

**LASER FLASH PHOTOLYSIS AND
MAGNETIC FIELD EFFECT ON
SOME CHARGE-TRANSFER REACTIONS**

**THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY (SCIENCE)
OF
JADAVPUR UNIVERSITY**

By

SANJUKTA AICH (nee SANYAL)

NUCLEAR CHEMISTRY DIVISION
SAHA INSTITUTE OF NUCLEAR PHYSICS
1/AF, BIDHANNAGAR
CALCUTTA-700 064

1997

Contents

| | |
|--|--------------|
| Chapter I : Electron Transfer and Magnetic Field Effect : An Overview | 1- 69 |
| 1.1 Introduction | 1 |
| 1.2 PET Reactions | 3 |
| 1.2.1 CT Intermediates in PET | 3 |
| 1.2.2 Examples on PET | 9 |
| 1.2.2.1 Intermolecular CT in Unlinked D-A Systems | 10 |
| 1.2.2.2 PET in Metal Complexes | 11 |
| 1.2.2.3 Intramolecular PET in Linked D-A Systems | 13 |
| 1.3 Basic ET Formulation: Marcus Theory | 16 |
| 1.3.1 Classical Marcus Theory | 17 |
| Quantum Mechanical Aspects | 22 |
| Notes on Solvent Dynamics | 24 |
| Some Comments on MIR | 25 |
| Rehm Weller Approach | 26 |
| 1.4 Magnetic Field Effect | 27 |
| 1.4.1 Introduction | