations that AN forms 2:2 complex with OA, and having realized that titration by addition of OA to AN in

buffer could not be carried out due to solubility problems to unequivocally identify the presence of 1:2 or any other complex by NMR, we performed the titration at much lower concentration and followed the complexation by emission of AN. In Figure 4.2.3.1 the emission spectra of AN upon slow addition of OA (from 0.5 to 50 μM) to a 5 μM solution of AN in borate buffer are displayed.

We believe the initial spectrum is that of AN aggregates suspended in water. The emission intensity of AN in aqueous buffer solution increases monotonously with increasing concentration of AN up to 0.24 μM (Figures 4.2.3.2a and b). Beyond that, AN is no more soluble in aqueous medium, which is evident from the large scattering observed in the absorption spectrum (see Figure 4.2.3.3 for absorption spectrum of 5 μM AN in aqueous buffer). Nevertheless, the emission intensity increases further, with a subtle change in the emission band structure (Figure 4.2.3.2a). Closer inspection reveals that the increase in emission intensity of peak 1 (380 nm) and peak 3 (420 nm) follows the same trend up to ca. 0.2 μM . After that the peak 1 intensity remains almost same, whereas peak 3 intensity increases steadily (Figure 4.2.3.2b). On the basis of these observations, we conclude that beyond 0.24 μM , AN molecule starts to form aggregates in aqueous buffer medium at the room temperature and stays in the medium as suspension. At 5 μM AN, the main contribution to the emission spectrum comes from the AN aggregate suspended in the aqueous buffer medium (Figure 4.2.3.2c).

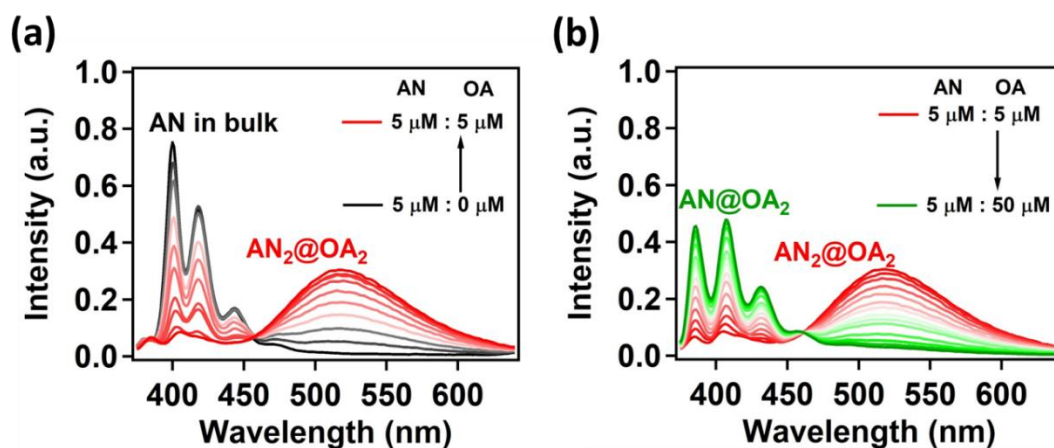


Figure 4.2.3.1. (a) Formation of $\text{AN}_2@\text{OA}_2$ complex (red) from bulk AN (black) followed by (b) formation of $\text{AN}@\text{OA}_2$ complex (green) upon addition of excess octa acid (OA) studied through steady-state emission upon exciting at 375 nm. We observe an equilibrium among AN in bulk water, $\text{AN}@\text{OA}_2$, $\text{AN}_2@\text{OA}_2$ and a particular species can be populated by choosing a desired ratio of AN and OA.

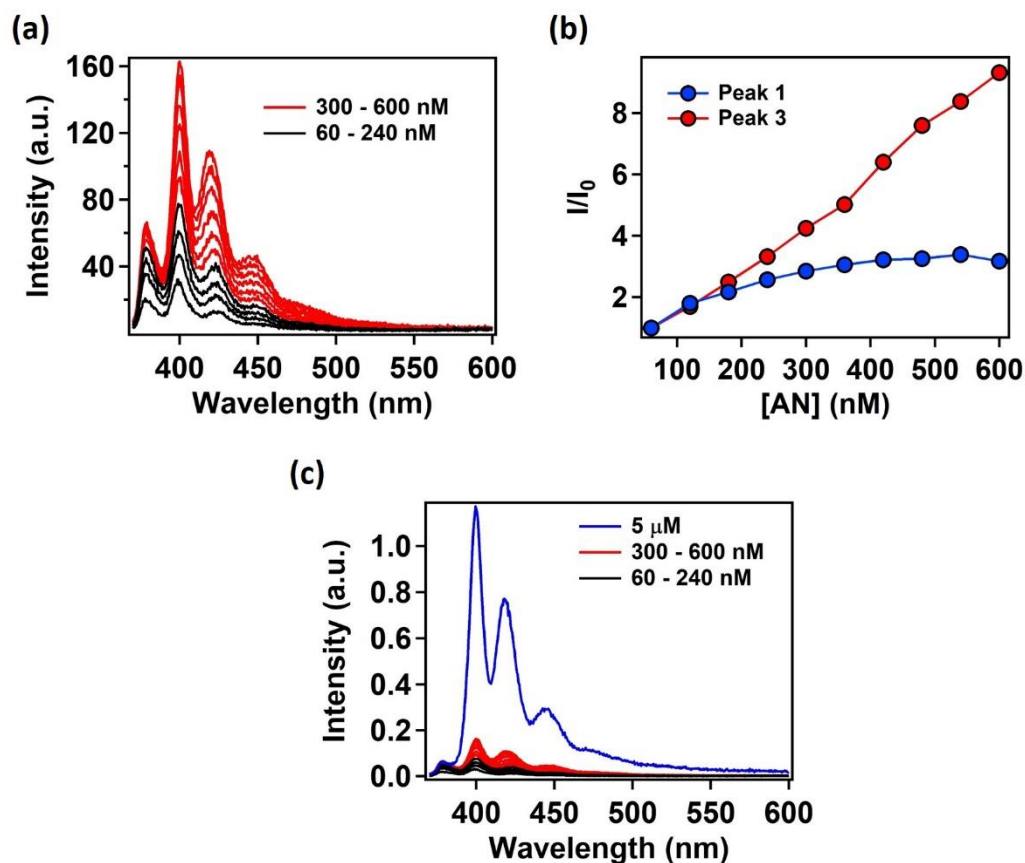


Figure 4.2.3.2. (a) Emission spectra ($\lambda_{ex} = 350$ nm) of AN in aqueous buffer (pH = 7.4) from 60 nM to 600 nM. (b) Plot of I/I_0 vs [AN] where I_0 is the intensity for 60 nM AN. (c) Emission spectrum ($\lambda_{ex} = 350$ nm) of 5 μM AN in aqueous buffer (pH = 7.4) appended with the emission spectra of 60 nM to 600 nM AN in aqueous buffer.

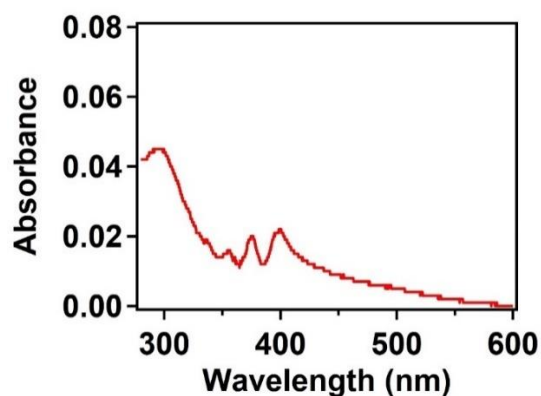


Figure 4.2.3.3. Absorption spectra (pathlength = 1 cm) of 5 μ M AN in aqueous buffer of pH = 7.4

Upon slow addition of OA, the intensity of the fluorescence around 400-420 nm decreased while at the same time a broad emission with a maximum at 520 nm appeared and intensified (follow the red spectra in Figure 4.2.3.1a) and reached a maximum at 5 μ M (1:1 equivalent). At this stage most emissions are broad and resembled the sandwich dimer (excimer) emission at 77 K reported by Chandross and others.^{10,19,43} Further addition of OA did not lead to total elimination of monomer emission but resulted in decrease of the broad emission and increase of monomer fluorescence (follow the green spectra in Figure 4.2.3.1b). Upon addition of 10 equivalents of OA the excimer emission disappeared leaving only the monomer emission. An immediate question arose, whether the final monomer emission (green in Figure 4.2.3.1b) and the one we started with (black in Figure 4.2.3.1a) are the same or different. Close examination of the emission peaks revealed the two are not identical. The excitation spectra of the two were also different (see Figure 4.2.3.4 and related discussion). The observed emission in presence of excess OA is similar to AN emission in benzene (for absorption and emission spectra in solvents see Figures 4.2.3.5). Considering the internal polarity of OA capsule is similar to that of benzene, similarity between the emissions within OA and in benzene is not surprising.⁴⁴ Apparently the monomer emission spectra in water and within OA capsule are not identical. Evidently, when excess OA is present, each AN molecule seeks out a capsule and forms a 1:2 complex. When OA is in short supply a single capsule accommodates two AN molecules. Based on the above titration experiments we believe buffer solutions containing mainly AN@OA₂ and AN₂@OA₂ could be prepared by controlling the amount of OA in solution. The dependence of the nature of the complex on OA concentration cautions one to avoid using more than an equivalent of OA to observe the AN excimer emission.

Careful perusal of Figure 4.2.3.1 reveals that although contribution of the monomer emission could be reduced, it could not be totally eliminated. For any given OA/AN ratio, a distribution between AN in water, AN@OA₂ and AN₂@OA₂

would be expected, thus the observation of monomer emission at all concentrations of AN is not surprising. This rises an important question: Whether the AN molecule present in 2:2 complex is also responsible for the monomer emissions seen in Figure 4.2.3.1. Knowing this, would help us to understand whether the excimer that is seen here is from an excited state complex or excited ground state complex.

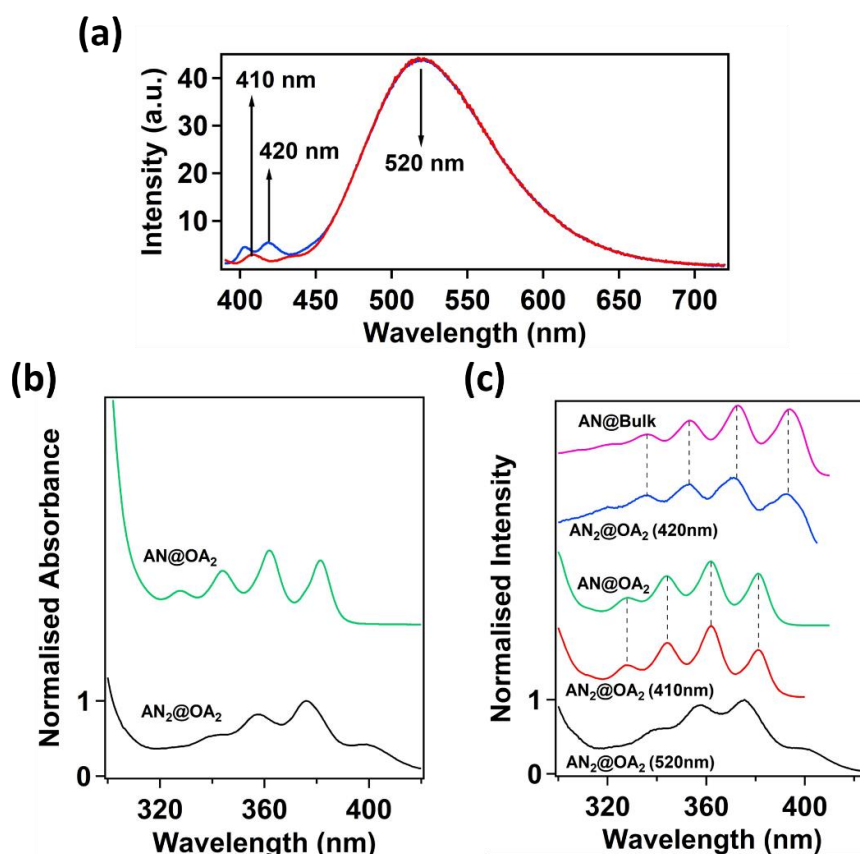


Figure 4.2.3.4. (a) Emission spectra of AN incubated in OA when AN:OA is slightly less than 1:1 (blue solid line) and AN:OA is slightly greater than 1:1 (red solid line). (b) Normalized absorption spectra of AN@OA₂ and AN₂@OA₂. (c) Comparison of the excitation spectra of free AN in bulk, AN@OA₂, monomeric and excimer emission for samples described in (a). For clarity purpose the excitation and absorption spectra were normalized to 1 and baseline offsets are used. Monomeric emission around 400-420 nm region does not come from AN₂@OA₂.

To answer this question two samples that show both monomer and excimer emissions were prepared. Interestingly, a small variation in the OA concentration resulted in change of the nature of the minor emission as seen by its maximum, 420

vs 410 nm in Figure 4.2.3.4 (a). We have included the absorption spectra of AN@OA₂ and AN₂@OA₂ in Figure 4.2.3.4 (b). Here we must state that due to solubility issues we could not record an absorption spectrum of AN monomer in aqueous buffer solution. The difference in the absorption spectra for AN@OA₂ and AN₂@OA₂ suggests that in case of 2:2 complex there is some sort of weak associative interaction present between the two AN in the ground state. In addition, in Figure 4.2.3.4 (c) the excitation spectra for emissions from AN in water as well as from AN@OA₂ and AN₂@OA₂ complexes are shown. The excitation spectra resemble well with the absorption spectra. Perusal of this reveals that the excimer excitation spectrum is distinctly different from those of the emissions from 1:2 complex and AN in water. Also, none of the excitation spectra of the monomer emissions resemble that of the excimer. This rules out the capsules containing two molecules of AN significantly contributing to the monomer emission with either 410 or 420 nm maxima. Further they suggest that excitation of AN₂@OA₂ capsules results mainly in excimer emission. For expanded absorption, excitation, and emission spectra of AN@OA₂ and AN₂@OA₂ complexes see Figure 4.2.3.6.

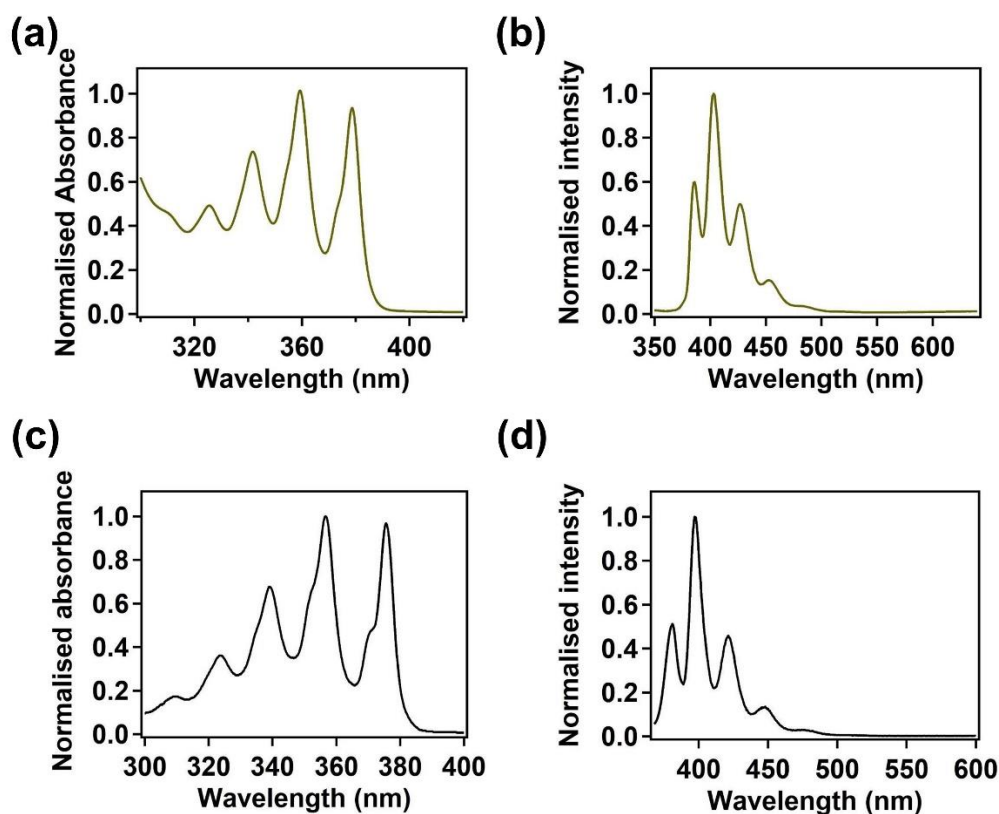


Figure 4.2.3.5. (a & b) Absorption and emission spectra ($\lambda_{exc} = 330 \text{ nm}$) of AN in benzene. (c & d) Absorption and emission spectra ($\lambda_{exc} = 350 \text{ nm}$) of AN in cyclohexane.

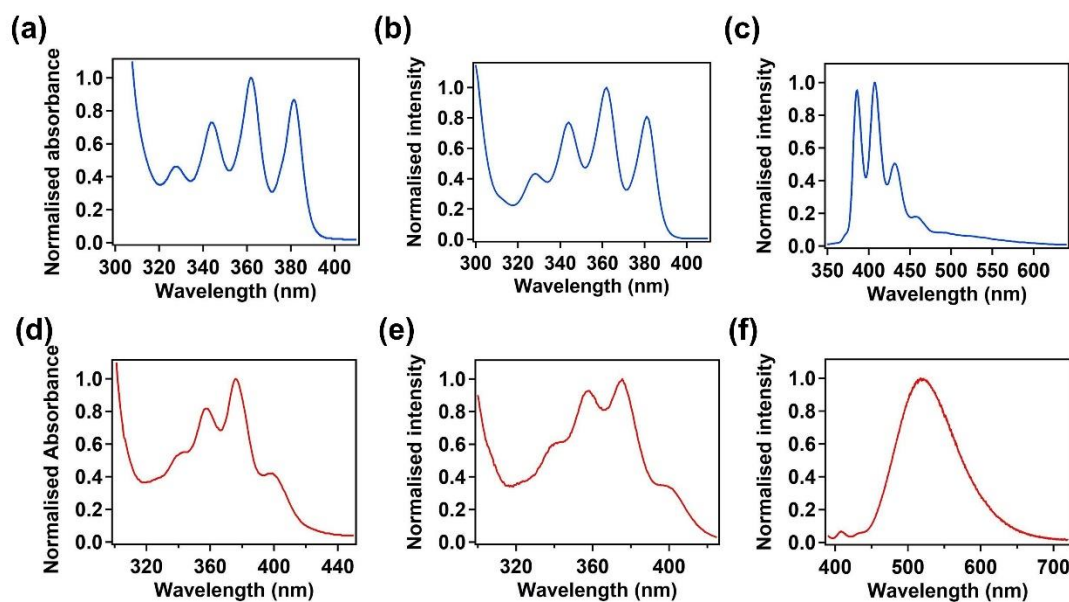


Figure 4.2.3.6. (a, b, c) Absorption, excitation ($\lambda_{em} = 410 \text{ nm}$), and emission ($\lambda_{exc} = 330 \text{ nm}$) spectra of AN@OA₂. (d, e, f) Absorption, excitation ($\lambda_{em} = 520 \text{ nm}$), and emission ($\lambda_{exc} = 375 \text{ nm}$) spectra of AN₂@OA₂.

Having established a procedure to generate AN excimer in solution at room temperature we were curious to compare its lifetime with the early reports that claimed to have recoded the excimer emission in solution at room temperature. Fluorescence transients of AN in cyclohexane, AN@OA₂ and AN₂@OA₂ under aerated conditions are shown in Figure 4.2.3.7. Lifetimes extracted from these decays are tabulated in Table 4.2.3.1. The long lifetime of 235 ns for emission with 520 nm maximum is closer to the values reported for sandwich dimers at 77 K (>200 ns)^{13-15, 20} and far away from the value reported for very weakly emissive excimer in solution at room temperature (<2 ns).²³⁻²⁵ The long lifetime suggests that the excimer experiences significant constraint within the capsule as in crystals and glassy matrix at 77 K.

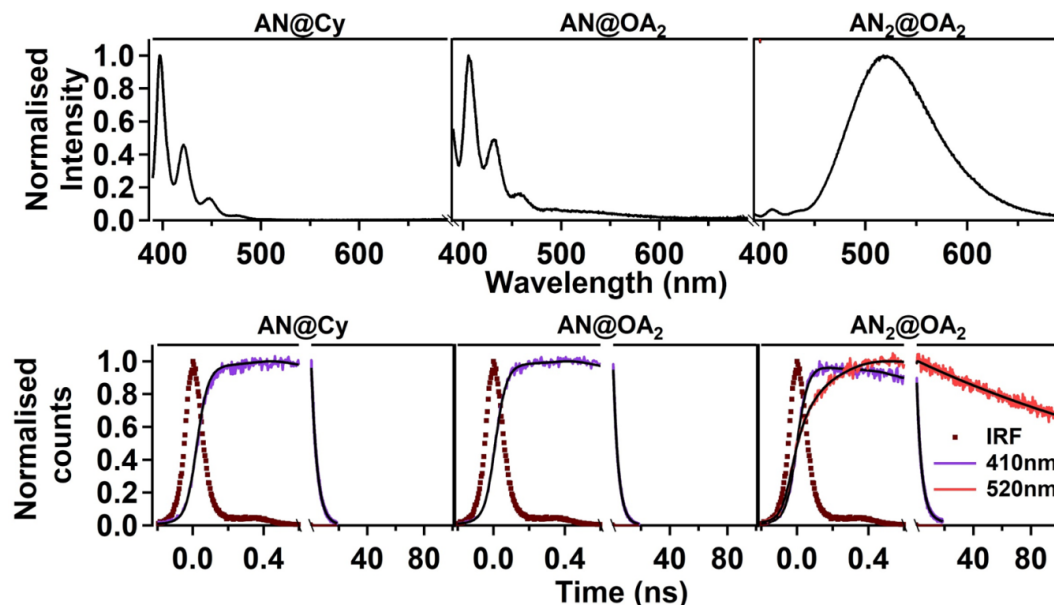


Figure 4.2.3.7. (Top) Emission spectra ($\lambda_{exc} = 375 \text{ nm}$) and (Bottom) fluorescent transient ($\lambda_{exc} = 375 \text{ nm}$) of AN in cyclohexane, AN in 1:2 complex and AN in 2:2 complex respectively.

Table 4.2.3.1. The average fluorescence lifetime of anthracene in bulk and in 1:2 and 2:2 complexes in aqueous buffer medium under aerated conditions.

Species	Wavelength (nm)	τ_{avg} (ns)
AN in cyclohexane	410	4.0
AN@OA ₂	410	3.6
AN ₂ @OA ₂	410	5.9
	520	235

4.2.4. Time-resolved Emission Experiments: Usually the excimer formation in isotropic solution medium is controlled by diffusion. In this respect, our system is quite unique like the sandwich dimer pre-prepared in crystals and organic glass at 77 K. Two monomers of AN being held together in close proximity inside the OA cavity nullifies the need for the two molecules to diffuse towards each other. This arrangement is ideal to investigate the dynamics of excimer formation excluding the first step of diffusion. Based on the structure shown in Figure 4.2.2.1a we realized

that at least two distinct motions are required to attain the favorable geometry for excimer formation. The two AN molecules must move closer (a-axis in Figure 4.2.2.1b) and slip along both b and c-axes to be fully on top of each other to attain total π - π overlap. Time-resolved experiments were performed to gain an insight into the nature of movements the AN*–AN pair within the confined space of OA to reach the above geometry.

We recorded fluorescence transients throughout the whole range of the broad band emission of AN₂@OA₂. Presence of a delay in the excimer emission build up (Figure 4.2.4.1a) confirms that only one of the two AN is excited and it reaches out for another ground state AN to form the excimer. As seen in Figure 4.2.4.1b, immediately upon excitation only monomer type emission dominates (violet and greenish blue lines) and with time excimer emission builds up. This is consistent with the conventional monomer-excimer buildup often displayed in textbooks.⁵ The most unusual feature of the time resolved spectra shown in Figure 4.2.4.1b is the maximum of broad excimer emission shifting with time. Such a behavior is not known in solution during excimer formation of any aromatic molecules. This we believe is an indication of the difference in the nature of the excited state surface connecting monomer and excimer within OA capsule and isotropic solution. To examine this further we analyzed mainly the excimer emission. The 400-420 nm region has been excluded from the analysis as contribution for this emission also comes from 1:2 complex and free monomer in solution (Figure 4.2.3.2 and Figure 4.2.3.4). Construction of time-resolved emission spectra (TRES) reveals a gradual shift of emission maxima from 458 nm to 520 nm with time (Figure 4.2.4.1c). One important point to note is that the time zero spectra (458 nm) is much red shifted and broad compared to the monomeric emission in bulk and 1:2 complex (410 nm maximum). The broadness suggests that the emission must involve two molecules interacting with one another. If it is due to a single molecule, one would expect it to be structured. Perhaps the very short distance between the two monomers trapped inside the capsule is the reason behind this feature.

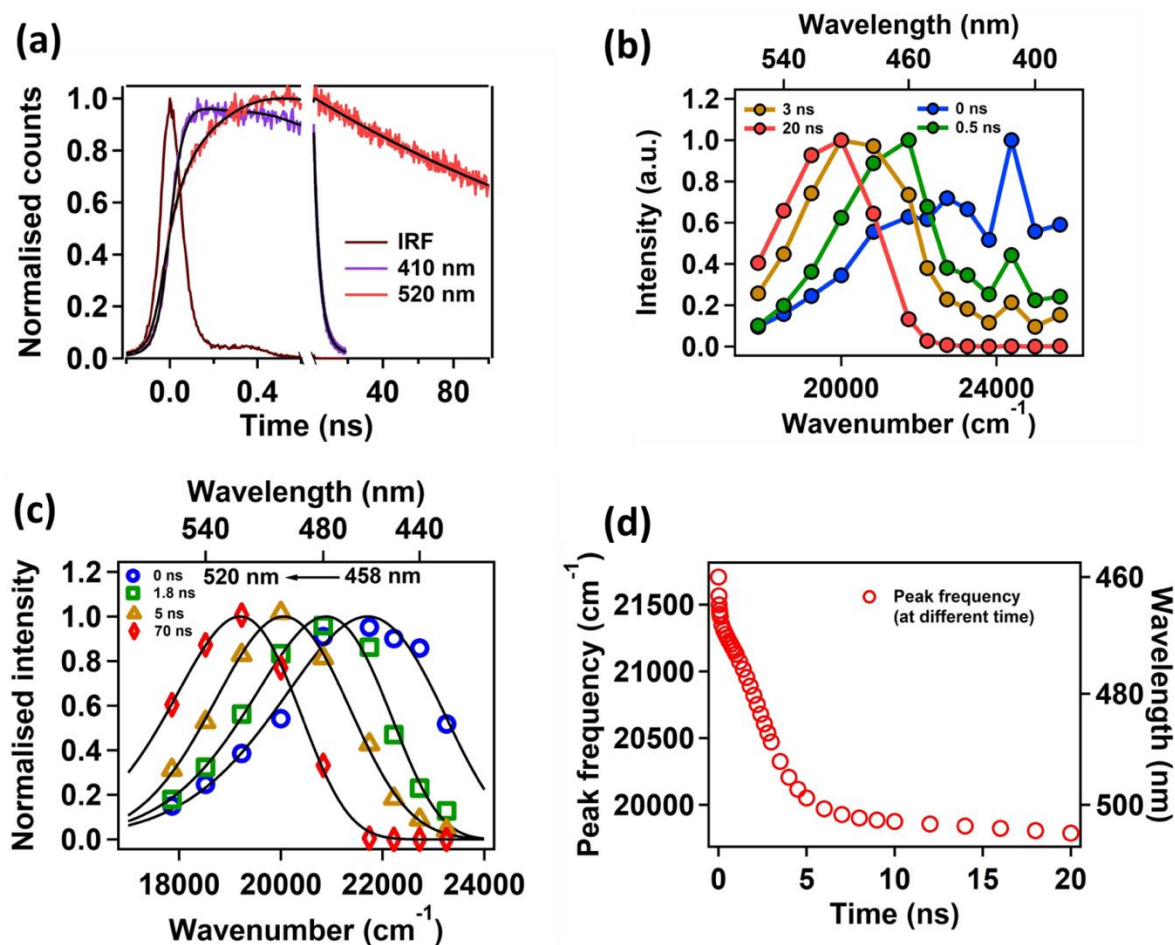


Figure 4.2.4.1. (a) Fluorescence transients of $\text{AN}_2\text{@OA}_2$ complex upon exciting at 375 nm. Multiexponential fitted lines to the transients are displayed in black. Fluorescence transient at 520 nm has a rise component. (b) Representative time resolved emission spectra, TRES, (blue: 0 ns; green: 0.5 ns; yellow: 3 ns; red: 20 ns) constructed from the fitting parameters of fluorescent transients at different wavelength along the steady state emission spectra (390-560 nm). (c) Some representative TRES in the excimer region (blue circles: 0 ns; green squares: 1.8 ns; yellow triangles: 5 ns; red diamonds: 70 ns) fitted to lognormal function (solid black lines). In this case we have excluded the wavelength region 390-420 nm which is mainly contributed by AN@OA_2 and free AN in bulk. We found that the excimer emission shifts to longer wavelength with time. (d) Variation of emission peak-frequency with time, which is not monotonous and suggests involvement of more than one step in the excimer formation process.

Appearance of excimers with different emission maxima suggests that the excited state surface must be shallow and the motion slow. Apparently, the radiative transition is able to compete with forward motion towards the stable excimer structure. Surprisingly the peak frequency vs time plot (Figure 4.2.4.1d) reveals that the shift of emission is not monotonous. This unusual behavior of variation of peak

frequency with time suggests that transformation of monomer to excimer on excited state surface may involve more than one step.

To probe this likelihood, time-resolved area normalized emission spectra (TRANES) were generated (Figure 4.2.4.2).⁴⁵⁻⁴⁷ Two isoemissive points were identified in the TRANES at two different wavelengths at two different time windows (see Figures 4.2.4.2a and 4.2.4.2c). This is a clear indication of a two-step process involving three states. From $t = 0$ to 0.1 ns time range the first isoemissive point appear at 448 nm. The second isoemissive point is at 487 nm in the time window of $t = 0.1$ ns to 16 ns. In order to determine the rate constant of the first step we plotted the ratio of the intensity of the peak at $t = 0$ ns to the intensity of the peak at $t = 0.1$ ns with time. From its exponential fitting we estimated the time constant of the first step to be 0.06 ns (Figure 4.2.4.2b). A similar approach was taken to determine the rate constant of the second step. Exponential fit to the intensity ratio against time plot gave the time constant as 2.65 ns (Figure 4.2.4.2d), which is indeed a much slower process compared to step 1. Based on the above observations a model shown in Figure 4.2.4.3 is proposed. As per this model, AN* soon after its generation interacts with the close-by ground state AN molecule and both molecules together start their journey from 'M' to 'O' via 'N'. A possible barrier from 'N' to 'O' is indicated in the Figure 4.2.4.3. In conclusion, encapsulation of two monomeric AN inside OA cavity nullifies the effect of diffusion in the excimer formation dynamics which enables us to look into the molecular dynamics prior to the excimer formation. We find the excimer formation to be a two-step process. The first step is barrierless while the second step has a barrier.

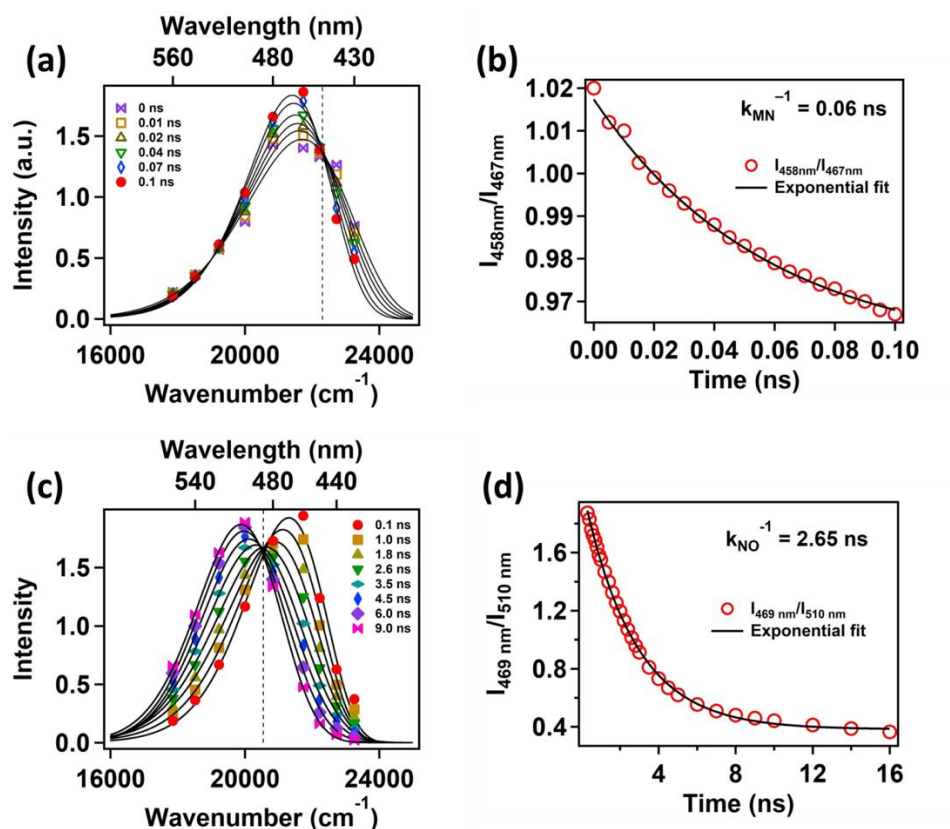


Figure 4.2.4.2. (a and c) TRANES showing the isoemissive point at different wavenumber at different time. Two different isoemissive points indicate the overall process of energy relaxation occurs through two different steps. (b and d) Time evolution of the ratio of the intensity of the initial state and the final state for each of these two steps. They were fitted exponentially. Fitted line is given in black. Presence of two isoemissive points at different wavelength at different time windows suggests a two-step process involving three states. The first step is ultrafast with time constant 0.06 ns and the second step is slow with a time constant of 2.65 ns.

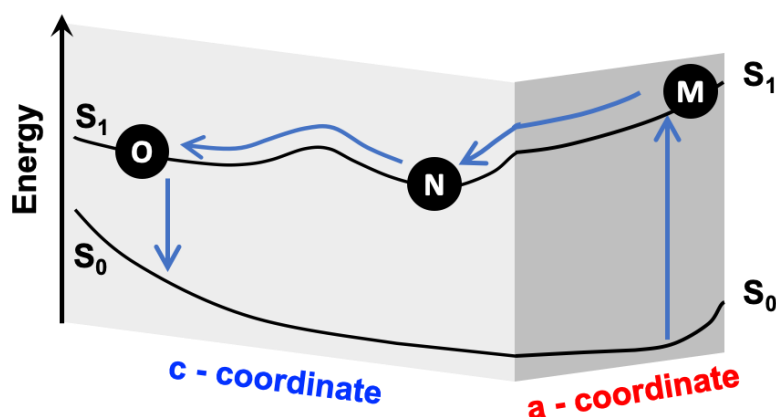


Figure 4.2.4.3. Kinetic model based on the result of TRES and the theoretically calculated PES.

4.2.5. Temperature Effect on Excimer Emission: To check the presence of energy barrier as per the model shown in Figure 4.2.4.3, we recorded emission spectra of AN₂@OA₂ from 278 to 343 K. The result obtained are displayed in figure 4.2.5.1. The excimer emission gradually decreased with increase in temperature. Though this result does not support our proposed model, such a result is not a surprise. Interestingly, after a close inspection of the results we conclude that it is not at all surprising. It has been previously reported that an increase in temperature well below the room temperature facilitates the excimer formation and the intensity of excimer emission (I_E) increases with a decrease in monomer emission intensity (I_M) but in the higher temperature range an increase in temperature decreases the excimer emission due to thermal decomposition¹⁻⁴. For example in case of pyrene depending upon the solvent the high temperature from where the excimer emission starts to decrease can vary from ~ 0 °C to ~ 40 °C.¹ In that case the $\ln \frac{I_E}{I_M}$ vs $\frac{1}{T}$ plot in the low-temperature region yields a straight line with a negative slope, $(-\frac{E_a}{k})$, which gives the activation energy (E_a) of excimer formation and in high-temperature region the plot yields a straight line with positive slope $(\frac{E_B}{k})$ that gives us the binding energy (E_B) of the excimer¹⁻⁴. In our case, we were unable to conduct experiment below 5°C due to experimental difficulties. With increasing temperature, the 520 nm emission decreases with increase in the intensity of the emission around 400-420 nm. Thus a plot of $\ln \frac{I_E}{I_M}$ vs $\frac{1}{T}$ in our case only has positive slopes. The interesting observation here is that it does not have one positive slope but two different slopes in two different temperature range. In the temperature range above room temperature, it has a larger slope whereas in the region below room temperature it has a much smaller slope. In this context this is to emphasize that here we need to consider two different types of bindings, one is the excimer, and the other is the 2:2 guest-host complex. As we have already discussed that the 400-420 nm emission comes from monomeric AN in bulk or 1:2 complex, a significant increase in the emission in that range indicates toward the thermal decomposition of the 2:2 complex. The AN₂@OA₂

complex is supposed to have larger binding energy with respect to the excimer inside it.

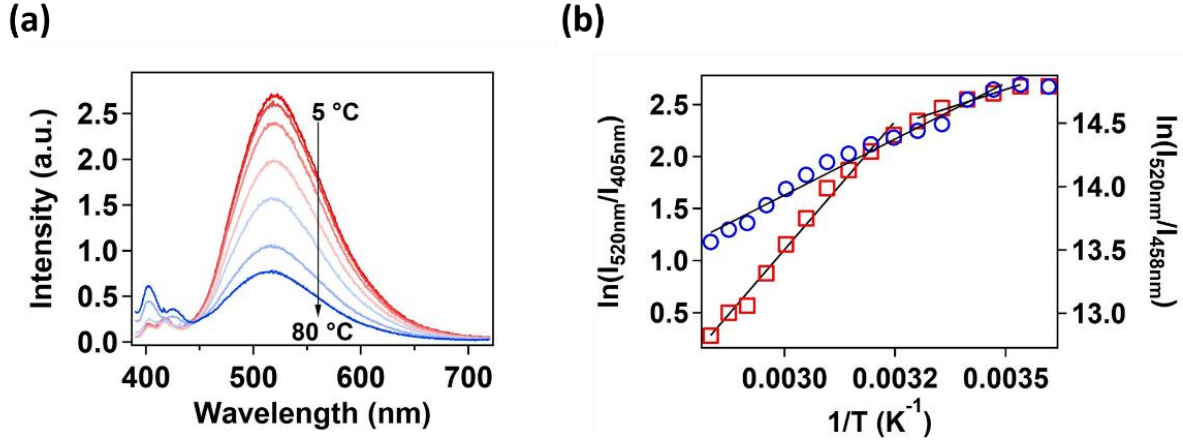


Figure 4.2.5.1. (a) Temperature-dependent emission spectra of AN₂@OA₂ (b) plot of $\ln \frac{I_{520nm}}{I_{405nm}}$ vs $\frac{1}{T}$ (red squares) and $\ln \frac{I_{520nm}}{I_{458nm}}$ vs $\frac{1}{T}$ (blue circles). Fitted lines are in black.

Thus, we assign that upon an increase in temperature initially the excimer decomposes leading to the straight line with a smaller slope and afterward at a higher temperature the whole 2:2 complex starts to decompose giving rise to the larger slope region in the $\ln \frac{I_E}{I_M}$ vs $\frac{1}{T}$ plot. From the initial slope, we have calculated the binding energy of the excimer as 1.91×10^{-20} J and from the second slope we calculated the binding energy of the AN₂@OA₂ complex as 6.81×10^{-20} J. From the TRES we know that the time zero spectra before the excimer formation is at 458 nm. We have done a similar analysis as the previous one. The only difference is that in this case, we used the intensity at 458 nm as the I_M . If the temperature change does not have any effect on the excimer binding as if the decrease in 520 nm emission intensity was solely due to breakage of the 2:2 complex, $\ln \frac{I_E}{I_M}$ should be invariable with $\frac{1}{T}$. But that is not the case. We obtained a straight line with a positive slope from which the binding energy of the excimer is estimated to be 2.44×10^{-20} J which is very similar to the value obtained from the previous analysis (1.91×10^{-20} J).

Furthermore, in isotropic solution, where the excited monomer–excimer equilibrium is established in the excited surface, the excimer shows a bimodal temperature dependence.^{9, 48-50} In one region the excimer emission increases and in the other it decreases with temperature. Thus, a wide temperature range is required to verify the temperature effect on excimer formation. However, since the stability of host-guest assemblies depends on the temperature we were unable to verify the model by monitoring the excimer emission intensity with respect to temperature. This prompted us to obtain an insight into the temperature effect on excimer formation by quantum chemical calculations. Results of this approach are discussed in a later section.

4.2.6. Photoinduced Electron Transfer against Excimer Formation: The above model as well as the presence of a rise time for excimer emission (Figure 4.2.4.1a) suggest that AN* has a transient existence before interacting with the adjacent ground state AN. If this is true it should be possible to quench it with an external quencher such as MV²⁺ before the start of the excimer emission. In Figure 4.2.6.1(c) steady state emission spectra of AN in 2:2 complex in presence of methylviologen²⁺ (MV²⁺) are displayed. Weak monomer and strong excimer emissions are seen. Upon incremental addition of MV²⁺ the intensities of both emissions (410 nm and 520 nm) decreased indicating quenching by MV²⁺ (see Figure 4.2.6.1 (c)). On the other hand, lifetimes of the monomer and excimer emissions are not significantly influenced by MV²⁺ (Figure 4.2.6.1 (a) & (b)). The Stern-Volmer plots shown in Figure 4.2.6.1 (d) by monitoring the emission intensity and excited state lifetime suggest that in ns time range the quenching is static in origin. In order to measure the rate constant of quenching we recorded the transient absorption spectra of the AN@OA₂ and AN₂@OA₂ following the addition of MV²⁺ by employing a fs transient absorption spectrometer. In the TA spectra for both the cases (Figure 4.2.6.2 (a) & (c)), we observe a positive signal developing around 615 nm, which is an indication of the formation of methyl viologen radical cation (MV^{•+}) as a product of photoinduced electron transfer (PET).⁴³ Time constant of formation of MV^{•+} is the rise component

obtained from fitting of the kinetics at 615 nm and gives the actual rate constant of PET (Figure 4.2.6.2 (b) and (d)). These rate constants of PET for AN@OA₂ and AN₂@OA₂ are measured as 0.196 and 0.189 ps⁻¹, respectively, which are nearly the same.

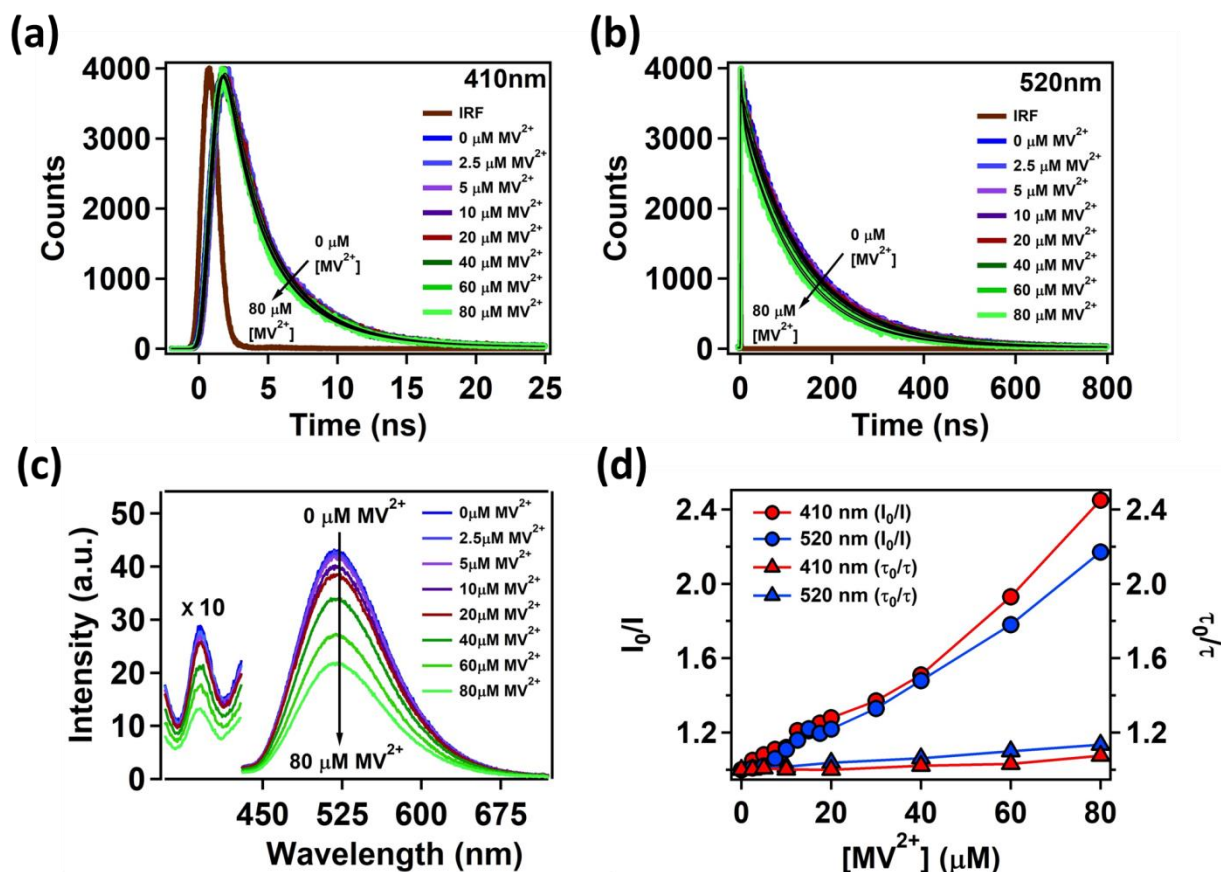


Figure 4.2.6.1. (a) Fluorescence transients at 410 nm and 520 nm (a & b, respectively), and (c) steady state emission spectra of AN₂@OA₂ with increasing concentration of MV²⁺. Spectra in the 390-430 nm region are shown as 10 times enlargements of the original data for better visualization. (d) Stern-Volmer plot for AN₂@OA₂ quenching with MV²⁺. The lines in the Stern-Volmer plots are to guide the eye. ([AN] = 25 μM and [MV²⁺] = 0 – 80 μM). Excimer emission of AN₂@OA₂ can be quenched by MV²⁺ and the Stern-Volmer quenching experiment suggests that the quenching is static in nature.

The higher than diffusion constant reported here is consistent with our recent studies on electron transfer between OA encapsulated aromatics and viologens present outside the capsule⁵¹ and is consistent with the conclusion that the quenching is static. In the case of AN₂@OA₂, the much higher rate constant of PET compared to that one associated with the excimer formation dynamics indicated earlier (Figure

4.2.4.1a) suggests that electron transfer takes place at the very early stages of the excimer formation process and $[AN^*+AN]$ do not get the chance to relax to the most stable excimeric conformation before the quenching process. The similarity in the rate constants of PET for $AN@OA_2$ and $AN_2@OA_2$ also suggests that at the time scale as small as ~ 5 ps it is possible that the emission from the FC state of $AN_2@OA_2$ may have much more similarity to the monomeric emission of $AN@OA_2$ than we estimated from the time-resolved studies in the earlier sections as time-resolved studies at ps-resolution is beyond the scope of our experimentation in case of such a slow process like excimer formation.

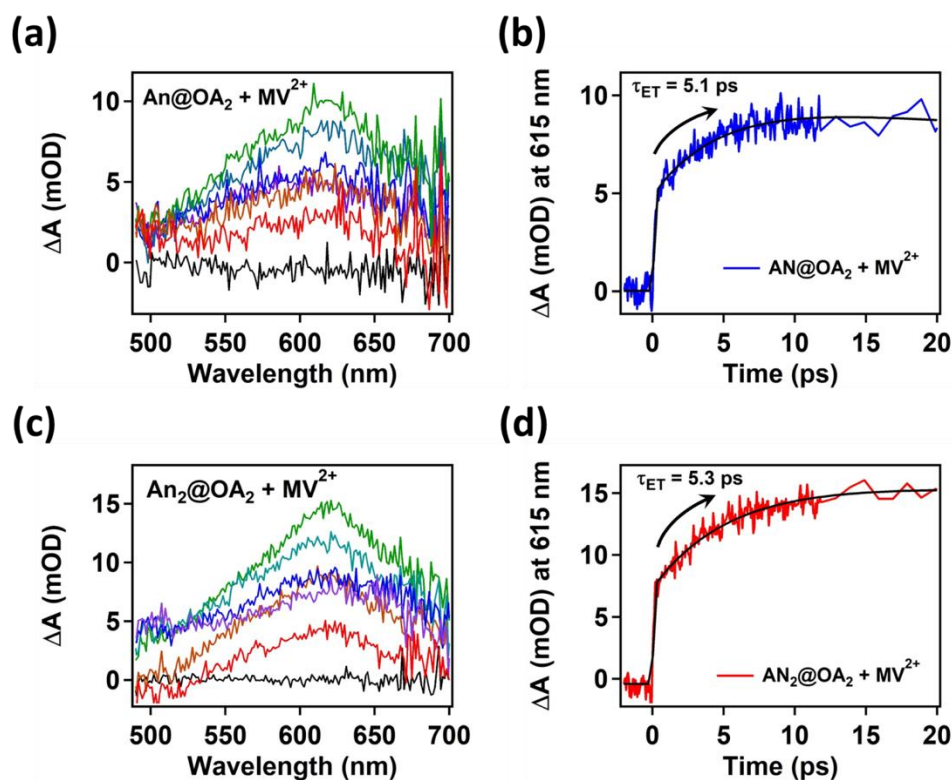


Figure 4.2.6.2. Transient absorption spectra (a & c) at some selected time delays (black: 0 ps; purple: 0.5 ps; blue: 1 ps; cyan: 5 ps; green: 20 ps; orange: 400 ps; red: 1000 ps) and fitted kinetics at 615 nm (b & d) for $AN@OA_2$ and $AN_2@OA_2$, respectively, in presence of MV^{2+} . ($[AN] = 100 \mu M$ and $[MV^{2+}] = 10 mM$). Formation of positive TA band around 615 nm indicates the formation of methyl viologen radical cation (MV^{+}) and hence confirms the PET process for both $AN@OA_2$ and $AN_2@OA_2$. Rate constants of PET for both the cases are similar and are much faster than the rate constant of excimer formation.

4.2.7. Quantum Mechanical Model for Excited State Dynamics: The DFT optimized ground state (S_0) structure of the complex is similar to the equilibrated

structure obtained in the MD simulations (Figure 4.2.2.1). The two AN molecules are in a slip-stacked configuration with a distance $a = 3.544 \text{ \AA}$ between their parallel planes and having relative displacements of $b = 1.003 \text{ \AA}$ and $c = 2.089 \text{ \AA}$ along the short and long axes, respectively. The molecules are oriented at 18 degrees to the axis of the OA cavity. Compared to the gas phase optimized structure (Table 4.2.7.1), the confined dimer is significantly more slipped along c .

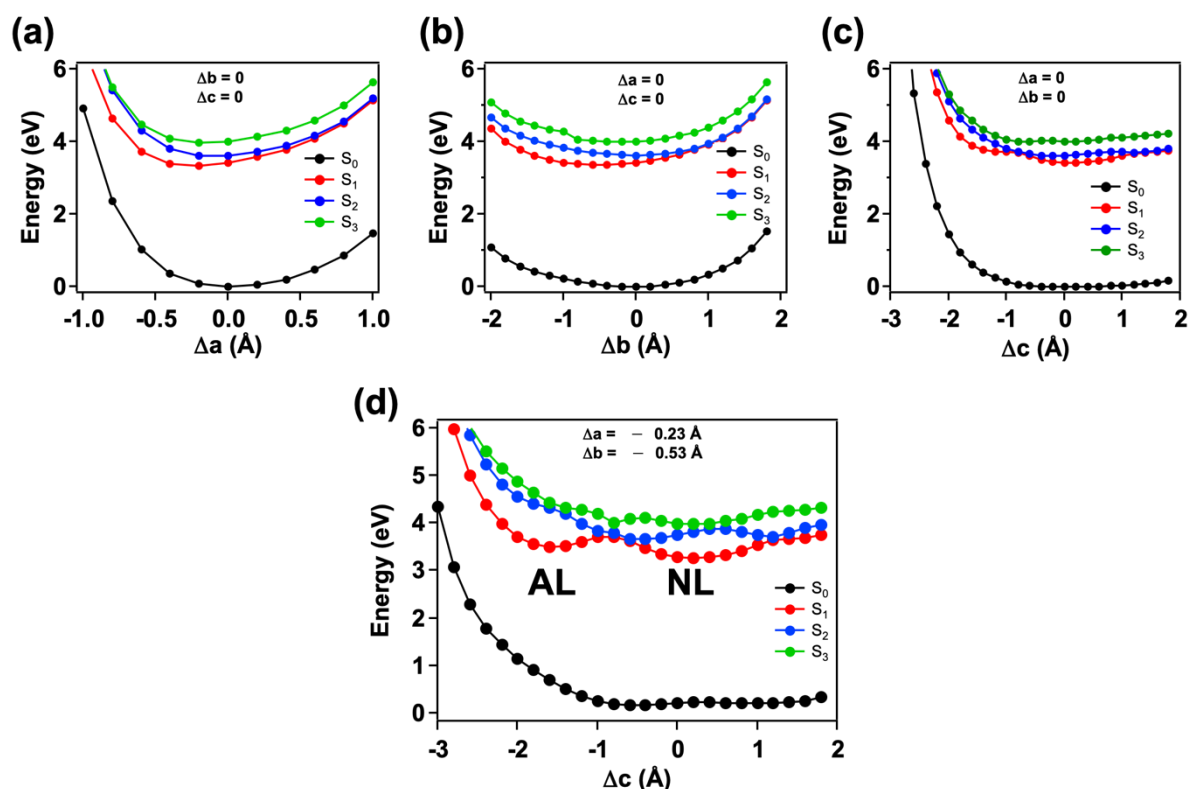


Figure 4.2.7.1. Potential energy curves for the confined anthracene dimer depicting the complex binding energies as a function of the displacement along (a) the a -coordinate (interplanar separation), (b) the b -coordinate (short axis) and (c) the c -coordinate (long axis) about the ground state optimized geometries ($a = 3.544 \text{ \AA}$, $b = 1.003 \text{ \AA}$ and $c = 2.089 \text{ \AA}$). (d) Potential energy curve along the c -coordinate with a and b assuming their minimal values on S_1 ($\Delta a = -0.23 \text{ \AA}$ and $\Delta b = -0.53 \text{ \AA}$). The locations of the anthracene-like (AL) and naphthalene-like (NL) excimer minima are marked. The energies and the displacements are plotted relative to their respective values in the optimized structure. This calculations were done by Prof. Varadharajan Srinivasan group in IISER Bhopal, India.

In order to understand the mechanism of excimer formation, we explored the ground and excited potential energy curves (PEC) of the two AN molecules in the OA cavity along the a , b and c coordinates (see Figure 4.2.2.1 (b) for axis notations). In

particular, the first three singlet excited states (S_1 , S_2 , and S_3) were tracked in the PEC along with the ground state (S_0). The results are plotted in Figures 4.2.7.1 (a)-(c). It was previously reported that anthracene dimer can form three types of excimers⁵² depending on the number of benzene rings that are π - π stacked in the excited state. Accordingly, these are termed as anthracene-like (AL), naphthalene-like (NL) and benzene-like (BL) excimers. Our gas-phase calculations (Figure 4.2.7.2) clearly show the existence of these three types of excimers with the AL excimer having the deepest minimum in S_1 .

Table 4.2.7.1. Structural parameters for anthracene dimer in the gas phase and the octaacid cage from density-functional theory ground state optimization at CAM-B3LYP-D3BJ/6-31G(d,p) level.⁵⁻⁷ For the gas phase, results from optimization at ω B97xD/6-31G(d,p) level are also shown. All gas-phase calculations were performed using the Gaussian 16 program⁸. This calculations were done by Prof. Varadharajan Srinivasan group in IISER Bhopal, India.

Displacement Direction	Gas-phase (Å)	Inside OA cage (Å)	
	CAM-B3LYP-D3BJ ^{5,6}	ω B97xD ⁷	
<i>a</i>	3.45	3.36	3.54
<i>b</i>	1.03	1.03	1.00
<i>c</i>	1.28	1.28	2.09

Unlike in the gas phase, the PECs for the slip displacements (*b* and *c*) in the confined AN dimer (Figure 4.2.7.1 (b) and (c)) are unsymmetrical about the sandwich-like arrangement. The S_1 PEC along *c* exhibits a minimum at $\Delta c = 0.24$ Å ($c = 2.33$ Å) corresponding to the NL excimer. Instead, AL excimer with all three rings π - π stacked is less stable than NL excimer in the OA cage. This is an important difference between the gas phase and OA-encapsulated AN excimers resulting from the interactions of the molecules with the hydrophobic walls of OA cage. The AL excimer could perhaps be stabilized by a reorganization of the solvated OA capsule in the excited state. However, it was not possible to model such effects in the present work due to computational limitations.

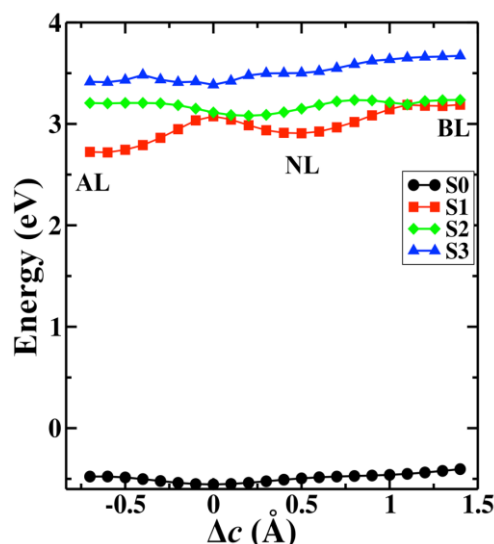


Figure 4.2.7.2. Potential energy curves along the c -coordinate (long axis displacement) for the gas phase anthracene dimer in the ground state and the first three excited singlet states, respectively. The dimer binding energy (computed at CAM-B3LYP-D3BJ/6-31G(d,p) level) is plotted in the vertical axes and the displacement along c -coordinate with respect to the ground-state optimized geometry is along the horizontal axis. The values of a and b displacements were fixed to their values in the ground state (see Table S1). The anthracene-like (AL), naphthalene-like (NL) and benzene-like (BL) excimer minima on S1 are marked in the plot. Note that, in the gas phase, the AL excimer occurs at $c=0$, i.e. with no slip along the long axis. This calculations were done by Prof. Varadharajan Srinivasan group in IISER Bhopal, India.

Table 4.2.7.2. Spectra of An₂@OA₂ complex with QM/MM .The QM part was described with CAM-B3LYP-D3BJ/6-31g(d,p) level of theory. This calculations were done by Prof. Varadharajan Srinivasan group in IISER Bhopal, India.

Excited State	Excitation wavelength (nm)	Excitation energy (eV)	Oscillator Strength
S1	363	3.42	0.00
S2	342	3.62	0.11
S3	309	4.01	0.00

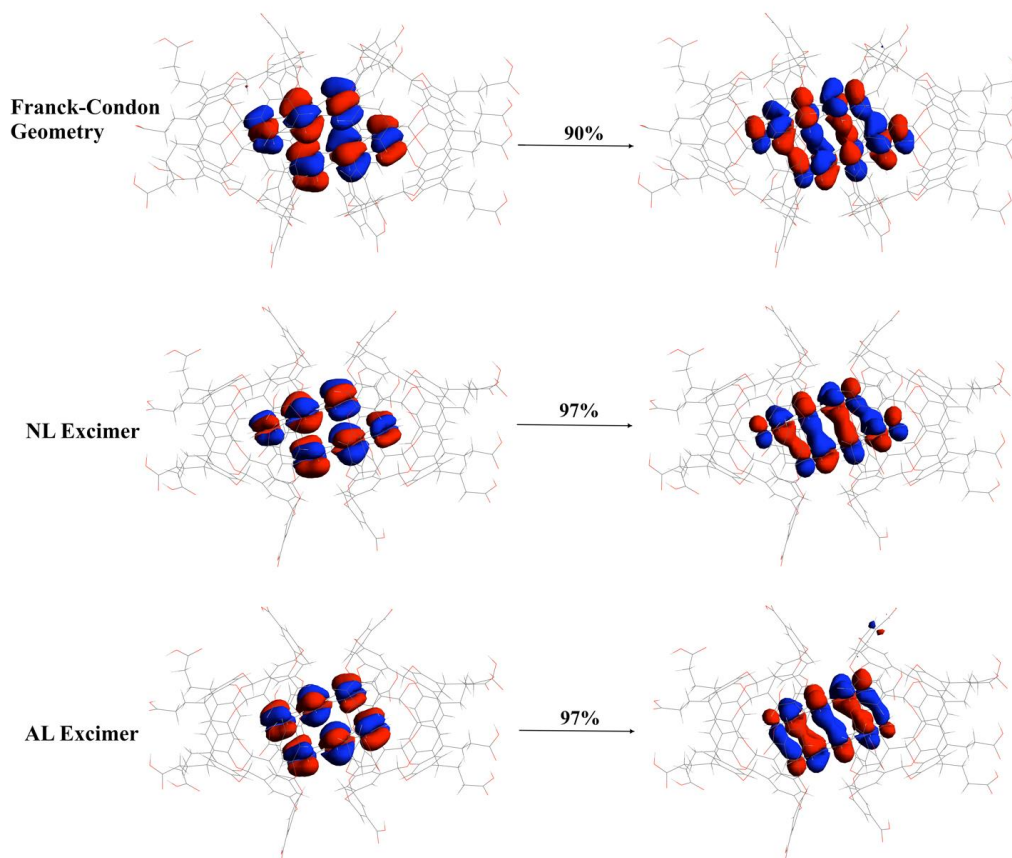


Figure 4.2.7.3. Natural Transition Orbitals (NTOs) corresponding to the $S_0 \rightarrow S_1$ transition in the confined anthracene dimer at Franck-Condon, NL and AL excimer geometries, respectively. The contribution of these electron (right) and hole (left) pairs to the excitation are mentioned above the arrows. The NTOs were obtained by performing a TDDFT/CAM-B3LYP-B3DJ/6-31G(d,p) calculation on the entire system ($AN_2@OA_2$) using Gaussian 16 followed by post-processing using the Multiwfn code⁹. The plots were made using the Avogadro software¹⁰. The NTOs indicate that while the absorption character is mostly local, the excimer emission involves a mixture of local and charge-transfer character. This calculations were done by Prof. Varadharajan Srinivasan group in IISER Bhopal, India.

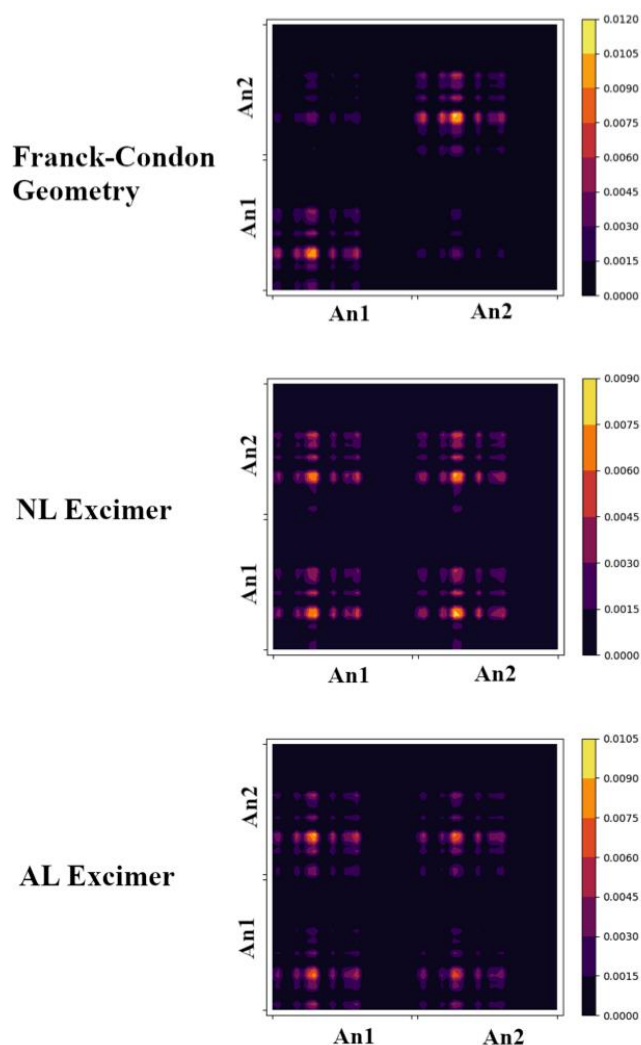


Figure 4.2.7.4. Transition density matrix (TDM) heat map plots corresponding to the $S_0 \rightarrow S_1$ transition in the confined anthracene dimer at Franck-Condon (FC), NL and AL excimer geometries, respectively. The TDM was obtained, in each case, by performing a TDDFT/CAM-B3LYP-B3DJ/6-31G(d,p) calculation on the entire system ($AN_2@OA_2$) using Gaussian 16⁸ followed by post-processing using the Multiwfn code⁹. The plots were made using our own python scripts. The axes in each plot are divided into regions belonging to the first (An1) and the second (An2) anthracene molecules, respectively. Diagonal contributions in the plot indicate local nature of transitions whereas off-diagonal contributions imply charge-transfer between the two molecules. The plots confirm the local nature of the excitation at the FC geometry and its mixed nature at the excimer geometries. This calculations were done by Prof. Varadharajan Srinivasan group in IISER Bhopal, India.

The theoretically predicted excitation wavelength to S_1 of 3.42 eV of $\lambda = 363$ nm (see Table 4.2.7.2) is in good agreement with the experiment ($\lambda = 376$ nm). The $S_0 \rightarrow S_1$ transition at the optimized geometry predominantly involves orbitals

localized on the individual AN molecules as is evident from plots of the hole and electron natural transition orbitals (NTOs) as well as the transition density maps (TDMs) shown in Figures 4.2.7.3 and 4.2.7.4, respectively. This explains the monomer-like absorption features seen in the experiment. A delocalized electron NTO and small off-diagonal contributions in the TDM are indicative of inter-monomer interaction in the excited state. This is likely responsible for the bathochromic shifts in the absorption peaks with respect to the AN monomer.

It is likely that after vertical excitation to the S_1 surface the system moves down without a barrier along the a , b and c coordinates to the NL excimer state. Along a -axis S_1 has a minimum at $3.31 \text{ \AA}$ ($\Delta a = -0.23 \text{ \AA}$) and along b -axis the minimum is at $0.47 \text{ \AA}$ ($\Delta b = -0.53 \text{ \AA}$). We recomputed the PEC along c with these optimal values for a and b (see Figure 4.2.7.1(d)) to locate two minima at $\Delta c = -1.43 \text{ \AA}$ and $\Delta c = 0.24 \text{ \AA}$ corresponding to the AL and NL excimers, respectively. From these minima, we estimate emission wavelengths of 441 nm for AL and 407 nm for the NL excimer. Note that this discrepancy between theoretical and experimental emission wavelengths is likely because of the oversimplified approach employed to guess the minimum along S_1 . A more accurate prediction of the emission wavelength would require an excited state optimization in S_1 which was prohibitive given the size of the system and limitations of the codes used. The NTOs and TDMs calculated for the same transition at these estimated NL and AL excimer geometries indicate a strong mixture of local and charge-transfer characters (see Figures 4.2.7.3 and 4.2.7.4). It is evident from the delocalized electron NTO plots that there is stronger interaction between the two AN monomers in the excited state giving rise to the CT character and strong binding. Excimer formation leads to significant overlap between the π -orbitals of the two monomers and likely leading to the observed intense excimer emission. This effect has also been seen previously in crystals of functionalized anthracene.⁵²

The TRANES experiments discussed above show that the formation of excimer is a two-step process that involves a barrier. This is consistent with the calculated PECs

which indicate that the NL excimer would form in the first process with a higher rate constant. In the second stage the NL excimer slowly converts to the AL excimer through a barrier, and subsequently resulting in the experimentally observed broad fluorescence centered at 520 nm.

4.3. Conclusions

Although numerous substituted anthracenes are well-established to show excimer emission, the parent unsubstituted anthracene generally do not show excimer emission in solution. In the 60's considerable effort was spent on understanding this anomalous behavior resulting in the development of an ingenious method involving photolytic decomposition of dianthracene in organic glass at 77° K. This approach enabled excimer emission from AN to be recorded at 77° K. However, recording excimer emission from AN at room temperature in solution continues to be challenging even now. In this report we have expanded our preliminary observation of a method that allowed recording intense emission from AN excimer at room temperature in aqueous solution.⁴¹ The confined environment provided by a synthetic organic capsule enhances the photophysical pathway (excimer emission) at the expense of photochemical reaction pathway, namely dimerization. The simple elegant strategy outlined here should be a valuable tool to record excimer emission from reluctant guest molecules.

Host-guest complexation as followed by NMR experiments suggested that AN forms two types of OA complexes, 1:2 and 2:2 (guest to host). The ratio of these complexes could be controlled by careful manipulation of the relative concentrations of OA and AN in solution. Excitation and absorption spectra of monomer and excimer emissions reveal that the AN molecules present in 2:2 complex show mainly excimer emission. One of the novel observations relates to the time dependent emission maxima of the excimer. For excimer formation in bulk solution the rate-limiting step being the diffusion, movements along the PES after the formation of the encounter

complex can not be traced. Interestingly, time resolved emission studies inside OA cavity has uncovered a unique feature thus far unknown with respect to excimer emission in solution. The time dependent AN excimer emission maxima suggest that the potential energy surface leading from excited monomer to excimer is not steep and the pathway within the OA capsule is tortuous. Time-resolved area normalized emission spectra reveal that the path should consist at least one potential energy barrier. Computational and quantum chemical calculations suggest that due to the restricted space within OA capsule the two AN molecules are not ideally placed in the ground state for excimer formation. The calculated potential energy curves are consistent with the experimental observations. The results presented here supports the conclusion that molecules when confined behave differently.⁵³⁻⁵⁶

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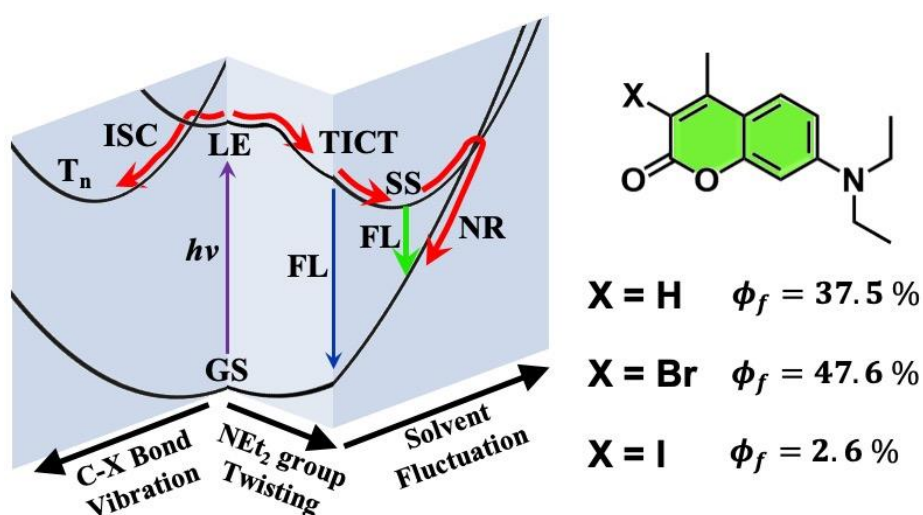
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Chapter 5

Vibration Assisted Intersystem Crossing in the Ultrafast Excited-State Relaxation Dynamics of Halo-Coumarins



Aritra Das, Sujit Kumar Ghosh, Vaidyanathan Ramamurthy, and Pratik Sen, *J. Phys. Chem. A* **2022**, 126, 1475-1485.

In this chapter, I have presented detailed steady state and femtosecond transient absorption studies along with theoretical calculation done to rationalize the unusual trend in fluorescence quantum yield among coumarin-1 and its bromo- and iodo-derivatives. I have found that the carbon-halogen bond length variation coordinate plays an important role in intersystem crossing (ISC) in these molecules. Barrierless singlet-triplet crossing along this coordinate leads to efficient ISC for iodo-derivative. Whereas presence of a significant barrier in the same coordinate hinders ISC in the bromo-derivative.

5.1. Introduction

Recent intense research on phosphorescence¹⁻⁵ could be traced to G. N. Lewis' statement to his student in 1942 namely, "You know, those triplet states that Mulliken was talking about in ethylene are probably the phosphorescent state".⁶ The experimental evidence for the existence of triplet states in phosphorescent materials by Kasha and Lewis in 1944 also revealed the importance of intersystem crossing (ISC) through spin-orbit coupling (SOC).⁷⁻⁹ The observation of heavy atom effect on phosphorescence by McClure in 1949 and the quadratic dependence of the SOC with the atomic number ($\propto Z^4$) found handy to tune the phosphorescence property of a system.¹⁰⁻¹² Halogen substitution in organic molecules like naphthalene, azulene, phenanthrene, quinoline, quinoxaline and anthracene is a preferred way to introduce heavy atom effect in the past.¹⁰⁻²² A change in orbital type from $\pi\pi^* \rightarrow n\pi^*$ or $n\pi^* \rightarrow \pi\pi^*$ has also been noted to facilitate ISC through stronger SOC (El Sayed rule).²³ However, El Sayed rule only considers the electronic aspect of the transition and ignores the vibrational component.²⁴ Depending on the extent of nuclear geometry difference between the singlet and triplet states, there can be two regimes of ISC.²⁵ When the difference between singlet and triplet geometries is small, it falls in the small coupling regime and the rate of ISC decreases exponentially with increasing energy gap (ΔE) between the two states.²⁶⁻²⁷ On the other hand, when the geometries of the singlet and triplet states differ significantly and their surfaces cross, it falls in the strong coupling regime and ISC rate constant follows a bell-shaped dependence with ΔE . This has similarity to the bell-shaped dependence described in the Marcus theory for electron transfer.²⁶⁻²⁷ If this is true, it should be possible to prove the applicability of Marcus theory for ISC in the strong coupling regime. In this context we note that there are reports of facile ISC without heavy atom effect, where crossing between singlet and triplet states is present.^{24,27}

The ISC trend of 1-halonaphthalene is an example in support of the idea that SOC is not the only factor that controls the ISC from excited singlet to the triplet.¹² The ratio of the square of SOC constants for 1-bromo and 1-iodonaphthalene is 1:4.2, whereas,

the ratio of their ISC rate constants is measured to be 1:9.3.^{10,12} The 2.2 times larger value of the ISC for 1-iodonaphthalene than the predicted value based on SOC suggests the involvement of other factor(s) associated with the heavy atom incorporation, which remains mostly unexplored. When the excited state is non-adiabatic in nature, we cannot consider the spin, electronic and vibrational contributions separately.²⁴ In such cases, the ISC cannot be described solely in terms of conventional SOC values and a change in the nuclear geometry may also dictate the course of relaxation following the photoexcitation. In general, vibration is likely to be important for an excited state process, which may also be the case in the singlet-triplet ISC process. Such examples are known: in the case of inorganic materials and metal complexes, such a phenomenon has been reported.²⁸⁻³¹ For example, in $[\text{Fe}(\text{bpy})_3]^{2+}$ the singlet triplet transfer occurs along the Fe-N distance coordinate.²⁸ Similarly, in $\text{Re}(\text{L})(\text{CO})_3^-$ the ISC is non-adiabatic in nature and coupled with the complex's low-frequency vibrational modes.²⁹ Similar vibronic involvement in ISC was speculated in cases of PtPOP-BF_2 and transition-metal trifluoride compounds like MnF_3 and CoF_3 .³⁰⁻³¹ Quantum dynamics simulation also predicted the role of prefulvene normal mode of benzene in ISC.³²⁻³⁴ Another important report in this direction is the ISC of a xanthone derivative, where spin mixing has been observed along the C=O elongation coordinate.³⁵

The above examples prompted us to probe this phenomenon further employing halogen substituted 7-diethylamino-4-methylcoumarins as probe molecules (Figure 5.1.1). If the C–X vibration plays a role in ISC, the HAE would be expected to be position dependent. To explore this, we carried out femtosecond transient absorption spectroscopic experiments and quantum chemical calculations with two halogen substituted 7-diethylamino-4-methylcoumarins as examples. Results suggest that the ISC rate is dictated by the carbon-halogen bond vibration. We have extrapolated the above conclusions to halonaphthalenes.

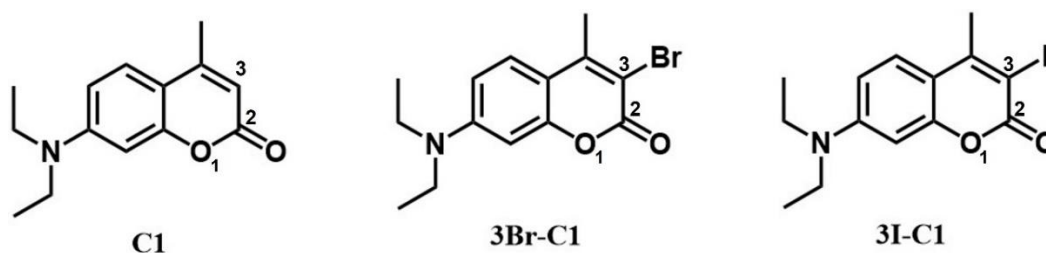


Figure 5.1.1. Molecular structures of coumarin 1 (C1), 3-bromo-coumarin 1 (3Br-C1) and 3-iodo-coumarin 1 (3I-C1). 3Br-C1 and 3I-C1 were synthesized by Prof. Ramamurthy group in University of Miami, USA.

5.2. Results

5.2.1. Steady State and TCSPC Experiments: In figure 5.1.1 the molecular structures of three coumarins used in this work are provided. The steady state absorption and emission spectra of the coumarins in methanol (MeOH) and cyclohexane (CHX) are included as figure 5.2.1.1.

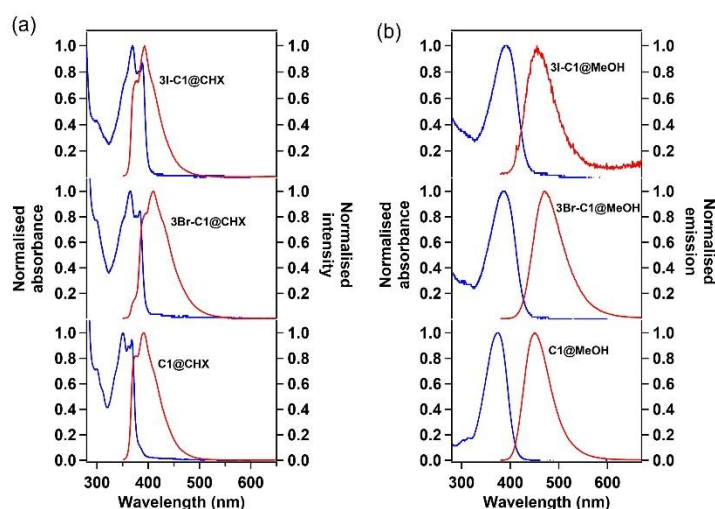


Figure 5.2.1.1. Steady state absorption (blue solid line) and emission (red solid line) spectra of C1, 3Br-C1, 3I-C1 in (a) CHX and (b) MeOH. For absorption spectra measurement, pathlength was 1 cm and concentration was 10 μ M. For emission spectra in CHX, λ_{exc} was 340 nm and in MeOH λ_{exc} was 340 nm.

The absorption and emission maxima with the calculated Stokes shifts in different solvents for the three coumarins are tabulated in table 5.2.1.1. All the halo-derivatives showed expected solvatochromic properties based on the behavior of the parent coumarin (C1). The fluorescence quantum yields (ϕ_f) of these coumarins

were estimated in different solvents (see table 5.2.1.1) using C1@ MeOH or C1@CHX as the standard.³⁶ The average fluorescence lifetimes of these three molecules were recorded using TCSPC method. The results are consolidated in table 5.2.1.1.

Table 5.2.1.1. Steady state absorption and emission parameters with average fluorescence lifetimes of coumarin 1 (C1), 3-bromo-coumarin 1 (3Br-C1) and 3-iodo-coumarin 1 (3I-C1) in methanol (MeOH) and cyclohexane (CHX).

Dye	Solvent	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Stokes shift (nm)	ϕ_f (%)	τ_{avg} (ns)
C1	MeOH	374.6	450	75.4	37.5	2.07
3Br-C1		387.0	471	84.0	47.6	2.46
3I-C1		391.1	455	64.1	2.6	1.69
C1	CHX	350.6	391	40.4	49.0	2.54
3Br-C1		364.8	410	45.2	55.3	2.59
3I-C1		369.6	393	23.4	15.3	2.43

5.2.2. Transient Absorption Spectroscopy: The femtosecond transient absorption (TA) spectroscopic study of C1, 3Br-C1 and 3I-C1 were performed in methanol. The TA spectra of C1, 3Br-C1 and 3I-C1 in methanol consist of stimulated emission (SE) bands respectively around 470 nm, 485 nm and 490 nm, and excited state absorption (ESA) bands >600 nm. Global fitting of the time evolution of the TA response provided three different kinetic parameters (hence three different time constants) for all three molecules in methanol. In table 5.2.2.1, the global fitting time constants are given. The TA spectra at different time delays along with the fitted kinetics at selected wavelengths for C1, 3Br-C1 and 3I-C1 in methanol are displayed in figures 5.2.2.1a, 5.2.2.1b, 5.2.2.1d, 5.2.2.1e, 5.2.2.1g and 5.2.2.1h, respectively. The decay associated spectra (DAS) for these three time constants for three molecules are showed in figures 5.2.2.1c, 5.2.2.1f and 5.2.2.1i.

Table 5.2.2.1. Time constants obtained from the global fitting of the transient absorption spectra (pump: 400 nm; probe: 470-750 nm) of coumarin 1 (C1), 3-bromo-coumarin 1 (3Br-C1) and 3-iodo-coumarin 1 (3I-C1) in methanol (MeOH).

Dye	τ_1 (ps)	τ_2 (ps)	τ_3 (ns)
C1	3.2	10.3	2.04
3Br-C1	0.9	12.6	2.14
3I-C1	0.9	61.8	2.00

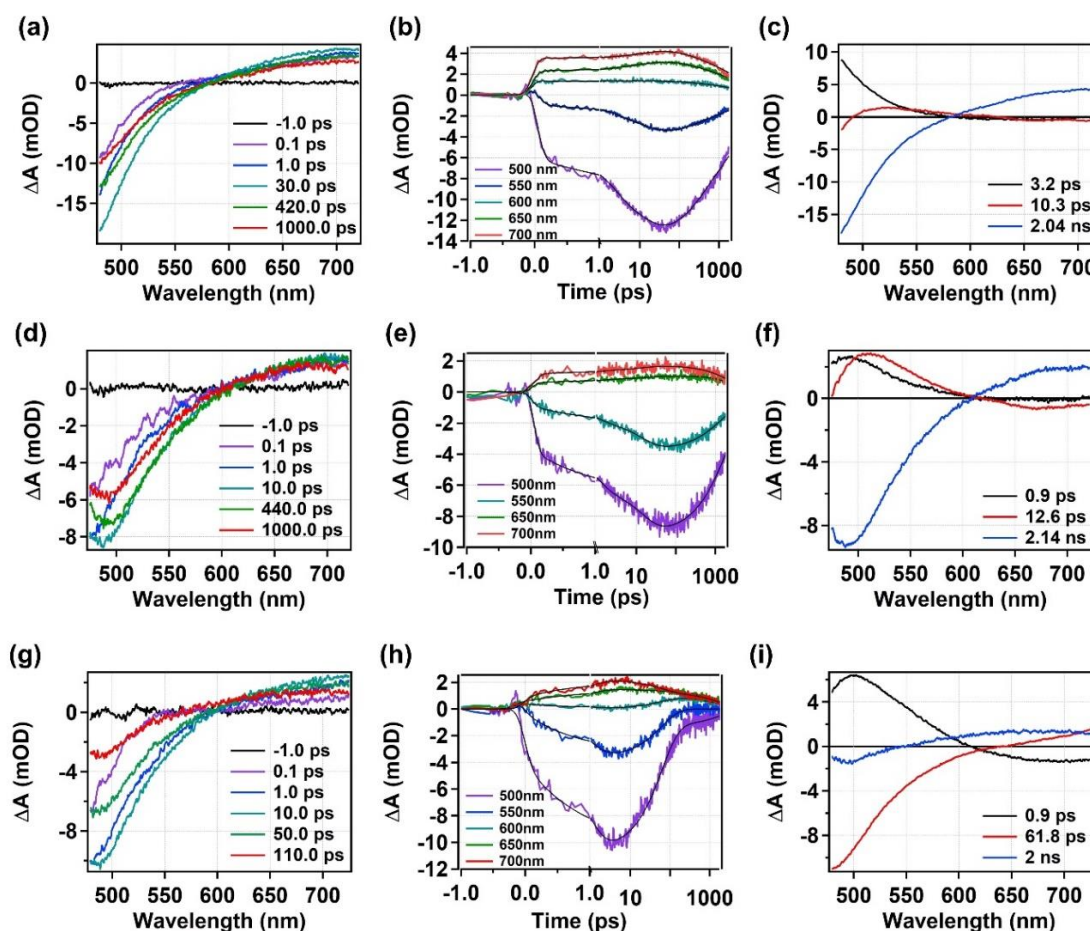


Figure 5.2.2.1. TA response (pump: 400 nm; probe: 470-750 nm) of C1, 3Br-C1 and 3I-C1 in methanol. (a, d, g) TA spectra at some representative delay times for C1, 3Br-C1 and 3I-C1 respectively. For C1, the TA spectra consists of a SE signal around 470 nm and an ESA around 700 nm. For 3Br-C1, The TA spectra consists of a SE signal around 485 nm and an ESA around 700 nm. For 3I-C1, The TA spectra consists of a SE signal around 490 nm and an ESA around 700 nm. (b, e, h) Globally fitted kinetics at some selected wavelengths for C1, 3Br-C1 and 3I-C1 respectively. For C1, obtained time constants from global analysis are 3.2 ps, 10.3 ps and 2.04 ns. For 3Br-C1, obtained time constants from global analysis are 0.9 ps, 12.6 ps and 2.14 ns. For 3I-C1, obtained time constants from global analysis are 0.9 ps, 61.8 ps and 2.0 ns. (c, f, i) Corresponding DAS obtained from global analysis for C1, 3Br-C1 and 3I-C1 respectively.

5.2.3. TD-DFT Calculations: All three molecules shown in figure 5.1.1 were optimized in methanol using PCM model, and their absorption wavelengths were calculated by TD-DFT method. The frontier molecular orbitals of these molecules are displayed in figure 5.2.3.1 and the absorption wavelengths are tabulated in table 5.2.3.1 along with experimentally obtained absorption wavelengths for comparison.

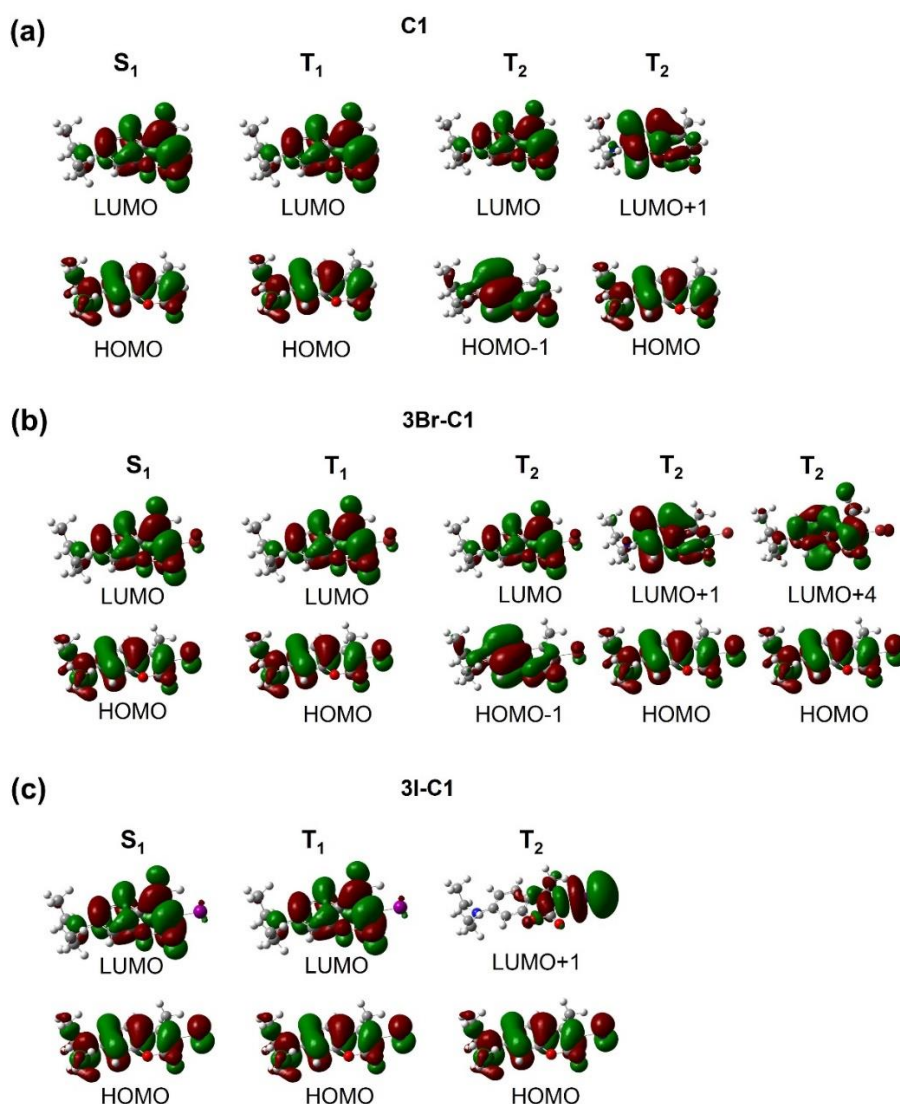


Figure 5.2.3.1. (a) Electronic structure of the S₁, T₁ and T₂ state of C1. Formation of all the states consists of electronic transitions between π orbitals. (b) Electronic structure of the S₁, T₁ and T₂ state of 3Br-C1. Formation of S₁ and T₁ states consists of electronic transitions between π orbitals. However, in the T₂ state there is mixing of π and n characters. (c) Electronic structure of the S₁, T₁ and T₂ state of 3I-C1. Formation of S₁ and T₁ states consists of electronic transitions between π orbitals. However, significant change in orbital character (π and n) happens in the T₂ state. We have used the B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for Br and I the DFT calculations. DFT calculations were performed using Gaussian 09 package.³⁷

Table 5.2.3.1. λ_{abs}^{max} (nm) obtained from TDDFT calculation and steady state absorption spectroscopy

Molecule	λ_{abs}^{max} in nm (calculated)	λ_{abs}^{max} in nm (experimental)
C1	363.9	374.6
3Br-C1	380.8	387.0
3I-C1	381.9	391.1

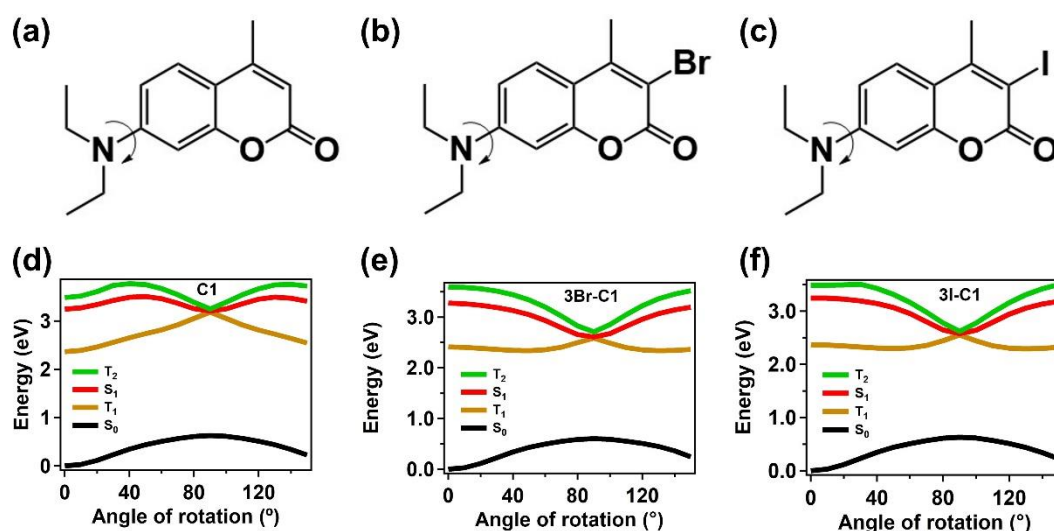


Figure 5.2.3.2. Molecular structures and the $-NEt_2$ group rotations (denoted by black arrows in the molecular structures) for (a) 7-diethylamino-4-methylcoumarin (C1), (b) 3-Bromo-7-diethylamino-4-methylcoumarin (3Br-C1), (c) 3-Iodo-7-diethylamino-4-methylcoumarin (3I-C1). Potential energy curves (PEC) along the angle of $-NEt_2$ group rotation of the (d) 7-diethylamino-4-methylcoumarin (C1), (e) 3-Bromo-7-diethylamino-4-methylcoumarin (3Br-C1), (f) 3-Iodo-7-diethylamino-4-methylcoumarin (3I-C1). We have used the B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for Br and I for the TD-DFT calculations to determine the PECs. PE scan was done taking methanol as solvent using PCM model. DFT calculations were performed using Gaussian 09 package.³⁷

Prompted by previous reports^{36,38-42} suggesting rotation of the diethylamino group as a potential deactivation channel for C1, potential energy scan by TDDFT calculation along the diethylamino group rotation coordinate for C1, 3Br-C1 and 3I-C1 was performed. The potential energy curves (PEC) thus obtained for different electronic states are shown in figure 5.2.3.2. The PEC along the carbon-halogen bond length was computed, and to our surprise, the PEC for C1, 3Br-C1 and 3I-C1

are observed to be different for the three (figure 5.2.3.3a,b,c). For C1, all the states are bound in nature and there is no crossing of different electronic states. In case of 3I-C1 (figure 5.2.3.3c) S_1 and T_2 state crosses with a slight elongation ($\sim 2\%$) of the C-I bond length. Once the molecule is in T_2 , it is on a downhill trajectory to reach the T_1 surface with 11.3% elongation of the bond length. For 3Br-C1, (figure 5.2.3.3b) the crossing between S_1 and T_2 requires 6.1% elongation of the C-Br bond length and eventually reaches the T_1 state. Interestingly, for 3Br-C1 there is a significant PE barrier of 0.110 eV for $S_1 \rightarrow T_2$ crossing, whereas for 3I-C1 the PE barrier is only 0.017 eV .

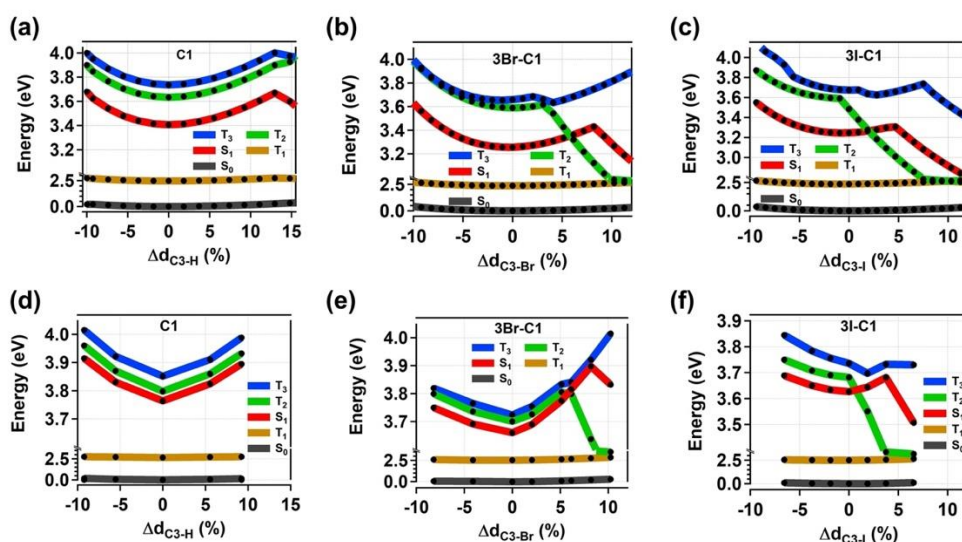


Figure 5.2.3.3. Potential energy curves (PEC) along the C3-X (X=H, Br, I) bond vibration coordinates of the (a) 7-diethylamino-4-methylcoumarin (C1), (b) 3-Bromo-7-diethylamino-4-methylcoumarin (3Br-C1), (c) 3-Iodo-7-diethylamino-4-methylcoumarin (3I-C1) without considering the effect of SOC. SOC-corrected PEC along the C3-X (X=H, Br, I) bond vibration coordinates of the (d) 7-diethylamino-4-methylcoumarin (C1), (e) 3-Bromo-7-diethylamino-4-methylcoumarin (3Br-C1), (f) 3-Iodo-7-diethylamino-4-methylcoumarin (3I-C1). For the PEC calculations without SOC correction, Gaussian 09 package was used. B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for Br and I were used for the TD-DFT calculations to determine the PECs. PE scan was done taking methanol as solvent using PCM model. DFT calculations were performed using Gaussian 09 package.³⁷ For the SOC-corrected PEC calculations, B3LYP exchange correlation functional and def2-TZVP basis set was used and calculations are done on Orca 4.2.1 package.⁴³ $\Delta d_{C3-X}(\%)$ denotes the % change in C3-X (X= H, Br, I) bond length (d_{C3-X}). $\Delta d_{C3-X}(\%) = (\Delta d_{C3-X}(\text{\AA})/d_{C3-X}^{eq}(\text{\AA})) \times 100\%$. d_{C3-X}^{eq} is the equilibrium C3-X bond length in electronic ground state. For molecular structures check figure 5.1.1.

Given a large atomic SOC constant of Br and I, we further included SOC in the PEC calculation (see figure 5.2.3.3d,e,f). Though the energy values and the position of surface crossings have changed to some extent, the general features of the SOC-neglected & SOC-incorporated PEC are same. For C1, all the states are bound in nature, as observed without incorporation of SOC (figure 5.2.3.3d). In case of 3I-C1, the crossing between S_1 and T_2 requires a tiniest of bond length modification, and the crossing is almost barrierless (figure 5.2.3.3f). For 3Br-C1, S_1 crosses T_2 after ~6 % C-Br bond elongation (figure 5.2.3.3e), with a barrier height of 0.138 eV.

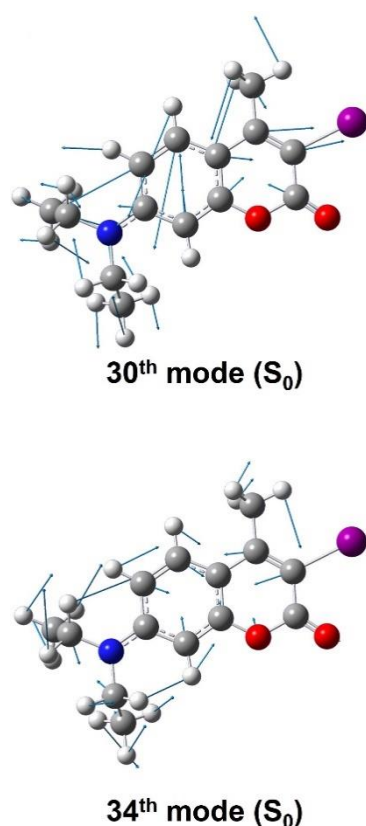


Figure 5.2.3.4. The 30th and 34th normal modes of vibration of 3I-C1 in S_0 state. Blue arrows are indicating displacement vectors. We have used the B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for I for the frequency calculations. DFT calculations were performed using Gaussian 09 package.³⁷

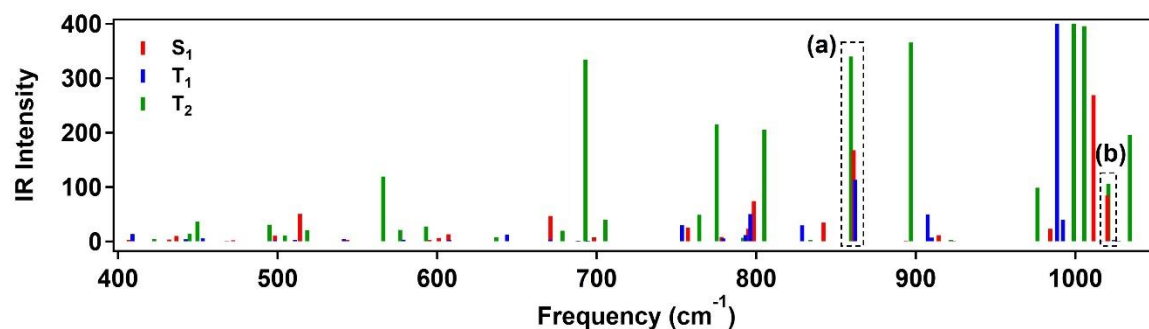


Figure 5.2.3.5. The IR spectra of 3I-C1 in S_1 , T_1 & T_2 generated by TD-DFT calculations. The IR signals for normal modes in resonance are squared by dotted line. Square (a) is at 860 cm^{-1} and square (b) is at 1020 cm^{-1} . Square (a) has the S_1 mode 39, T_1 mode 39 and T_2 mode 42 in resonance and square (b) has the S_1 mode 46 and T_2 mode 48 in resonance. B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for I were used for the frequency calculations. DFT calculations were performed using Gaussian 09 package.³⁷

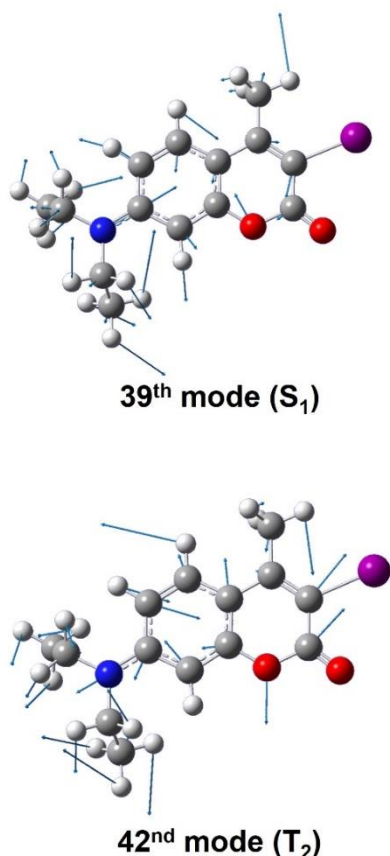


Figure 5.2.3.6. The 39th mode in S_1 and 42nd mode in T_2 of 3I-C1. Blue arrows are indicating displacement vectors. B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for I were used for the frequency calculations. The 39th Mode of S_1 and the 42nd mode of T_2 are resonant (860 cm^{-1}). Close inspection reveals that C-I bond length variation increases as we move from the S_1 to T_2 through these two resonating modes. DFT calculations were performed using Gaussian 09 package.³⁷

The normal modes of 3I-C1 were computed and it was found that in the ground electronic state 30th & 34th modes lead to change in the carbon-iodine bond length (figure 5.2.3.4). The normal modes in the excited electronic states (S_1 , T_1 and T_2) at the ground state geometry of 3I-C1 revealed that S_1 normal modes 39 and 46 are in resonance with the T_2 normal modes 42 and 48, respectively (figure 5.2.3.5). However, T_1 and S_1 are in resonance only through the 39th mode of vibration (figure 5.2.3.5). Most importantly, a close inspection of these normal modes reveals that C-I bond length increases as we move from the S_1 to T_2 manifold through S_1 -39: T_2 -42 resonating mode (figure 5.2.3.6). The frequency calculations strongly suggest an involvement of bond length variation during ISC, which supports the requirement of the PEC calculations (figure 5.2.3.3) along the varying carbon-halogen bond length.

5.2.4. Steady State and Time-Resolved Emission Studies of Octa Acid (OA) Encapsulated 3-iodo and 3-bromo 7-diethylamino-4-methylcoumarins:

Synthetic host octa acid has been established to form closed host-guest capsular complex with C-1 in borate buffer solution.⁴⁴ Several guest molecules included within OA capsule are known to phosphoresce at room temperature in solution. To examine the feasibility of phosphorescence from 4-iodo and 4-bromo 7-diethylamino-4-methylcoumarins they were included within OA capsule and emission recorded. NMR study confirmed that all the coumarin derivatives used in this study form a 2:1 (octa acid:coumarin) complex in aqueous buffer medium of pH=7.4 (see figure 5.2.4.1). As seen in figure 5.2.4.1 expected upfield shift of the signals upon complexation is observed (see signals even below δ -1).

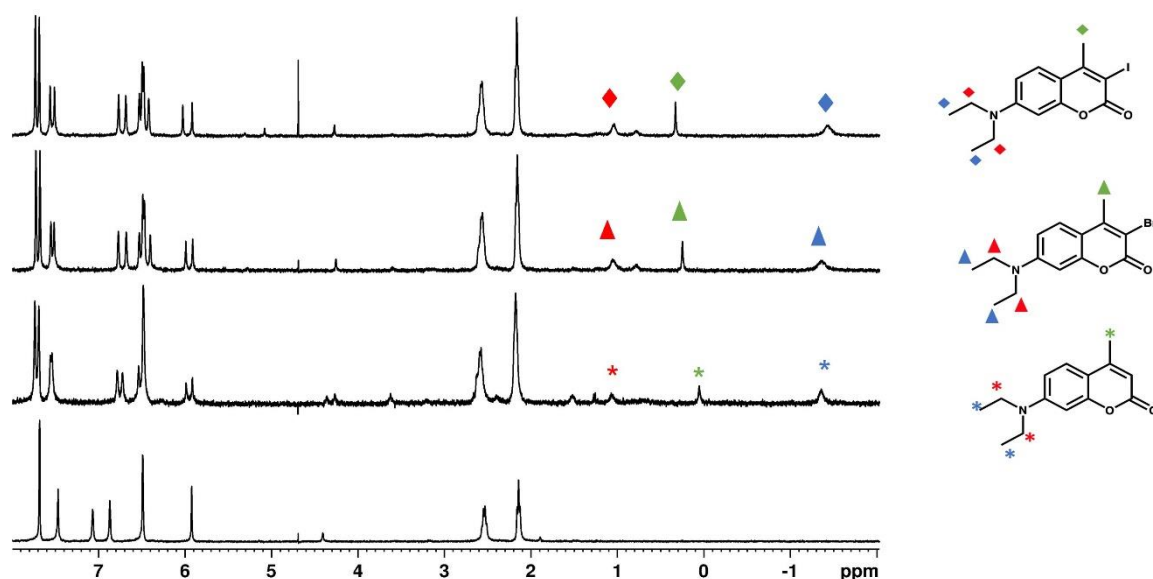


Figure 5.2.4.1. Fig: ^1H NMR (400 MHz, 10 mM $\text{Na}_2\text{B}_4\text{O}_7$ buffer/ D_2O , pH = 8.7) spectra of (Bottom to top) (i) 7-(diethylamino)-4-methyl-2H-chromen-2-one, (ii) 3-bromo-7-(diethylamino)-4-methyl-2H-chromen-2-one, (iii) 3-iodo-7-(diethylamino)-4-methyl-2H-chromen-2-one in presence of octa acid (OA). This experiment was performed by Prof. Ramamurthy group in University of Miami, USA.

The steady state emission of 3Br-C1@OA_2 and 3I-C1@OA_2 were recorded and are shown in figure 5.2.4.2a. For 3Br-C1@OA_2 , a single intense band centered at 440.5 nm is observed. In case of 3I-C1@OA_2 , a weak emission band around 580 nm was present along with the intense band centered at 440 nm. With decrease in the temperature, the 580 nm band intensified in the case of 3I-C1@OA_2 (Figure 5.2.4.2b), whereas, for 3Br-C1@OA_2 no change in the emission spectrum is observed. Recorded spectrum of 3I-C1 at 77 K in a glass forming liquid (ethanol-methanol mixture) applying a 500 ns time delay after the excitation showed an intense emission centered at 540 nm confirming the longer wavelength emission to be phosphorescence (see figure 5.2.4.2c). Thus, it is clear that while 3I-C1@OA_2 show phosphorescence at room and low temperature, 3Br-C1@OA_2 does not under both conditions.

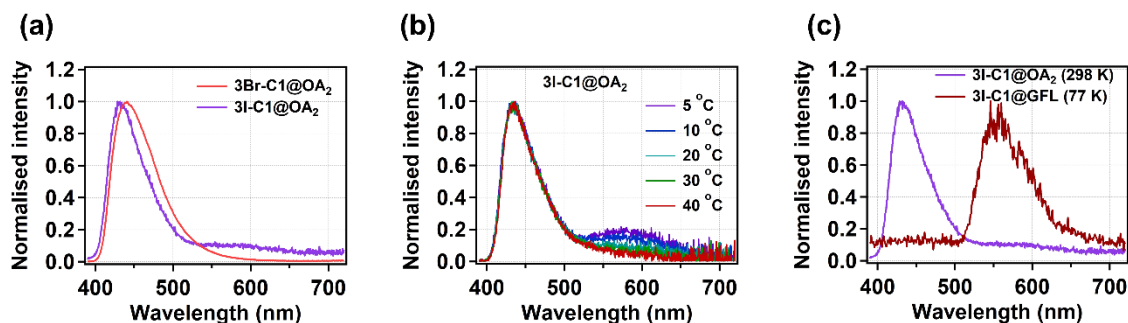


Figure 5.2.4.2. (a) Steady state emission of 3I-C1@OA₂ and 3-Br-C@OA₂ (b) temperature dependence steady state emission of 3I-C1@OA₂ (c) Steady state emission of 3I-C1@OA₂ compared with the phosphorescence spectra of 3I-C1 in glass forming liquid at 77 K. For 3I-C1@OA₂, there is a weak band around 580 nm which is completely absent in case of C1Br@OA₂. This weak emission band for C1I@OA₂ intensifies with decreasing temperature. Phosphorescence spectra recorded for C1I in glass forming liquid (Ethanol-methanol mixture) at 77 K confirms the weak band at 580 nm for C1I@OA₂ as a phosphorescence band.

The TA spectra of 3Br-C1@OA₂ have a strong SE band associated with an ESA band (figure 5.2.4.3). The global fitting analysis of the TA data yielded two time constants of 13.5 ps and 4.6 ns. The TA spectra and the fitted kinetics for some selected time delay and wavelengths and decay associated spectra (DAS) of 3Br-C1@OA₂ are depicted in figure 5.2.4.3a, b, c. On the other hand, the TA spectra for 3I-C1@OA₂ mainly features a broad ESA band, which is stretched throughout the observation window, although in early time a weak SE like feature is observed (figure 5.2.4.3d). The ESA band does not decay in the time delay available in our experimental setup (2 ns). A global fitting analysis yields two time constants, 11.9 ps and >10 ns. In figure 5.2.4.3e we provide fitted kinetics at selected wavelengths and the DAS are shown in figure 5.2.4.3f.

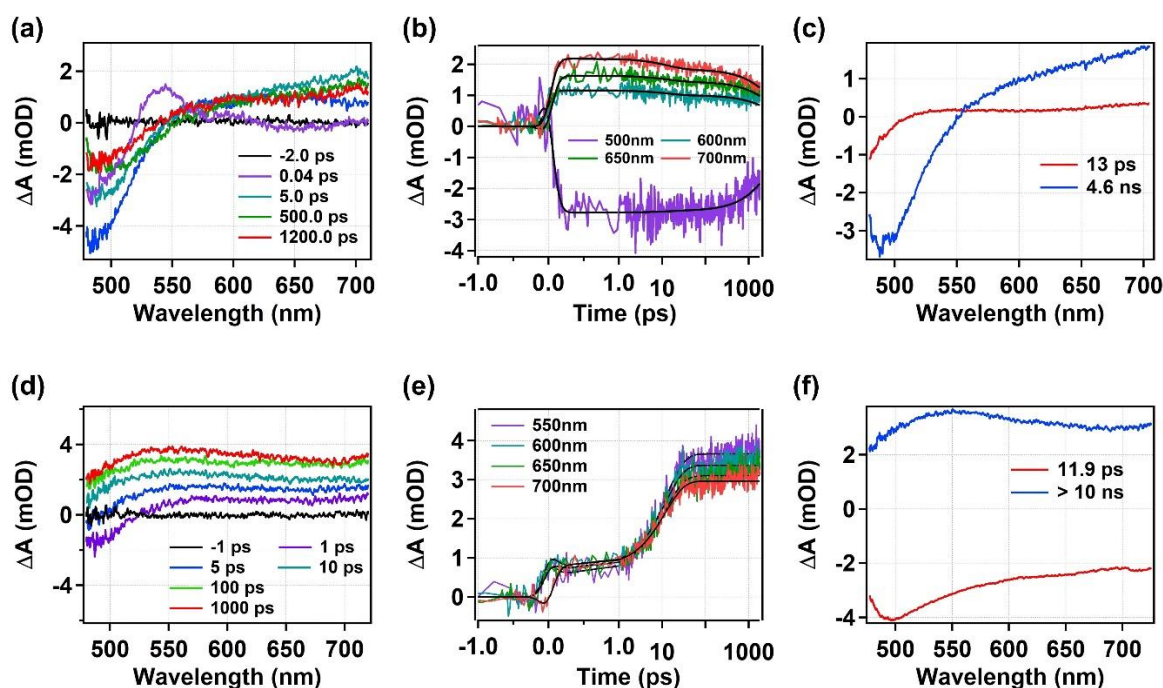


Figure 5.2.4.3. TA response ($\lambda_{ex} = 400 \text{ nm}$; probe: 470-750 nm) of 3Br-C1 and 3I-C1 inside OA cavity. (a, d) TA spectra at some representative delay times for 3Br-C1@OA₂ and 3I-C1@OA₂ respectively. For 3Br-C1@OA₂, the TA spectra consists of a SE signal around 500 nm and an ESA around 600-700 nm. For 3I-C1@OA₂, the TA spectra consists entirely of a broad ESA signal throughout the probe window. (b, e) Globally fitted kinetics at some selected wavelengths for 3Br-C1@OA₂ and 3I-C1@OA₂ respectively. For 3Br-C1@OA₂, obtained time constants from global analysis are 13.0 ps and 4.6 ns. For 3I-C1@OA₂, two time constants were obtained from global analysis. One is of 12 ps and the other is a long time constant > 10 ns. (c) Corresponding DAS obtained from global analysis for 3Br-C1@OA₂ and 3I-C1@OA₂ respectively.

5.3. Discussion

From the steady state experiments, in the case of 3I-C1 we observed a decrease in ϕ_f in methanol and cyclohexane, whereas an increase in ϕ_f was observed in case of 3Br-C1 with respect to C1 (Table 5.2.1.1). This observation is not in line with the heavy atom effect, where the ϕ_f is expected to decrease with increasing atomic number of the incorporated halogen. It is known that the introduction of heavy atoms not only promotes the ISC but also facilitates the back intersystem crossing (BISC) process.⁴⁵⁻⁴⁶ One could attribute the enhanced fluorescence in 3Br-C to BISC. However, presence of BISC for 3Br-C1 but not for the iodo derivative is surprising.

Based on the rationale that increasing atomic number should increase both ISC and BISC, one would expect ϕ_f decrease even in the case of 3I-C1.

Explicit analysis of transient absorption data was necessary to understand the photophysics of these coumarins. For C1 in methanol, three time constants from TA analysis were obtained (Table 5.2.2.1). The DAS for 10.3 ps and 2.04 ns components have a prominent SE feature, where the amplitude of the former is smaller compared to the latter (figure 5.2.2.1c). Earlier studies of C1 in polar solvent methanol indicate the operation of a twisted intramolecular charge transfer (TICT) mediated deactivation of the excited state through non-radiative channels.³⁸ Keeping this in mind, we suspect that the 10.3 ps time component and the associated DAS is of the TICT state of C1 in methanol. The 3.2 ps DAS does not show any SE feature (figure 5.2.2.1c), and we propose this time component is that of the locally excited (LE) state. The SE feature of the 2.04 ns DAS (figure 5.2.2.1c) closely matches with the steady state emission, and hence, we designate it as the solvated TICT state (SS) of C1 in methanol. We attribute the short lifetime of the LE state to rapid shift of the LE population towards the TICT state by twisting and finally to the SS state by solvation.

On the other hand, for 3I-C1, the 0.9 ps DAS looks exactly similar to the short lifetime DAS of C1 and we assign this to the LE state (figure 5.2.2.1i). An SE like feature is observed in both the 61.8 ps and 2.00 ns DAS of 3I-C1. However, unlike in the case of C1, here the 2.0 ns DAS has a low amplitude compared to that of 61.8 ps DAS. The 61.8 ps DAS is the most intense among all and suggests that this state dominates the relaxation process of the excited 3I-C1 leading to a weak fluorescence quantum yield compared to C1. Based on the wavelength of the SE band, the longest amongst the two, we assign the 2.0 ns DAS to the fully solvated state (SS). However, the weak DAS signal of this state suggests that a very small number of molecules reach this state. We speculate that the decreased intensity is due to the excited 3I-C1 following some other coordinate to reach the triplet state. We cannot confirm the occurrence of ISC solely from this data as we have not seen any DAS associated with this triplet state.

The feature of all three DAS of 3Br-C1 look similar to that of the C1 (figure 5.2.2.1f). Following the assignment in case of C1, we assign the 0.9 ps and 2.14 ns DAS to be associated with the LE and SS states, respectively. The 12.6 ps DAS of 3Br-C1 is also very similar in feature with that of 10.3 ps DAS of C1, and we assign it to the TICT state of 3Br-C1. Careful examination reveals that the SE feature has been cut off beyond 480 nm due to interference by the probe light. We suspect that though this SE feature is not observed in the measurement window, it is present and can be observed with an extended probe pulse. Unlike 3I-C1, the DAS for SS is the most intense in the case of 3Br-C1. This suggests that the ISC is unfavorable for 3Br-C1, allowing most molecules to reach the SS state.

Earlier reports proposed that the rotation of the diethylamino group of C1 is the predominant coordinate for the formation of the TICT state from the LE state.³⁸⁻⁴² This led us to scan the PE along the rotation of the diethylamino group of the C1, 3Br-C1 and 3I-C1. Examination of figure 5.2.3.2 reveals that the corresponding potential energy curves (PEC) in different electronic states are very similar for the three coumarins. This implies the presence of another coordinate along the PEC that accounts for the variation in ϕ_f . Basically, the studied coumarin derivatives only differ in the substitution at the 3-position of the C1, which hardly affects the twisting of diethylamino group present at the 7-position. This led us to consider a coordinate where the effect of halogen is prominent. There are several reports suggesting how normal mode of vibrations in a molecule can affect ISC as discussed in the introduction section.^{12,24} This information prompted us to speculate that the carbon-halogen bond vibration may influence the ISC in the coumarins investigated here. PE scan along this vibrational coordinate showed that the PEC of the electronic states of C1 (in this case there is no halogen substitution, C-X refers to C-H), 3Br-C1 and 3I-C1 are distinctly different for all three (figure 5.2.3.3 in results section). As for C1, all the states are bound in nature, preventing ISC from S_1 (figure 5.2.3.3a). Whereas in case of 3Br-C1 and 3I-C1, crossing between S_1 and T_2 states are present (figures 5.2.3.3b,c). The S_1 - T_2 surface crossing requires much smaller bond deformation for 3I-C1 (~2 %) compared to 3Br-C1 (6.1 %). Most importantly, the

PE barrier height for $S_1 \rightarrow T_2$ crossing for 3Br-C1 is significant (0.110 eV) and 6.5 times higher than 3I-C1, which has a PE barrier of 0.017 eV that is achievable at room temperature. To check the role of SOC on the computed PECs, we have also computed the SOC corrected PECs (Figures 5.2.3.3d,e,f). The nature of the ordering, shapes and intersections of the electronic states remain essentially same. A crossing between S_1 and T_2 was observed in cases of 3Br-C1 and 3I-C1 (figures 5.2.3.3e,f). The higher barrier in 3Br-C1 probably slows the ISC process favoring fluorescence. This could be a possible reason for higher ϕ_f for 3Br-C1 in comparison to 3I-C1. Moreover, excited state frequency calculation for 3I-C1 suggests that certain modes of vibration in S_1 and T_2 are in resonance with each other (figure 5.2.3.5) but the C-I bond length change is much more prominent in case of T_2 compared to S_1 (figure 5.2.3.6). Thus, S_1 to T_2 jump must involve the C-I bond length variation coordinate.

The TA analysis along with TD-DFT calculations have provided a glimpse of the photophysics associated with halogen derivatives of C1. However, the association of state mixing and solvation process have made the problem somewhat difficult to address. The poor stability of triplets due to oxygen quenching makes the experimental measurements slightly difficult.⁴⁷ It has been established earlier that one could protect the phosphorescent molecules by including it within an organic capsule formed from octa acid (OA) host.⁴⁸⁻⁴⁹ The internal OA cavity of OA capsule is established to be non-polar in nature.⁵⁰⁻⁵¹ Consistent with the non-polar character and the tightness of the cavity no solvation of the excited coumarin occurred within the OA cavity.⁵² It is also known that molecular oxygen do not penetrate the OA cavity.⁵³ Most importantly, the small OA cavity with very little free space will not allow the large amplitude motion of the diethylamino group twisting and the TICT state will not be expected. Thus, we can anticipate phosphorescence from OA encapsulated 3I-C1 and 3Br-C1 if any triplet state is involved in the excited state deactivation of these molecules. In case of 3I-C1@OA₂, the presence of a broad band emission at longer wavelength (580 nm) along with the usual fluorescence (440 nm) and its gradual increase with lowering of temperature (figure 5.2.4.2) confirm

the long wavelength emission to be phosphorescence from the triplet. Time-delayed low temperature emission (77 K) of 3I-C1 in the glass forming liquid (ethanol-methanol mixture) shows an emission band around 540 nm. This also supported that the longer wavelength temperature dependent weak broadband emission observed for 3I-C1 inside OA cavity is room temperature phosphorescence.

In the transient absorption signal of 3I-C1@OA₂, the broad ESA band along with the long lifetime component clearly indicates the existence of the triplet state in case of 3I-C1@OA₂ (figure 5.2.4.3). Usually, the triplet states are closely spaced in terms of electronic energy and thus it is not surprising that the ESA band for a triplet state being broad in nature. We assign the >10 ns component as the triplet state and the 11.9 ps component to the S₁ state of 3I-C1@OA₂ the precursor for the triplet state. Based on the above observations, we propose that in 3I-C1@OA₂ it is the C-I vibration that takes the system to the T₁ state. We believe that due to this bond vibration mediated channel the S₁ state has a very short lifetime of 11.9 ps.

For 3Br-C1@OA₂, the 4.6 ns DAS has a strong SE feature (figure 5.2.4.3c), and we assign it to the lifetime of the S₁ state of 3Br-C1@OA₂. The short lifetime (13.5 ps) DAS mostly consists of an ESA band with a SE band at the blue edge of the observation window (figure 5.2.4.3c). We suspect this short lifetime component is associated with another emissive state, which resides on a completely different nuclear coordinate on the PES. At this stage we have no knowledge of its structure. The above theoretical and experimental studies suggest that the C–X (X=Br/I) bond vibration coordinate plays an important role on the fate of the excited singlet state of 3Br-C1 and 3I-C1. This also rationalizes the unusually high ϕ_f of 3Br-C1 compared to 3I-C1. However, the higher ϕ_f of 3Br-C1 compared to the parent C1, cannot be explained either by the C–X vibration or by the diethylamino twisting coordinates. We consider two reasons for this unusual behavior. First, we believe the reason lies on a different reaction coordinate, namely the solvent polarization coordinate. From the previous works we know that for similar coumarins like C1, there is an extra relaxation path from TICT→ground state via solvent fluctuation.⁵⁴ The nonradiative transition from the TICT to the GS happens to be PE barrier

mediated. The difference in this barrier height for C1 and 3Br-C1 is a plausible reason behind the higher ϕ_f of 3Br-C1 compared to C1. Secondly, from earlier reports it is evident that fluorescence quantum yield (ϕ_f) is related with the π -conjugation length (A_π).⁵⁵⁻⁵⁶ Longer the conjugation more efficient is the fluorescence.⁵⁵⁻⁵⁶

Upon photoexcitation of molecule from the S_0 to the S_1 state, permanent dipole generates at the S_1 state. This dipole can be represented as the π -conjugation length (A_π).⁵⁵⁻⁵⁶

From the excited S_1 state molecule can come back to the ground S_0 via radiative or non-radiative transitions. The radiative rate constant is given by⁵⁵⁻⁵⁶

$$k_r = A_{1,0} \quad (5.3.1)$$

where $A_{1,0}$ is the Einstein's transition rate constant for spontaneous emission.

Correlating the non-radiative rate constant to the relaxation of the induced dipole, we can use the Hush equation to write k_{nr} as,⁵⁵⁻⁵⁶

$$k_{nr} = k_0 e^{-\beta R} \quad (5.3.2)$$

Where, R is the distance between two charges (length of the dipole), β is a phenomenological constant and k_0 is the non-radiative rate constant when $R = 0$.

At $R = 0$, the k_{nr} has the highest possible value which means when $R=0$ the probability of transition from S_1 to S_0 is highest. Thus k_{nr} at $R = 0$ can be considered equal to the Einstein's transition rate constant for stimulated emission ($B_{1,0}$). Thus, we get⁵⁵⁻⁵⁶

$$k_{nr} = B_{1,0} e^{-\beta A_\pi} \quad (5.3.3)$$

Assuming the value of β to be 1 from the literature, we obtain⁵⁵⁻⁵⁶

$$k_{nr} = B_{1,0} e^{-A_\pi} \quad (5.3.4)$$

As,

$$B_{0,1} = B_{1,0} = \frac{c^3}{8\pi h \nu^3} A_{1,0} \quad (5.3.5)$$

Equation 5.3.4 modifies as⁵⁵⁻⁵⁶

$$k_{nr} = \frac{c^3}{8\pi h \nu^3} A_{1,0} e^{-A_\pi} \quad (5.3.6)$$

where c is the speed of light, h is the Planck constant and ν is the frequency of fluorescence maximum.

Using equation 5.3.1, we get⁵⁵⁻⁵⁶

$$\frac{k_{nr}}{k_r} = \frac{c^3}{8\pi h \nu^3} e^{-A_\pi} \quad (5.3.7)$$

$$\Rightarrow \frac{k_{nr}}{k_r} + 1 = \frac{c^3}{8\pi h \nu^3} e^{-A_\pi} + 1$$

$$\Rightarrow \frac{1}{\frac{k_{nr}}{k_r} + 1} = \frac{1}{\frac{c^3}{8\pi h \nu^3} e^{-A_\pi} + 1}$$

$$\Rightarrow \frac{k_r}{k_r + k_{nr}} = \frac{1}{\frac{c^3}{8\pi h \nu^3} e^{-A_\pi} + 1}$$

$$\Rightarrow \phi_f = \frac{1}{\frac{c^3}{8\pi h \nu^3} e^{-A_\pi} + 1} \quad (5.3.8)$$

The parameter A_π can be think of as the change in dipole moment ($\Delta\mu = \mu_e - \mu_g$) upon photoexcitation.⁵⁵⁻⁵⁶ From Lippert-Mataga formulation we can write

$$\Delta\mu \propto (\bar{\nu}_a - \bar{\nu}_f)^{1/2} a^{3/2} \quad (5.3.9)$$

Hence, equation 5.3.8 reforms into

$$\phi_f = \frac{1}{\frac{c^3}{8\pi h \nu^3} e^{-(\bar{\nu}_a - \bar{\nu}_f)^{1/2} a^{3/2}} + 1} \quad (5.3.10)$$

Where $\bar{\nu}_a$ is the wavenumber of absorption and $\bar{\nu}_f$ is the wavenumber of fluorescence, which are known from the steady state data. The a is the molecular radii and was determined from the DFT calculations. Using all these inputs, we find that the $\Delta\mu$ trend for the three coumarins are 3Br-C1 $\approx$ 3I-C1>C1. Therefore, the ϕ_f order should also be 3Br-C1 $\approx$ 3I-C1>C1.

This estimated ϕ_f order will only be valid for a set of molecules for which there is no extra non-radiative deactivation channel operational for any one of them. In case of 3I-C1, the ISC channel is extremely favourable, which decreases the actual ϕ_f of 3I-C1 from the value estimated by equation 5.3.9. On the other hand, as in case of both C1 and 3Br-C1, ISC is unfavourable, the estimated ϕ_f order between them holds in reality. This explains the higher ϕ_f of 3Br-C1 compared to C1.

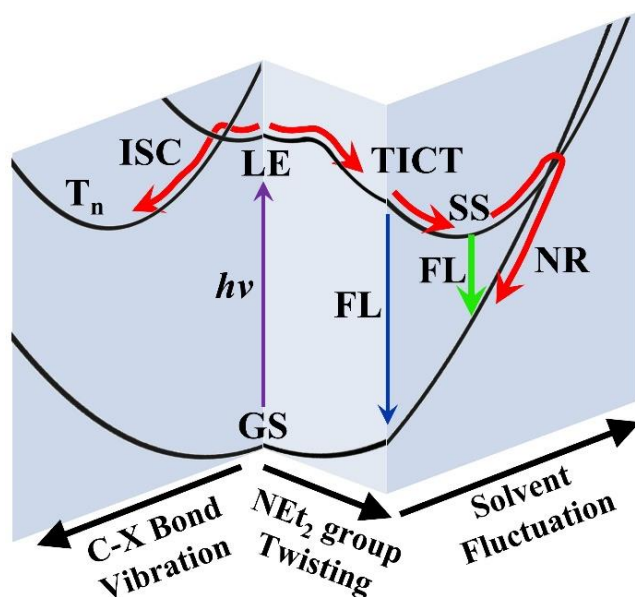


Figure 5.3.1. A general relaxation scheme for photo-excited 3X-C1 (X= H, Br, I). Depending upon X and medium, the PE barrier on each coordinate varies. Thus, for a particular molecule in a particular medium relaxation through some coordinate becomes predominant whereas relaxation through the other paths become negligible.

We present a scheme for the overall relaxation processes of photoexcited 3X-C1 (X= H, Br, I) in figure 5.3.1. Following excitation, they can follow the diethylamino twisting coordinate to reach the TICT state followed by solvation of the TICT to SS. At the same time, the system can also reach the triplet state through a different coordinate namely carbon-halogen bond vibration. The propensity of ISC path along the vibration coordinate depends on the barrier height present along the bond vibration coordinate. According to the results presented above, the preferred relaxation channel depends strongly on the nature and position of halogen substitution. For example, as the barrier height between the singlet (S_1) and triplet (T_2) states along the bond vibration coordinate is negligible for 3I-C1 (see figure 5.2.3.3c), it prefers to follow this path rather than the one which leads to SS. It explains the lack of fluorescence in 3I-C1. On the other hand, in 3Br-C1 the barrier height between the same singlet and triplet states along the C-Br vibration coordinate is significant (see figure 5.2.3.3b). Most likely this forces the molecule to avoid this path relative to TICT pathway leading to SS. Similar is the case for C1. In this case there is no crossing between singlet and triplet surfaces and therefore it reaches the

SS via the only available diethylamino twisting coordinate (see figure 5.2.3.3a). In figure 5.3.1, only the relaxation of the most stable form of the TICT along the solvent fluctuation coordinate is shown. Due to solvent fluctuation, the SS state crosses with the GS through an energy barrier at a particular solvent orientation where the solvated TICT (i.e. SS) and GS are isoenergetic.⁵⁴ We propose that the difference in this barrier height is a plausible explanation of higher ϕ_f value for 3Br-C1 than C1. The figure 5.3.1 will depend on the medium. For example, inside OA capsule the solvent fluctuation coordinate will be insignificant as the capsule interior lacks any solvent.⁵²

To examine whether the involvement of C–X bond vibration in ISC is a general feature, a similar approach was taken to a completely different yet simpler molecular system, namely 1-iodonaphthalene, 1-bromonaphthalene and 2-bromonaphthalene (1I-Nap, 1Br-Nap, and 2Br-Nap, respectively). The ratio of the square of SOC constant to ISC rate constants for 1I-Nap and 1Br-Nap—are 0.5 and 1.1, respectively.^{10,12} The PECs along the C–X bond length coordinate of all the three molecules were constructed by TD-DFT calculation (see figure 5.3.2). For 1I-Nap a crossing between S_1 and T_4 states has been noticed around the LE state, and its difference compared to the Br-counterparts are distinctly visible. On the other hand, both 1Br-Nap and 2Br-Nap must undergo bond elongation before reaching the crossing point between S_1 and T_5 . The difference in the PE barrier to the triplet crossing for 1Br-Nap and 2Br-Nap is evident, where it is smaller in the former. The experimental observation of ϕ_f of 1Br-Nap (0.67%) and 2Br-Nap (1.25%) are proposed to be due to the difference in PE barrier along the C-Br bond vibration coordinate. However, for a precise comment on this, higher level theoretical calculations are necessary. This agreement between theoretical prediction and experimental result indicates that this model based on molecular vibrations should be useful for future studies on the effect of position dependent substitution on the ISC rate.

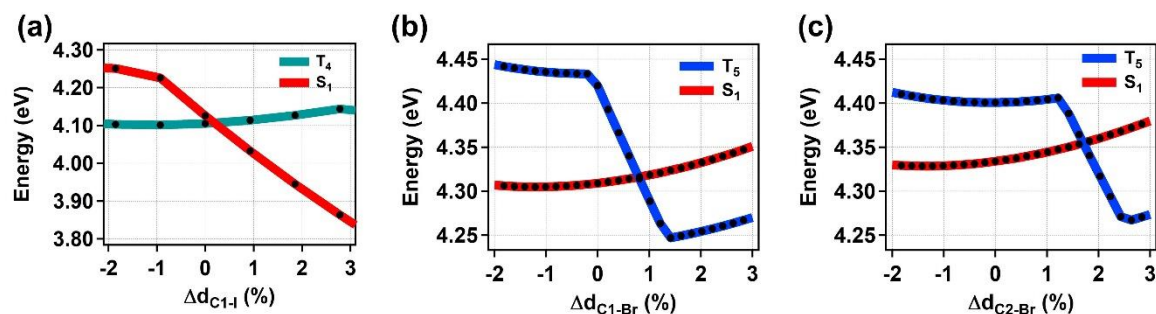


Figure 5.3.2. Potential energy curves (PEC) along the Cn-X (n=1, 2; X=Br, I) bond vibration coordinate for the (a) 1-Iodo-naphthalene (1I-Nap), (b) 1-Bromo-naphthalene (1Br-Nap) and (c) 2-Bromo-naphthalene (2Br-Nap). For better clarity only the S₁ and T₄ surfaces for 1I-Nap and the S₁ and T₅ surfaces for 1Br-Nap and 2Br-Nap were plotted. B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C & H and LANL2DZ basis set for Br and I were used for the TD-DFT calculations to determine the PECs. DFT calculations were performed using Gaussian 09 package.³⁷ $\Delta d_{Cn-X}(\%)$ denotes the % change in Cn-X (n=1, 2; X=Br, I) bond length (d_{Cn-X}). $\Delta d_{Cn-X}(\%) = (\Delta d_{Cn-X}(\text{\AA}) / d_{Cn-X}^{eq}(\text{\AA})) \times 100\%$. d_{Cn-X}^{eq} is the equilibrium Cn-X bond length in electronic ground state.

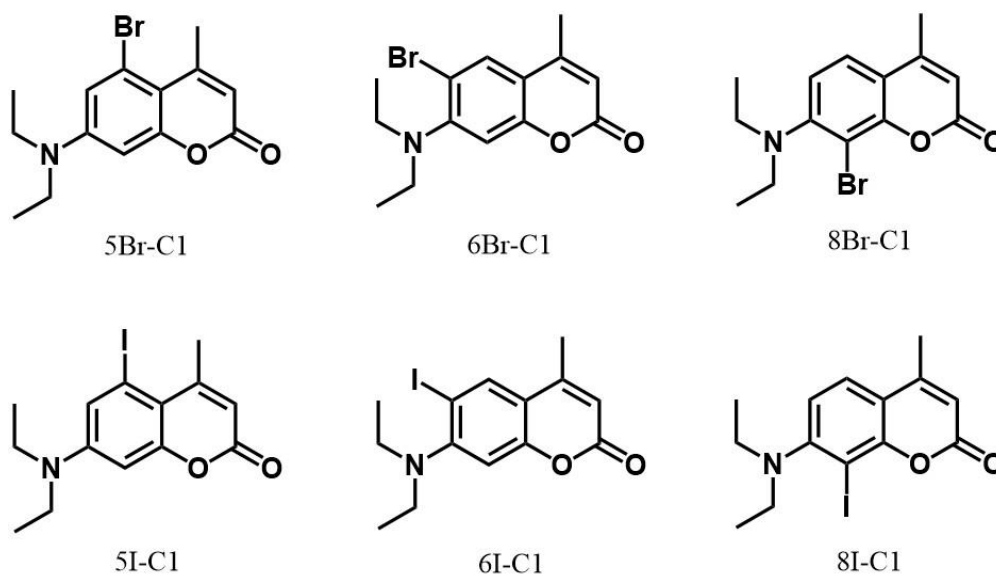


Figure 5.3.3. Structures of the molecules used for TD-DFT calculations

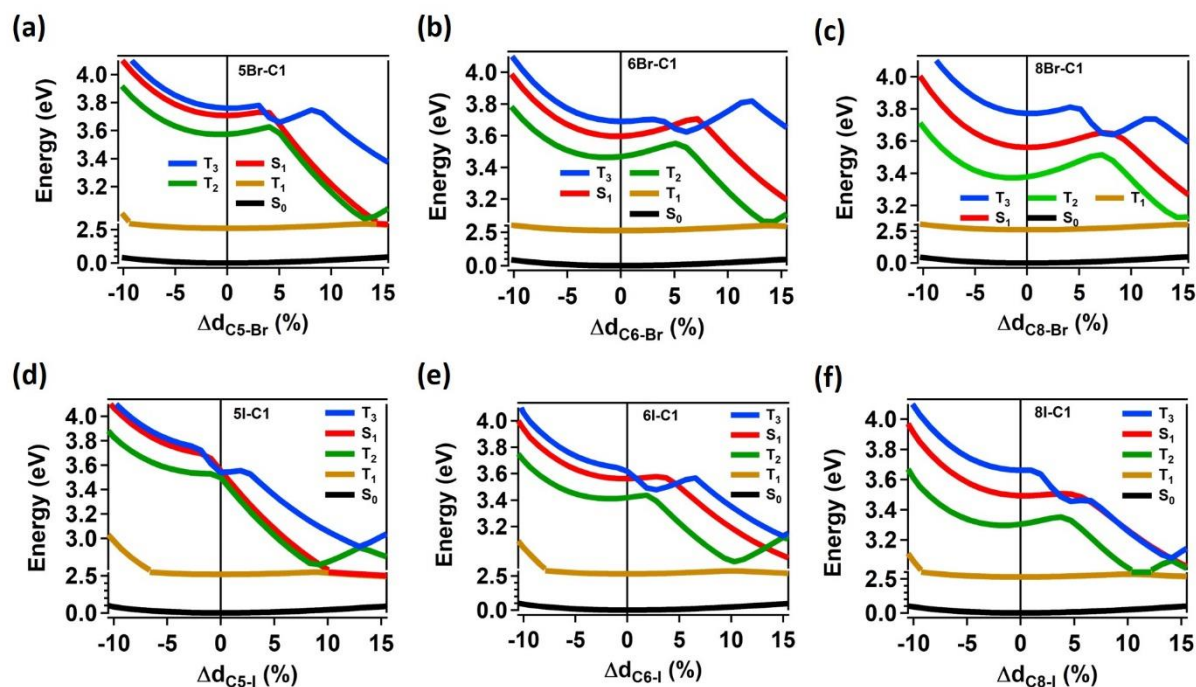


Figure 5.3.4. Potential energy curves (PEC) along the bond length variation coordinate of the (a) C5-Br bond of the 5-Bromo-7-diethylamino-4-methylcoumarin, (b) C6-Br bond of the 6-Bromo-7-diethylamino-4-methylcoumarin, (c) C8-Br bond of the 8-Bromo-7-diethylamino-4-methylcoumarin, (d) C5-I bond of the 7-Diethylamino-5-iodo-4-methyl coumarin, (e) C6-I bond of the 7-Diethylamino-6-iodo-4-methyl coumarin and (f) C8-I bond of the 7-Diethylamino-8-iodo-4-methyl coumarin. We have used the B3LYP exchange correlation functional and 6-311++G (d,p) basis set for C, H, N, O and LANL2DZ basis set for Br and I for the TD-DFT calculations to determine the PECs. DFT calculations were performed using Gaussian 09 package.³⁷ $\Delta d_{Cn-X}(\%)$ denotes the % change in $Cn-X$ ($n=5, 6, 8$; $X=Br, I$) bond length (d_{Cn-X}). $\Delta d_{Cn-X}(\%) = (\Delta d_{Cn-X}(\text{\AA})/d_{Cn-X}^{eq}(\text{\AA})) \times 100\%$. d_{Cn-X}^{eq} is the equilibrium $Cn-X$ bond length in electronic ground state.

We also use this approach to predict the trend of ISC and ϕ_f for the other possible halo-substituted coumarin 1 derivatives, namely 5-bromo-coumarin 1 (5Br-C1), 6-bromo-coumarin 1 (6Br-C1), 8-bromo-coumarin 1 (8Br-C1), 5-iodo-coumarin 1 (5I-C1), 6-iodo-coumarin 1 (6I-C1) and 8-iodo-coumarin 1 (8I-C1). The structures of these molecules are given in figure 5.3.3. The PECs along the C-halogen bond length for these halo-derivatives are displayed in figure 5.3.4. For all these molecules crossing of S_1 and T_3 states can be found at some point of the C-X ($X=Br/I$) bond length variation coordinate. At this level of theory, a precise prediction of the values of PE barrier is not possible. However, it is obvious that the barrier height to reach the S_1 - T_3 crossing is different for all these molecules that depends on the position of

the Br/I substitution. We expect the fluorescence quantum yields to increase or decrease as the PE barriers decrease or increase. To check the validity of the above results, synthesis of these molecules and the subsequent determination of their fluorescence quantum yield is necessary, which is reserved for the future.

Present study suggests that for the molecular systems where a strong coupling between states is present along the vibrational coordinates, Marcus theory is valid and rate constant of ISC and free energy barrier should be correlated. We believe that with proper choice of a molecular system one can experimentally verify this prediction. We plan to pursue this line of approach in the near future.

5.4. Conclusions

Iodo substitution of the parent coumarin C1 decreases the fluorescence quantum yield to large extent as expected, whereas the bromination of C1 surprisingly increases the fluorescence quantum yield. This anomalous observation could not be described from the viewpoint of SOC constants alone. Detailed TA study and TD-DFT calculation reveals that C-X bond vibration largely controls the ISC in these halo-coumarins and hence dictates the whole excited state relaxation process of 3Br-C1 and 3I-C1. The rate constant of ISC for 3I-C1 is 11.9 ps whereas ISC is forbidden in case of 3Br-C1 due to presence of a 0.12 eV PE barrier on the C3-Br bond vibration coordinate. Vibration controlled ISC was also observed for halo-naphthalenes, where SOC approach fails to fully predict the extent of ISC, but bond vibration model does. We also have successfully predicted the position dependency of halogen insertion on fluorescence quantum yield using the model. Overall, we propose that C-X bond vibration plays a crucial role in ISC. It also explains the effect of heavy atom insertion in different position of a molecule. We believe that while engineering RTP molecules using heavy atom, one should always consider the position dependence of heavy atom insertion. Constructing PES by TD-DFT calculation for the targeted molecules, should reveal the position in which halogen insertion will give most efficient ISC. We are optimistic that Marcus inversion in ISC will be observed in the future by examining a series of molecules chosen based

the C-X vibrational model discussed here. To achieve this goal extensive experimental, theoretical and synthetic studies are required.

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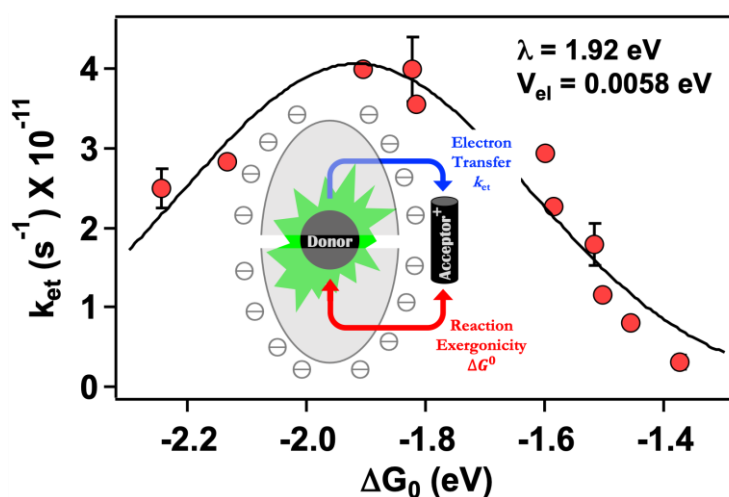
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Chapter 6

Marcus Relationship Maintained During Ultrafast Electron Transfer Across a Supramolecular Capsular Wall



Aritra Das, Nareshbabu Kamatham, A. Mohan Raj, Pratik Sen and V. Ramamurthy, *The Journal of Physical Chemistry A*, **2020**, 124 (26), 5297-5304

In this chapter, I have proved the existence of Marcus inverted region for electron transfer (ET) reaction between photo-excited donor and acceptor separated by the molecular wall of octa acid (OA). I have determined the rate constant of ET by tracking the transient absorption signal of the viologen radical cation formed as the product of ET. Electronic coupling value obtained from the fitting of Marcus bell-shaped plot was significant. This suggests despite being separated by molecular wall, there is electronic coupling between the donor and acceptor. Comparison with previous report has enlightened the role of OA molecular wall on the ET.

6.1. Introduction

Electron transfer plays a prominent role in several important events such as photosynthesis, solar energy storage, metabolic and respiratory processes, photocatalysis, electrical conduction in organic materials and several organic and inorganic reactions.¹⁻⁶ In such studies occurrence of electron transfer at short as well as long distances have been noted. The rate of electron transfer that occurs via classic tunneling mechanism is established to exponentially increase with decrease in donor-acceptor distance.⁵ Challenging long distance electron transfer investigations have involved protein,⁷⁻¹² DNA¹³⁻¹⁶ and hydrocarbon chains as scaffolds and covalently linked donor-acceptor systems.¹⁷⁻²⁰ In these systems electron transfer occurs either through hopping or *via* super-exchange mechanism involving σ or π bonds. In addition to these, there are systems wherein electron transfer occurs through non-covalent interactions,¹⁷ in frozen and free solvents,²¹⁻²⁴ with the help of a solvent molecule trapped between a C-clamp molecule²⁵⁻²⁸ and in mixed donor-acceptor melts.²⁹⁻³¹ Inter-protein electron transfer that involves solvent mediation belong to this category.¹⁰⁻¹² These studies suggest that for electron transfer to occur donor and acceptor molecules need not be within collisional distance or covalently linked. Presence of another molecule in between a donor and an acceptor apparently would not inhibit the electron transfer and its presence, in fact, is better than vacuum.²⁰

Among supramolecular assemblies, to our knowledge, the Cram-type carcerand³² is an unique assembly where the donor and acceptor molecules could be well separated by the host wall. Energy and electron transfer have been established to occur between the donor and acceptor molecules, one trapped within the Cram-type carcerand and the other free outside in solution.³³⁻³⁹ In fact, results reported with these systems have laid the groundwork for the current undertaking. Unfortunately, since the interior of the Cram-type carcerand is small its generality is limited. Most guests need to be included during the synthesis of the carcerand.

In the current study, we employ a synthetic host known as octa acid (OA)⁴⁰ whose structure and internal dimensions are provided in figure 6.1.1. Unlike Cram-type

carcerand, the OA capsule is made up of two molecules of OA that assemble in presence of a hydrophobic guest molecule. This plus larger internal dimension allow inclusion of a wider variety of guest molecules.⁴¹ Importantly, the capsule is tight and takes a few milliseconds to partially open and close.⁴²⁻⁴³ Therefore, during the time of electron transfer between encapsulated excited donor and the acceptor the capsule remain tightly closed similar to that of Cram-type carcerand.⁴⁴

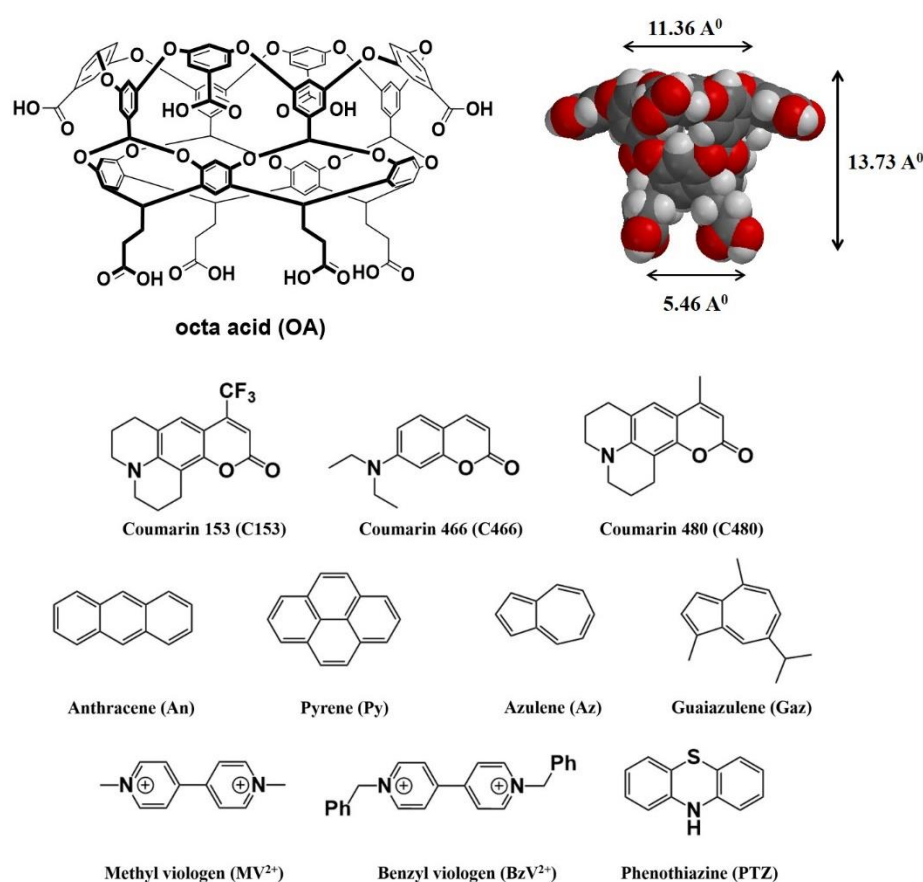


Figure 6.1.1. Chemical structure of donor and acceptor molecules used in the present study. OA was synthesized by Prof. V. Ramamurthy Group in University of Miami, USA.

Furthermore, prior studies have established the interior of the capsule to be dry and not to contain water molecules.⁴⁴⁻⁴⁵ These would mean that prior to and after the electron transfer only the interior wall of OA would surround the donor molecule. Because of the tightness of the capsule, at no stage during the excited state life-time of the donor there is direct contact between the donor and acceptor molecules as well as between the donor and exterior water molecules. Therefore, the OA system we

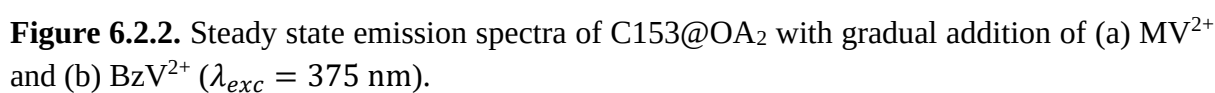
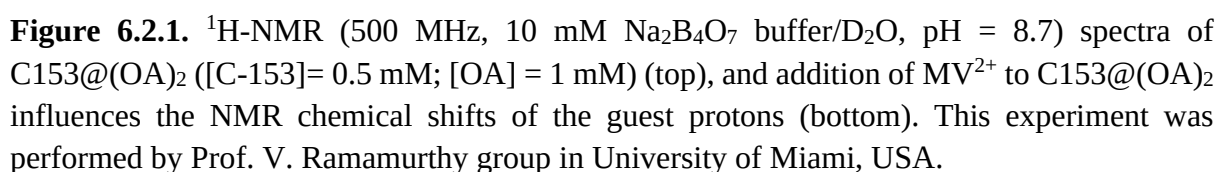
have chosen allows probing the importance of a permanent organic molecular wall during electron transfer between the encapsulated donor and free acceptor. One could visualize this to be a model for electron transfer across a solvent molecule that is permanently placed between the donor and the acceptor. Similarity between the current assembly and solvent mediated C-clamp system,²⁷ Cram-type carcerand assembly³⁵ and the solvent separated radical ion pairs⁴⁶ is obvious. At the same time, the OA capsule based system is unique: the wall is permanent and the donor and acceptor are held closer by Coulombic attraction that makes the electronic coupling between the donor and acceptor stronger. We believe the electronic coupling required for electron transfer between the encapsulated donor and nearby acceptor must involve the host wall.

We have recently demonstrated the occurrence of photoinduced electron transfer between OA encapsulated donors (stilbene, coumarins and azulenes) and methyl viologen acceptor in phosphate/borate buffer solution (pH $\sim$ 7.4 and 8.7).⁴⁷⁻⁵² Through time resolved experiments we have identified the formation of methyl viologen radical cation as well as stilbene radical cation, the products of electron transfer. With the help of ultrafast time resolved experiments the forward electron transfers were found to occur with time constants between 1-25 ps. Although the above experiments unequivocally established the occurrence of electron transfer across the capsular wall the mechanism is not clear. Based on known lower β values of solvents such as tetrahydrofuran and water ($1.2 \text{ \AA}^{-1}$ and $1.68 \text{ \AA}^{-1}$, respectively) with respect to vacuum ($3.5 \text{ \AA}^{-1}$)^{22-23, 53} we believe that the capsular wall can transport electron from the encapsulated excited donor to free acceptor and will not be passive. Similar to solvent molecules one would expect the OA frame that is made up of electron rich benzyl units to have lower β value, certainly well below vacuum. However, unlike solvent molecules the OA frame is not soft and flexible.⁵⁴ Because of this the OA cavity would not be expected to help prepare the excited donor for electron transfer (conversion of D to D⁺•) although it might help transport an electron across the wall. The current experiments are directed towards understanding: (a) whether the electron transfer occurs by super-exchange

mechanism involving the host wall or via the classic tunneling by-passing the wall, (b) whether it proceeds via adiabatic or nonadiabatic pathway, *i.e.*, how strong is the electronic coupling (V_{el}) between the reactant and the product, and (c) what is the value of reorganization energy (λ) as defined by the Marcus equation.⁵⁵⁻⁵⁹ We expected study of a series of donor-acceptor pairs with varying ΔG° values would provide answers to the above questions. With this in mind, we have investigated electron transfer between donors and acceptors listed in figure 6.1.1. In the following sections results of these experiments are presented and discussed. Interestingly the Marcus relationship between the rate and ΔG° was noted and a non-zero value for V_{el} was calculated from the plot. Unexpectedly higher λ value (reorganization energy) was revealed, which is possibly a consequence of the rigidity surrounding the donor.

6.2. Results

Chemical structures of seven donors and two acceptors used in this study are provided in figure 6.1.1. Complexation of the donors with the host OA was confirmed from their ^1H NMR spectra. Several OA-guest complexes probed here have been characterized earlier during our other investigations.^{48-51, 60} Expected upfield shift of the guest signals was observed upon inclusion within OA. In addition, the diffusion constants measured by DOSY NMR were consistent with that of capsular assembly.^{45, 61} ^1H NMR titration experiments confirmed the OA-guest complex to be 2:1. In presence of OA, although the ^1H NMR chemical shifts of the donors, as expected, shifted upfield, that of acceptors MV^{2+} and BzV^{2+} were not affected by OA.^{48, 60} However, diffusion constants of the viologens in presence of donor@OA₂ were same as that of the complex. These suggested that MV^{2+} and BzV^{2+} were not included within OA but remained attached to the capsule. Interestingly, upon addition of MV^{2+} to C153@OA₂ complex in borate buffer (D_2O) the signals of C153 shifted upfield (Figure 6.2.1). This indicated that MV^{2+} influenced the extent of diamagnetic shielding provided by the capsular wall.



Obviously the electronic/magnetic effect of MV^{2+} is able to penetrate the capsular wall and reach the guest molecules present within the capsule. Additional information regarding the interior of the capsule came from the emission maxima of the coumarins⁶² and I_1/I_3 value of the pyrene fluorescence.⁶³ These suggested that the capsular interior has no water molecules and the guest alone is present within the OA capsule.⁴⁴⁻⁴⁵

Fluorescence of OA encapsulated guest molecules were quenched by viologen acceptors present in aqueous solution. As representative examples, the spectra for $C153@OA_2$ in presence of varying amounts of MV^{2+} and BzV^{2+} are provided in Figure 6.2.2. As seen in the figure, upon addition of the viologens the coumarin emission intensity decreases. Given the excited singlet state energies of the viologens are higher than that of the entrapped guests, we conclude the observed decrease is not due to energy transfer. Confirmation that the quenching is due to electron transfer came from identification of the products of electron transfer, the donor cation radical and the viologen mono-cation radical. Due to experimental difficulties the transient absorption spectra of the cation radicals of the coumarins and aromatics listed in figure 6.1.1 could not be recorded. However, we have unequivocally identified the formation of stilbene cation radical in $stilbene@OA_2 - MV^{2+}$ system by recording the transient absorption of stilbene cation radical.⁶⁰ Based on this observation we conclude that electron transfer is the primary cause of fluorescence quenching in the donor-acceptor systems investigated here. The transient absorption spectra of mono-cation radicals of methyl viologen and benzyl viologen (i.e. $MV^{+\bullet}$ and $BzV^{+\bullet}$), the products of electron transfer from the encapsulated excited donors to MV^{2+} and BzV^{2+} , recorded in this study supported this conclusion. Representative transient spectra recorded in the case of $C153@OA_2 - MV^{2+}$ are provided in Figure 6.2.3. Thus, upon excitation the donor present within the ‘dry’ OA capsule transfers an electron to the acceptor attached to the exterior wall.

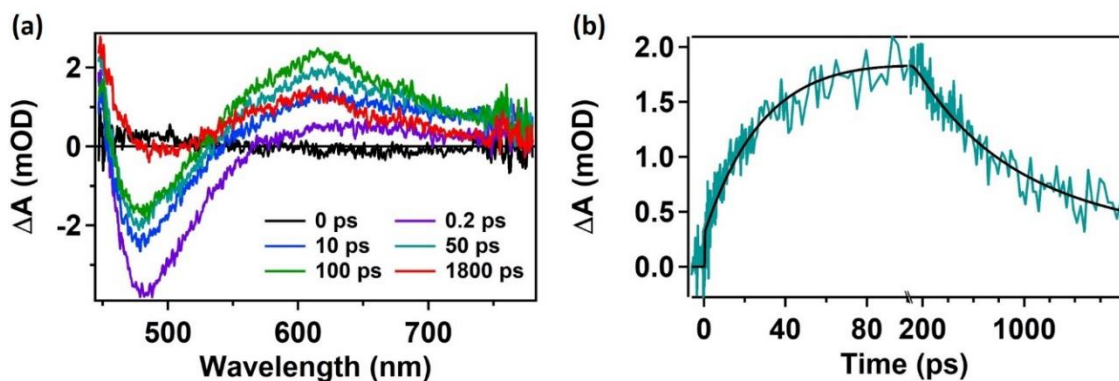


Figure 6.2.3. Plot of (a) transient absorption spectra at different time delay (in the early time stimulated emission of the C153 can be seen and with time it decreases and the absorption band at 610 nm which is due to the formation of $MV^{+\bullet}$, starts to increase) and (b) kinetic trace at 610 nm along with the fit (black solid line) for C153@OA2 in presence of 10 mM MV^{2+} (pump pulse: 400 nm, probe: 450-760 nm)

The rates of photoinduced electron transfer (PET) were estimated by monitoring the rise and decay of $MV^{+\bullet}$ and $BzV^{+\bullet}$ by recording their transient spectra following excitation of the encapsulated donors. For these experiments, phosphate buffer (pH ~ 7.4) solutions of 100 μM 1:2 donor@OA₂ complexes and 10 mM viologen (MV^{2+} and BzV^{2+}) were used. To initiate the PET reaction, the encapsulated guest was excited with a 400 nm pump pulse. To ensure the detection of the viologen radical cation that absorbs around 610 nm, transient absorption spectra were recorded from 450-760 nm. In Figure 6.2.3 the transient absorption spectra for C153@OA₂ in presence of MV^{2+} recorded at different time delays following pumping are displayed. In the figure 6.2.4, the data for remaining systems are depicted. Quenching of C153 stimulated emission in concurrence with the rise of a new absorption band centered at 610 nm due to $MV^{+\bullet}$ are clearly visible. The rate constants of the formation and decay of the $MV^{+\bullet}$ were extracted from the plot of the change in absorbance at 610 nm with respect to the delay time (Figure 6.2.3b). After deconvoluting the Gaussian shaped instrument response function with 150 fs FWHM, the above curve was fitted with sum of three exponential functions. The same procedure was followed for all donor@OA₂-acceptor systems (Figure 6.2.4). The fitting parameters are tabulated in Table 6.2.1. For all cases, three exponentials were necessary to satisfactorily fit the data. Of the three, one is the rise component

and other two are decay components. We assign the rise component as the inverse of the bimolecular PET rate constant (k_{et}).

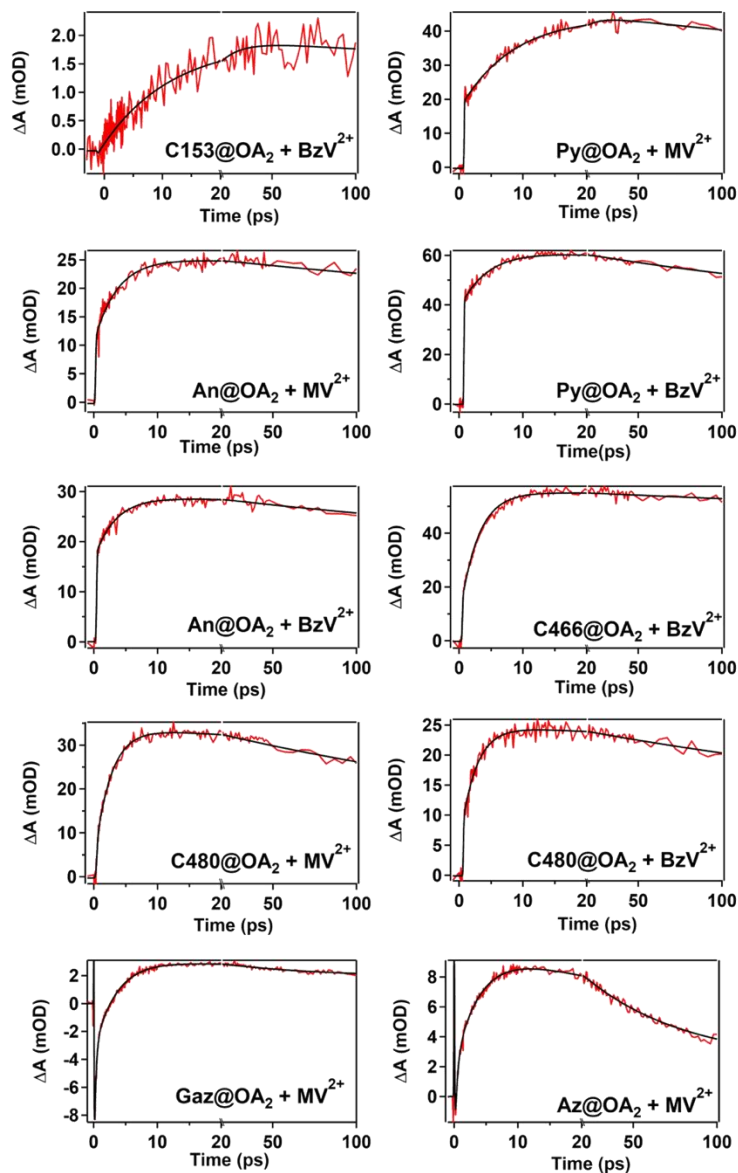


Figure 6.2.4. Plot of kinetic traces at 610 nm along with the best fit (black solid line) for the following pairs: C153@OA₂ + BzV²⁺, Py@OA₂ + MV²⁺, An@OA₂ + MV²⁺, Py@OA₂ + BzV²⁺, An@OA₂ + BzV²⁺, C466@OA₂ + BzV²⁺, C480@OA₂ + MV²⁺, C480@OA₂ + BzV²⁺, Gaz@OA₂ + MV²⁺ and Az@OA₂ + MV²⁺. (pump pulse : 400nm, IRF = 110 fs, probe: 450-760 nm)

In order to correlate k_{et} with free energy change (ΔG°) of electron transfer as per Rehm-Weller equation (see chapter 1 for details).^{6, 64} we needed to know the

oxidation potential of the donor (E_{D/D^+}), reduction potential of the acceptor (E_{A^{2+}/A^+}), Coulombic term ($\frac{e^2}{\epsilon_s r_0}$) and the excitation energy ($E_{0,0}$).

$$\Delta G^0 = E_{D/D^+} - E_{A^{2+}/A^+} - E_{0,0} - \frac{e^2}{\epsilon_s r_0} \quad (6.2.1)$$

Table 6.2.1. Fitting parameters of the kinetic traces at 610 nm and Rehm Weller parameters for all the donor-acceptor pairs

Pairs	a_1	$\tau_1(\text{ps})$	a_2	$\tau_2(\text{ps})$	a_3	$\tau_3(\text{ps})$	E_{D/D^+} in ACN (eV)	E_{D/D^+} in OA (eV)	E_{A^{2+}/A^+} in OA (eV)	$E_{0,0}$ (eV)	$\frac{e^2}{\epsilon_s r_0}$ (eV)	ΔG^0 (eV)	$k_{et}(\text{s}^{-1})$ $\times 10^{-12}$
C153+MV ²⁺	- 0.00179	31.1	0.00145	694	0.00066	3430	0.89	0.505	-0.655	2.78	0.245	-1.375	0.032
C153+BzV ²⁺	- 0.00204	12.2	0.00143	830	0.00054	2878	0.89	0.505	-0.573	2.78	0.245	-1.457	0.082
Py+MV ²⁺	- 0.02629	8.6	0.02198	416	0.02402	3580	1.4	1.015	-0.655	3.42	0.245	1-.505	0.116
An+MV ²⁺	- 0.01393	5.5	0.01237	447	0.01331	3640	1.185	0.8	-0.655	3.22	0.245	-1.52	0.180
Py+BzV ²⁺	- 0.02064	4.4	0.02336	195	0.03944	6500	1.4	1.015	-0.573	3.42	0.245	-1.587	0.227
An+BzV ²⁺	- 0.01118	3.4	0.01021	275	0.01899	4720	1.185	0.8	-0.573	3.22	0.245	-1.602	0.294
C466+BzV ²⁺	- 0.04031	2.8	0.00547	285	0.05029	4550	0.92	0.535	-0.573	3.17	0.245	-1.817	0.357
C480+MV ²⁺	- 0.02612	2.5	0.02373	264	0.01071	2070	0.72	0.335	-0.655	3.06	0.245	-1.825	0.400
C480+BzV ²⁺	- 0.01547	2.5	0.01341	270	0.01161	2300	0.72	0.335	-0.573	3.06	0.245	-1.907	0.400
GAz+MV ²⁺	- 0.00664	3.5	0.00128	61	0.00193	8550	0.65	0.265	-0.655	3.3	0.245	-2.135	0.285
Az+MV ²⁺	- 0.01020	4.0	0.00805	55	0.00273	1150	0.71	0.325	-0.655	3.47	0.245	-2.245	0.250

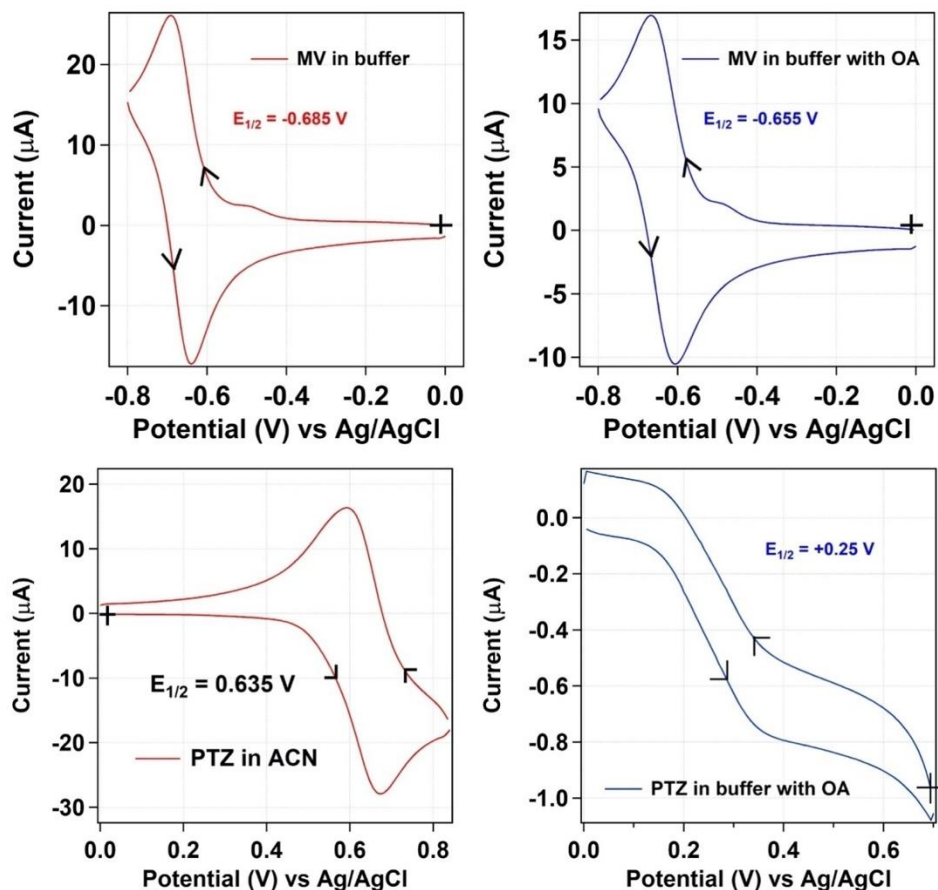
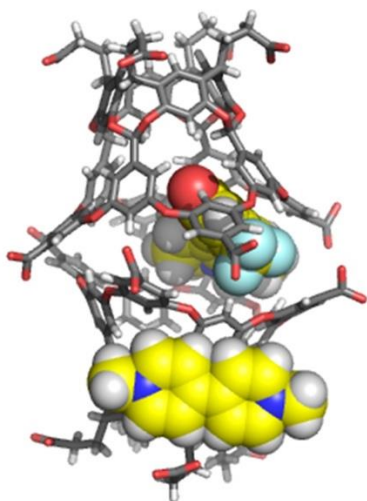


Figure 6.2.5: Cyclic voltammetry of methyl viologen (MV^{2+}) in absence and in presence of OA in aqueous buffer solution and of phenothiazine (PTZ) in acetonitrile (ACN) and inside OA cavity. All the oxidation and reduction potentials were measured with respect to Ag/AgCl electrode.

It is important to note that oxidation of the donor occurs within the non-polar OA capsule while the reduction occurs in aqueous phosphate/borate buffer, under two different environments. In addition, it should be noted that the location of reduction is the exterior of OA capsular wall where the acceptor is Coulombically attached. Also, following reduction since the charge reduces only by a unit (from $2+$ to $1+$), $\text{MV}^{+•}$ would still be attached to the capsule. Therefore, it is important to measure the reduction potential of acceptors in aqueous buffer in presence of OA and the oxidation potential of the donors within OA capsule. Cyclic voltammetry (CV) was used to estimate the oxidation and reduction potentials of the donor and acceptors in presence of OA. The reduction potential of MV^{2+} in water with respect to Ag/AgCl is found to be 0.685 V . In OA medium it decreased to 0.655 V (ref: Ag/AgCl; for

cyclic voltammogram (see Figure 6.2.5). The same shift in reduction potential was assumed for BzV^{2+} as well.

However, measurement of the oxidation potentials of donors encapsulated within OA cavity required an indirect approach. Oxidation potentials of the all coumarin derivatives, anthracene, pyrene, azulene and guaiazulene are greater than 0.8 V⁶⁵ whereas the electrochemical window for water is only up to 0.8 V.⁶⁶ This limited the direct measurement of oxidation potential of donor@OA₂ in water. To overcome this problem, we adopted an indirect method. Employing phenothiazine (PTZ), whose oxidation potential is less than 0.8 V,⁶⁷ as the standard we corrected the oxidation potential of others. The oxidation potential of PTZ in acetonitrile with respect to Ag/AgCl was measured to be 0.635 V (Figure 6.2.5). On the other hand, the oxidation potential of PTZ included within OA capsule was found to be 0.25 V. Comparing the oxidation potential of PTZ in acetonitrile with that in OA capsule, it is clear that the oxidation potential decreased by 0.385 V. Using this as the correction factor we converted the oxidation potential in acetonitrile (Ag/AgCl) of donors to that within OA₂ capsule. The excitation energy ($E_{0,0}$) required in eq. 1 was calculated from the 0-0 band of steady state absorption and emission spectra. For the calculation of the last term in eq. 1, we needed the values of electronic charge (e), permittivity of the solvent (ϵ_s), which is the product of permittivity of vacuum (ϵ_0) and the relative permittivity of the solvent (ϵ_r), and the separation distance (r_0) between the donor and the acceptor. The separation distance r_0 was estimated to be 8.9 Å for C153@OA₂ – MV²⁺ by MD simulation (Figure 6.2.6).⁴⁸ The MD simulation suggests that MV²⁺ resides at the bottom of the capsule rather on the side. Given that all the donors are within the OA cavity and the structures of MV²⁺ and BzV²⁺ are nearly the same, we have used the same value of r_0 for all other pairs. Considering the nature of the OA wall, ϵ_r is taken as relative permittivity of methyl benzoate (6.6).⁶⁸ The estimated values of the Coulombic term are tabulated in Table 6.2.1.



C153@OA₂ - MV²⁺ complex

Figure 6.2.6. MD simulated structures of C-153@OA₂—MV²⁺ ternary complex. MD simulation carried out with OPLS-AA force field and GROMACS software package. (Figure reproduced with permission from Chuang, C.-H.; Porel, M.; Choudhury, R.; Burda, C.; Ramamurthy, V., Ultrafast Electron Transfer across a Nanocapsular Wall: Coumarins as Donors, Viologen as Acceptor, and Octa Acid Capsule as the Mediator. *J. Phys. Chem. B* **2018**, 122, 328-337)

6.3. Discussion

Results accumulated thus far on donor@OA₂—acceptor systems are summarized below: (a) Photoinduced electron transfer across the OA capsular wall does occur with rate constants varying between 3.2×10^{10} and $4 \times 10^{11} \text{ s}^{-1}$ (Table 6.2.1). (b) Rate of photoinduced electron transfer shows a Marcus type correlation with ΔG^0 (Figure 6.3.1). (c) Remarkably, the above plot exhibits Marcus inversion. (d) NMR spectra supports the existence of electronic/magnetic interaction between the capsuled donor (C153) and the acceptor (MV²⁺) present outside the capsule (Figure 6.2.1). (e) Molecular dynamics (MD) simulation carried out previously with OPLS-AA force field and GROMACS software package suggested that the MV²⁺ is located closer to the OA capsule containing three different coumarins (C153).⁴⁸ The modeled structure shown in Figure 6.2.6 is consistent with the NMR spectra mentioned above (Figure 6.2.1). (f) Quantum chemical calculations employing time-dependent density functional theory (TDDFT) using the polarizable continuum

model (PCM) carried out earlier suggest that OA capsule acts as a charge acceptor upon excitation of the encapsulated C153.⁴⁷ Apparently, upon excitation the electron density shifts from C153 to the wall. This unusual behavior is an early indication of what is likely to happen when there is an acceptor adjacent to the wall. (g) Electron rich character of OA is revealed by fluorescence quenching of excited acceptors such as N-methylacridinium iodide, dimethyldiazapyrenium iodide and dimethyldiazaphenanthrenium iodide by OA.⁶⁹ Based on these the oxidation potential of OA was estimated to be ~ 1.5 eV. Thus OA by nature is a good electron donor. (h) With the help of fluorescence probes such as pyrene, pyrene aldehyde and coumarin 1, the interior of the capsule is concluded to be non-polar and free from water molecules.⁴⁵ This suggests that the donor molecule's immediate environment would only be the rigid capsular wall. (i) Results of NMR and EPR studies revealed that the OA encapsulated guest molecule have limited freedom of motion within the capsule and it is not frozen as in a glass or solid.⁶¹ (j) Ultrafast solvation dynamic studies have established that the OA capsule containing guest such as C153 do not disassemble and water do not penetrate into the capsule even in the time scale of 3000 ps following excitation. This implies that the capsule would remain closed during the excited state lifetimes of the donor.⁴⁴ We have found these information to be valuable to interpret the observed correlation between ΔG° and the rates of electron transfer (Figure 6.3.1).

The fact that a bell-shaped curve is obtained upon plotting the rate of electron transfer (k_{et}) against ΔG° suggests that the electron transfer across an organic wall investigated here follows the Marcus classical equation. We have calculated the two most important parameters the reorganization energy (λ) and electronic coupling matrix element (V_{el}) using the following equation.

$$k_{et} = \frac{4\pi^2}{h} \frac{V_{el}^2}{\sqrt{4\pi\lambda k_B T}} \exp \left\{ -\frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T} \right\} \quad (6.3.1)$$

In the above equation h is the Planck constant, V_{el} is the electronic coupling matrix element, k_B is the Boltzmann constant, T is the temperature in K . By fitting the data in Figure 6.3.1 into the above-mentioned equation we have estimated the λ to be 1.918 eV and the pre-exponential term A to be $4.074 \times 10^{11} \text{ s}^{-1}$. By carrying out the simple arithmetic the V_{el} was estimated to be 0.0058 eV.

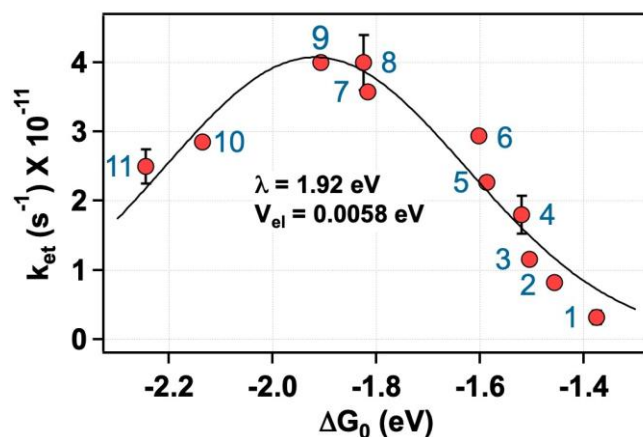


Figure 6.3.1. Plot of k_{et} obtained from transient absorption spectroscopy vs the estimated ΔG^0 for different donor/OA₂-acceptor pairs from 1-11. The pairs from 1-11 are respectively C153@OA₂ + MV²⁺, C153@OA₂ + BzV²⁺, Py@OA₂ + MV²⁺, An@OA₂ + MV²⁺, Py@OA₂ + BzV²⁺, An@OA₂ + BzV²⁺, C466@OA₂ + BzV²⁺, C480@OA₂ + MV²⁺, C480@OA₂ + BzV²⁺, Gaz@OA₂ + MV²⁺ and Az@OA₂ + MV²⁺. The plot was fitted with equation 6.3.1. The fitted line is displayed in black solid line. Experimental error for three representative points is also given.

We are aware that the λ consists of solvent and nuclear reorganization energies ($\lambda = \lambda_s + \lambda_i$).⁶ As discussed above, the encapsulated donor within OA capsule is surrounded only by the electron rich rigid capsular organic wall. This rigid wall would not help preparing the excited donor for electron transfer. Thus λ_s with respect to the donor part is negligible. The acceptor that is already doubly charged (2+) is located adjacent to the capsular exterior wall in water. The acceptor must be surrounded by water molecules and hydrogen bonded to the carboxylate anion of OA. Even after the electron transfer the solvation is not expected to change significantly around the acceptor since the acceptor would still be positively charged (1+) after accepting an electron from encapsulated donor molecule and would be

attached to the OA wall. Therefore, the solvent reorganization energy term (λ_s) with respect to acceptor part is also expected to be small. Thus the λ_s term is negligible during the electron transfer process. Based on these we believe that the observed λ of 1.918 eV is entirely due to the internal reorganization (λ_i). In rigid media such as glass and melts as well as within OA capsule the donor cation radical would be formed in a rigid higher energy environment.^{24, 70-72}

To get an insight into the electron transfer process in a rigid confined environment we reexamined the Marcus theory of electron transfer. According to this theory, λ is defined as the free energy of the product parabola at the equilibrium nuclear configuration of the reactant parabola as shown in Figure 6.3.2. Let us consider two sets of reactant and product parabolas. The first set is named set-1 and colored in black, whereas the other one is named set-2 and is colored in red. The only difference between these two sets is that the red parabolas are steeper than the black ones. For both of them the coordinate of the equilibrium positions of the reactant and product are respectively at $x = 0$ and $x = d$. Thus, the equations defining the free energy of the reactant ($G_i^R(x)$) and the product ($G_i^P(x)$) parabolas for the i -th set can be written as

$$G_i^R(x) = \frac{1}{2}k_i x^2 \quad (6.3.2)$$

$$G_i^P(x) = \frac{1}{2}k_i(x + d)^2 \quad (6.3.3)$$

where, k_i is the force constant of the parabolas for the i -th set. The solution of the product parabola for $x = 0$ will give the form of λ in terms of k_i and d and is given by

$$\lambda = \frac{1}{2}k_i d^2 \quad (6.3.4)$$

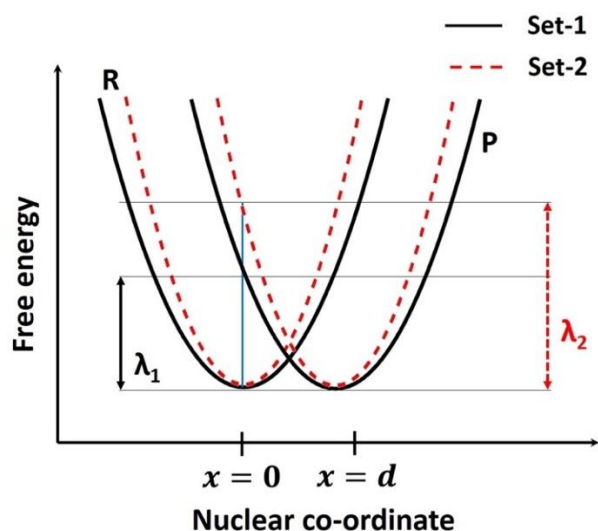


Figure 6.3.2. Dependence of reorganization energy on the steepness of the reactant and product parabolas in the Marcus formulation.

Examination of equation 6.3.4 reveals that λ increases linearly with increasing k_i . In other words, λ increases as the reactant and product parabolas become steeper. Comparison of the two curves in Figure 6.3.2 reveals that when the parabola is steeper (or constricted) more energy will be required to reach the product compared to a wider one, for same nuclear geometry. In a confined environment like as in the present case, where the structural modification is highly restricted, the reactant and product parabolas are expected to be steeper, leading to a higher value of reorganization energy. In support of our argument we would like to mention the work on a system of simple harmonic oscillator trapped inside a box and showed the energy of the oscillator increases with decrease in the box length, leading to a steeper potential.⁷³

Similar higher value for λ has been reported in the literature. A high value for λ (2.13 eV) has been noted during reverse electron transfer of radical ion pair by Gould and Farid.⁴⁶ In their case, solvent separated radical ion pair (SSRIP) possessed higher λ_s (1.63 eV) than contact radical ion pair (CRIP; 0.48 eV) where the radical cation and radical anion are almost touching each other. In fact, the structure of SSRIP has some similarity to the radical ion pair generated in this supramolecular environment with one exception. In our case the wall between

radical ions is permanent and rigid while in SSRIP it is flexible and soft.⁵⁴ The high λ in this study must all be λ_i while in SSRIP most of it is likely to be due to λ_s .

The second most important parameter we have retrieved from the Marcus plot is V_{el} . The value of V_{el} depends on the extent of orbital overlap between the donor and the acceptor. For the cases where the orbital overlap for the donor and acceptor is larger, greater will be the value of V_{el} . In our example like in SSRIP there is no direct overlap between the donor and the acceptor. A direct comparison between capsular wall separated radical ion pair with SSRIP is revealing. The V_{el} for CRIP and SSRIP are reported to be 0.093 and 0.00143 eV.⁴⁶ As mentioned earlier, in CRIP the orbitals of radical ion pair overlap while in SSRIP there is a solvent molecule in between. Presence of a solvent molecule decreases the orbital overlap and decreases V_{el} . Slightly higher value of V_{el} (0.0058 eV) obtained in our system could be due to the rigidity of the three component system – donor, capsule and acceptor. Most likely neither the donor, the acceptor nor the capsule has much freedom. This is distinctly different from that of SSRIP. We are pleased that our value of V_{el} is closer to that of SSRIP than CRIP.

Another model resembling our system is the C-clamp trapped solvent mediated electron transfer.²⁵⁻²⁸ One must recognize that unlike the solvent molecule trapped in the C-clamp, the capsular wall that serves as the mediator between donor and acceptor has no flexibility or freedom. The electronic coupling between the donor and acceptor in the C-clamp system is shown to depend on the electronic and steric properties of the solvent. The value of V_{el} vary between 0.0035 eV to 0.0068 ± 0.00161 eV.²⁷ Our value is on the higher side and this could be attributed to the dynamic nature of the C-clamp–solvent vs the static nature of the donor@)OA₂ – acceptor system. Other examples that has some resemblance to ours are the systems in which electron transfer occurs under solvent free and diffusion less conditions.^{29, 31} Under these conditions, the donor and acceptor molecules are pre-positioned adjacent to each other. The examples include dyes adsorbed on single crystals of aromatic molecules and melts of dyes with aromatic molecules. The V_{el} values varied between 0.0023 and 0.0043 eV. The electronic coupling reported for these

systems is slightly smaller than what we have calculated for OA wall mediated electron transfer.

The system that is directly relevant to the current study is the Cram hemicarcerand system investigated by Piotrowiak³⁶ and Balzani.³⁹ Electron and energy transfer across this hemicarcerand' wall have been investigated. However, it is important to note that the electron exchange matrix elements calculated for energy transfer between incarcerated triplet biacetyl and aromatic and olefinic acceptors vary between 0.00001 and $0.00003 \pm 10\%$ eV and are much smaller than what we have noted in the current system.^{37, 39} The difference most likely is due to the fact that the acceptors in our system are Coulombically bound to the exterior of the capsule while in the Cram hemicarcerand system the acceptors are free in solution. Because of the lack of any specific attraction between the hemicarcerand and the acceptor molecules, the contact time between the acceptor and carcerand will be short while in our case it is quite long. Interestingly, the electronic coupling is shown to depend on the internal cavity dimension of the Cram type hemicarcerands.³⁸ Smaller the capsule stronger the coupling. Clearly close interaction between the guest biacetyl and the walls of the hemicarcerand favors stronger coupling.

Expectedly, the V_{el} noted here is smaller than for systems wherein donor and acceptor are covalently linked. The observed smaller value is consistent with the expectation that lack of direct σ/π link would decrease the electronic coupling. An interesting but not so obvious feature one should note is that the wall of OA is electron rich. This is likely to increase the barrier for the electronic coupling between the donor and the acceptor through the wall and reduce the electronic coupling. This is in accordance with what has been noted in the C-clamp-solvent systems. A correlation between electronic coupling and the electron affinity of the solvent has been noted in C-clamp systems.²⁷ Interestingly solvent molecules with low electron affinity have smaller electronic coupling. We believe a similar effect may be reducing the coupling between the excited donor and electron rich capsular wall. However, the calculated V_{el} in this study higher than that in SSRIP and seems sufficient to bring about electron transport across the capsular wall.

6.4. Conclusions

Overall one could visualize the OA encapsulated donor and Coulombically linked acceptor system to be capable of undergoing photoinduced electron transfer. The capsular wall participates in the electron transfer process. Since the interior of the capsule is dry and rigid, medium reorganization is not expected to provide a driving force.⁵⁴ The observed λ value is higher than expected while V_{el} is reasonable for the current system. The preliminary quantum chemical calculation suggested that upon excitation of encapsulated coumarin the charge shift towards the wall. It seems that when there is an acceptor adjacent to the wall the charge from the wall moves to the acceptor. While the model we propose is qualitatively consistent with the observed results, a better understanding is needed and we are currently pursuing theoretical understanding of the observed phenomenon through collaboration.

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Chapter 7

Conclusions and Future Outlook

The fate of a photo-excited molecule strongly depends on the nature of its surrounding and the properties of its surrounding environment are inherently connected. A smart utilization of this connection has been the key to novel understanding about both.¹⁻⁵

In this thesis, I have studied four excited state processes in the nano-cavity octa acid (OA). By studying solvation dynamics of guest molecules trapped inside the OA cavity, I found that the core of OA cavity is primarily dry. Only when the size of the guest molecules is increased to a point where firm guest-host complexation is hindered, solvation dynamics was observed. This work solidifies the already established applicability of solvation dynamics as the tool to map unknown media.¹⁻⁵

Being diffusion-limited, the excimer formation dynamics remained unknown in bulk medium.¹⁻³ I have used the capability of the OA cavity to sandwich two anthracene molecules in its core and observed excimer formation dynamics for the first time. This system nullified the role of diffusion and made the unprecedented observation possible. In this system, I observed a two-step formation dynamics of anthracene excimer. Effect of other confined environment for different excimers can be explored. Similar studies on exciplex is also required.

Spin-orbit coupling (SOC) is always a necessary for the intersystem crossing (ISC).⁶ Insertion of heavy atom in molecule should enhance the SOC and hence the ISC.⁷ However, I have found some reported data suggesting that in some cases the heavy atom is underperformed to facilitate ISC.^{7,8} I further observed an unusual fluorescence quantum yield trend for coumarin-1 and its bromo- and iodo-derivative. Detailed femtosecond transient absorption study along with theoretical calculations suggested crucial involvement of the carbon-halogen bond length variation coordinate in ISC. Singlet triplet crossing along this coordinate is barrierless for the iodo-coumarin. For the bromo-coumarin, this path has a significant barrier and hinders ISC. The same model has also successfully predicted the photo-behaviour of the halogen-substituted naphthalenes. I predicted the position dependent of the

halogen substitution on the rate constant of ISC. However, target synthesis with photophysical studies must be done in future to confirm the prediction. According to the model, observation of Marcus inversion for ISC is a possibility. Extensive research on this subject is pending.

I proved the existence of Marcus inverted region for photoinduced electron transfer reaction between donor and acceptor separated by the OA molecular wall. The result revealed that even being separated by a molecular wall there is a significant electronic coupling between the donor and the acceptor. The role of the OA capsule has been speculated to resembles as that of a C-clamp trapped solvent molecule. Future work on this topic is needed. In a general way, research associated with Marcus inversion will be always welcome as the inverted mechanism of electron transfer can be proven crucial for delaying charge recombination and efficient harvesting of energy.⁹⁻¹¹

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List of Publications

- *16. Vibration-Assisted Intersystem Crossing in the Ultrafast Excited-State Relaxation Dynamics of Halocoumarins
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- 15. A Novel Quinoline Derivative for Selective and Sensitive Visual Detection of PPB Level Cu²⁺ in an Aqueous Solution
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- 14. Marcus Inversion is Observed for Excited State Proton Transfer in the Adiabatic Limit using Naphthol based Photoacids
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- *13. Dynamics of Anthracene Excimer Formation within a Water-Soluble Nanocavity at Room Temperature
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9. A Novel Quinoline Derivative for Selective and Sensitive Visual Detection of PPB Level Cu^{2+} in an Aqueous Solution

Nilimesh Das, Tanmoy Khan, **Aritra Das**, Vipin Kumar Jain, Joydev Acharya, Md. Serajul Haque Faizi, Joseph Daniel, Pratik Sen, *Curr. Anal. Chem.* **2022**, *18*, 196-203.

8. Chiral Induction on the Ultrafast Event of Excited State Proton Transfer Can Probe Its Mechanism

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7. β -carboline-based turn-on fluorescence chemosensor for quantitative detection of fluoride at PPB level

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4. Solvation Dynamics in SDS Micelle Revisited with Femtosecond Time Resolution to Reveal the Probe and Concentration Dependence

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2. Ultrafast Excited State Deactivation Channel of Thioflavin T Adsorbed on SDS Micelle: A Combined Femtosecond Fluorescence and Transient Absorption Study

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Puspal Mukherjee, **Aritra Das**, Arunava Sengupta, Pratik Sen. *J. Phys. Chem. B*, **2017**, 121, 1610–1622.

Works in this thesis are based on the publications marked with asterisk.

Front pages of these four published articles are given in the following pages.

Vibration-Assisted Intersystem Crossing in the Ultrafast Excited-State Relaxation Dynamics of Halocoumarins

Published as part of *The Journal of Physical Chemistry virtual special issue "Kankan Bhattacharyya Festschrift"*.

Aritra Das, Sujit Kumar Ghosh, Vaidhyanathan Ramamurthy,* and Pratik Sen*

Cite This: *J. Phys. Chem. A* 2022, 126, 1475–1485

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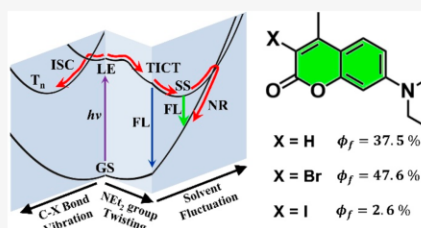
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ABSTRACT: Due to its numerous applications, triplet formation and resulting phosphorescence remain a frontier area of research for over eight decades. Facile intersystem crossing (ISC) is the primary requirement for triplet formation and observation of phosphorescence. The incorporation of a heavy atom in molecules is one of the common approaches employed to facilitate ISC. A detailed study of the excited state dynamics that governs ISC is necessary to understand the mechanism of heavy atom effect (HAE). Incorporation of iodine at the 3 position of coumarin-1 reduces fluorescence quantum yield (ϕ_f) drastically as expected, whereas bromine substitution at the same position increased the ϕ_f . Such a contrasting effect of the two heavy atoms suggests that there are other features yet to be discovered to fully understand the HAE. Detailed steady state and femtosecond transient absorption studies along with theoretical calculations suggest that the C3-X (X = Br, I) bond vibration plays an important role in the ISC process. The study reveals that while in the case of the iodo-derivative there is no energy barrier in the singlet triplet crossing path, there is a barrier in the case of the bromo-derivative, which slows the ISC process. Such an unexpected phenomenon is not limited to halocoumarins as this rationalizes the photobehavior of 1-bromo-/iodo-substituted naphthalenes as well.



INTRODUCTION

Recent intense research on phosphorescence^{1–5} could be traced to G. N. Lewis' statement to his student in 1942 namely, "You know, those triplet states that Mulliken was talking about in ethylene are probably the phosphorescent state".⁶ The experimental evidence for the existence of triplet states in phosphorescent materials by Kasha and Lewis in 1944 also revealed the importance of intersystem crossing (ISC) through spin–orbit coupling (SOC).^{7–9} The observation of heavy atom effect on phosphorescence by McClure in 1949 and the quadratic dependence of the SOC with the atomic number ($\propto Z^4$) found handy to tune the phosphorescence property of a system.^{10–12} Halogen substitution in organic molecules like naphthalene, azulene, phenanthrene, quinine, quinoxaline, and anthracene is a preferred way to introduce heavy atom effect in the past.^{10–22} A change in orbital type from $\pi\pi^* \rightarrow n\pi^*$ or $n\pi^* \rightarrow \pi\pi^*$ has also been noted to facilitate ISC through stronger SOC (El Sayed rule).²³ However, El Sayed rule only considers the electronic aspect of the transition and ignores the vibrational component.²⁴ Depending on the extent of nuclear geometry difference between the singlet and triplet states, there can be two regimes of ISC.²⁵ When the difference between singlet and triplet geometries is small, it falls in the small coupling regime, and the rate of ISC decreases exponentially with increasing energy gap (ΔE) between the

two states.^{26,27} On the other hand, when the geometries of the singlet and triplet states differ significantly and their surfaces cross, it falls in the strong coupling regime and ISC rate constant follows a bell-shaped dependence with ΔE . This has similarity to the bell-shaped dependence described in the Marcus theory for electron transfer.^{26,27} If this is true, it should be possible to prove the applicability of Marcus theory for ISC in the strong coupling regime. In this context we note that there are reports of facile ISC without heavy atom effect, where crossing between singlet and triplet states is present.^{24,27}

The ISC trend of 1-halonaphthalene is an example in support of the idea that SOC is not the only factor that controls the ISC from excited singlet to the triplet.¹² The ratio of the square of SOC constants for 1-bromo and 1-iodonaphthalene is 1:4.2, whereas, the ratio of their ISC rate constants is measured to be 1:9.3.^{10,12} The 2.2 times larger value of the ISC for 1-iodonaphthalene than the predicted

Received: September 27, 2021

Revised: February 16, 2022

Published: March 1, 2022



Dynamics of Anthracene Excimer Formation within a Water-Soluble Nanocavity at Room Temperature

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Cite This: *J. Am. Chem. Soc.* 2021, 143, 2025–2036



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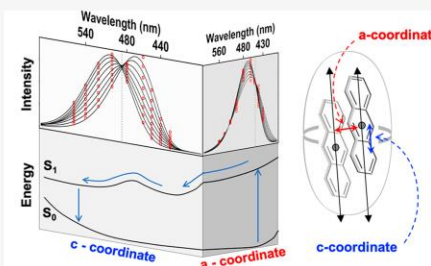
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ABSTRACT: Excited anthracene is well-known to photodimerize and not to exhibit excimer emission in isotropic organic solvents. Anthracene (AN) forms two types of supramolecular host–guest complexes (2:1 and 2:2, H:G) with the synthetic host octa acid in aqueous medium. Excitation of the 2:2 complex results in intense excimer emission, as reported previously, while the 2:1 complex, as expected, yields only monomer emission. This study includes confirming of host–guest complexation by NMR, probing the host–guest structure by molecular dynamics simulation, following the dynamics AN molecules in the excited state by ultrafast time-resolved experiments, and mapping of the excited surface through quantum chemical calculations (QM/MM-TDDFT method). Importantly, time-resolved emission experiments revealed the excimer emission maximum to be time dependent. This observation is unique and is not in line with the textbook examples of time-independent monomer–excimer emission maxima of aromatics in solution. The presence of at least one intermediate between the monomer and the excimer is inferred from time-resolved area normalized emission spectra. Potential energy curves calculated for the ground and excited states of two adjacent anthracene molecules via the QM/MM-TDDFT method support the model proposed on the basis of time-resolved experiments. The results presented here on the excited-state behavior of a well-investigated aromatic molecule, namely the parent anthracene, establish that the behavior of a molecule drastically changes under confinement. The results presented here have implications on the behavior of molecules in biological systems.



INTRODUCTION

Anthracene (AN) and pyrene (PY) occupy a special place in the history of the photochemistry^{1,2} and photophysics of aromatic molecules.^{3,4} The concepts that currently prevail concerning the excited-state chemistry of aromatic molecules could be traced back to these two molecules serving as exemplars in the development of concepts related to excimers and photodimerizations.^{1,2,5–7} A century ago AN was established to photodimerize with a limiting quantum yield of 1 in solution at room temperature.^{1,2} On the other hand, PY is known not to photodimerize under any conditions. However, it shows a concentration- and temperature-dependent emission, in addition to fluorescence and phosphorescence, in solution at room temperature even at 10^{−4} M.⁸ The intense structureless broad emission with a lifetime of 90 ns initially recorded by Forster and Kasper^{8,9} was established to originate from an excited dimer (excimer). In contrast, AN, which photodimerizes from the excited singlet state mainly fluoresces and phosphoresces in isotropic solution.³ Recognizing the anomaly between AN and PY, Chandross devised an ingenious method by which excimer emission from anthracene could be recorded at 77 K in an organic glass.^{10–12} He generated

“sandwich” dimers (two AN molecules placed side by side with the long and short axes parallel to each other) via photolytic decomposition of dianthracene (covalent dimer of AN; Scheme 1), which upon excitation gave an intense broad emission red-shifted with respect to fluorescence. This was attributed to an excimer and found to have a long lifetime (~185–225 ns).^{13–16} Following this, Ferguson showed that excimer emission could be recorded in the crystalline state as well as in a KBr matrix by following the above procedure.^{17–20} As expected, the excitation spectrum corresponded to the absorption spectrum of the AN monomer. While the “sandwich” dimer showed intense excimer emission at 77 K, when warming the matrix was warmed, the excimer emission disappeared and dianthracene was formed with a near-unit quantum yield at room temperature.²¹ The above observations

Received: November 20, 2020

Published: January 20, 2021



Marcus Relationship Maintained During Ultrafast Electron Transfer Across a Supramolecular Capsular Wall

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Cite This: *J. Phys. Chem. A* 2020, 124, 5297–5305



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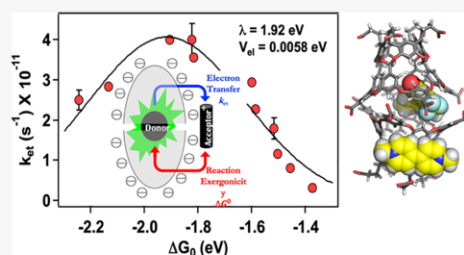
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ABSTRACT: Photoinduced electron transfer across an organic capsular wall between excited donors and ground-state acceptors is established to occur with rate constants varying in the range $0.32\text{--}4.0 \times 10^{11} \text{ s}^{-1}$ in aqueous buffer solution. The donor is encapsulated within an anionic supramolecular capsular host, and the cationic acceptor remains closer to the donor separated by the organic frame through Coulombic attraction. Such an arrangement results in electron transfer proceeding without diffusion. Free energy of the reaction (ΔG°) and the rate of electron transfer show Marcus relation with inversion. From the plot, λ and V_{el} were estimated to be 1.918 and 0.0058 eV, respectively. Given that the donor remains within the nonpolar solvent-free confined space, and there is not much change in the environment around the acceptor, the observed λ is believed to be because of “internal” reorganization rather than “solvent” reorganization. A similarity exists between the capsular assembly investigated here and glass and crystals at low temperature where the medium is rigid. The estimated electronic coupling (V_{el}) implies the existence of interaction between the donor and the acceptor through the capsular wall. Existence of such an interaction is also suggested by ^1H NMR spectra. Results of this study suggest that molecules present within a confined space could be activated from outside. This provides an opportunity to probe the reactivity and dynamics of radical ions within an organic capsule.



INTRODUCTION

Electron transfer plays a prominent role in several important events such as photosynthesis, solar energy storage, metabolic and respiratory processes, photocatalysis, electrical conduction in organic materials, and several organic and inorganic reactions.^{1–6} In such studies, occurrence of electron transfer at short as well as long distances has been noted. The rate of electron transfer that occurs via the classic tunneling mechanism is established to exponentially increase with decrease in the donor–acceptor distance.⁵ Challenging long-distance electron transfer investigations have involved protein,^{7–12} DNA,^{13–16} and hydrocarbon chains as scaffolds and covalently linked donor–acceptor systems.^{17–20} In these systems, electron transfer occurs either through hopping or via superexchange mechanism involving σ or π bonds. In addition to these, there are systems wherein electron transfer occurs through noncovalent interactions,¹⁷ in frozen and free solvents,^{21–24} with the help of a solvent molecule trapped between a C-clamp molecule,^{25–28} and in mixed donor–acceptor melts.^{29–31} Interprotein electron transfer that involves solvent mediation belongs to this category.^{10–12} These studies suggest that for electron transfer to occur, donor and acceptor molecules need not to be within collisional distance or covalently linked. The presence of another molecule in between a donor and an acceptor apparently would not inhibit

the electron transfer, and its presence, in fact, is better than vacuum.²⁰

Among supramolecular assemblies, to our knowledge, the Cram-type carcerand³² is a unique assembly, where the donor and acceptor molecules could be well separated by the host wall. Energy and electron transfers have been established to occur between the donor and acceptor molecules, one trapped within the Cram-type carcerand and the other free outside in solution.^{33–39} In fact, results reported with these systems have laid the groundwork for the current undertaking. Unfortunately, because the interior of the Cram-type carcerand is small, its generality is limited. Most guests need to be included during the synthesis of the carcerand.

In the current study, we employ a synthetic host known as octa acid (OA),⁴⁰ whose structure and internal dimensions are provided in Figure 1. Unlike Cram-type carcerand, the OA capsule is made up of two molecules of OA that assemble in

Received: May 3, 2020

Revised: June 3, 2020

Published: June 10, 2020



ACS Publications

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5297

<https://dx.doi.org/10.1021/acs.jpca.0c03944>
J. Phys. Chem. A 2020, 124, 5297–5305

Ultrafast Solvation Dynamics Reveal that Octa Acid Capsule's Interior Dryness Depends on the Guest

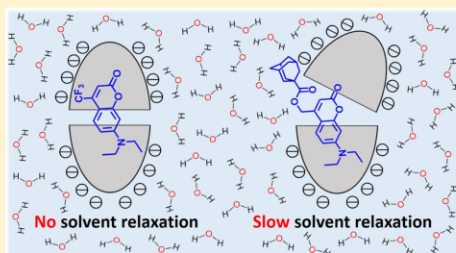
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[§]Supporting Information

ABSTRACT: Coumarins are well-known to exhibit environment-dependent excited-state behavior. We have exploited this feature to probe the accessibility of solvent water molecules to coumarins (guest) encapsulated within an organic capsule (host). Two sets of coumarins, one small that fits well within the capsule and the other larger that fits within an enlarged capsule, are used as guests. In our study, the two sets of coumarins serve different purposes: one is employed to explore electron transfer across the capsule and the other to release photoprotected acids into the aqueous environment. The capsule is made up of two molecules of octa acid (OA) and is soluble in an aqueous medium under slightly basic conditions. Molecular modeling studies revealed that while the OA capsule is fully closed with no access to water in the case of smaller coumarins, with the larger molecules, the capsule is not tight and the guest is in contact with water molecules, the number being dependent on the size of the coumarin. We have used the ultrafast time-dependent Stokes shift method to understand the solvent dynamics around the above guest molecules encapsulated within an OA capsule in an aqueous medium. Results depict that for the smaller sets of coumarins, water cannot access the guests within the OA cavity during their excited state lifetime. However, the case is completely different for the larger coumaryl esters. Distorted capsule structure exposes the guest to water, and a dynamics Stokes shift is observed. The average solvation time decreases with the increasing size of guests that clearly indicates accessibility of the encapsulated guests toward greater number of water molecules as the capsule structure distorts with increasing size of the guests. Results of the ultrafast solvation dynamics are consistent with that of molecular dynamics simulation.



INTRODUCTION

During the last three decades, interest in understanding the physicochemical behavior and dynamics of molecules in confined spaces has grown steadily.^{1–4} In this context, various organic and inorganic well-defined hosts have been employed as reaction space.^{5–8} Our long-standing interest in exploring the photochemical and photophysical behavior of molecules in confined spaces^{9,10} led us to use a synthetic molecule, octa acid (OA, Scheme 1), as the reaction medium.^{11–13} In the presence of a guest molecule, two molecules of OA are assembled to form a capsule with the host to guest ratio of 2:1 or 2:2 in aqueous solution under basic conditions.¹⁴ A variety of fluorescent as well as electron paramagnetic resonance active nitroxide probes revealed the interior of the capsule to be nonpolar and the micropolarity to be similar to that of benzene.^{15,16} Considering that the capsule is present in an aqueous medium, absence of water molecules within the capsule was unanticipated. Fluorescence probes revealed that during the measurement time, the capsule neither disassembled nor partially opened to expose the probe molecules to the aqueous exterior. On the other hand, phosphorescence

quenching of a variety of encapsulated guest molecules by oxygen indicated that the capsule partially opened and closed in the time scale of 5 μ s.¹⁷ The disassembling–assembling of the OA capsule takes place in the time-scale of 2.7 s that is 5 orders of magnitude slower than the partial opening and closing.¹⁸ Thus, although in a nanosecond timescale, the capsule is intact, in a microsecond timescale, it partially opens and closes, and in a second time scale, it disassembles and assembles. The above conclusion is based on probes that are presumed to form a tight 2:1 capsule. Given that well-known hosts such as micelles, cyclodextrins, cucurbiturils, calixarenes, and related organometallic cavitands are permeable to water molecules, absence of water within the OA capsule is unique and provides an opportunity to conduct photochemical and photophysical studies under “dry” conditions even in an aqueous medium.

Received: May 15, 2019

Revised: June 17, 2019

Published: June 19, 2019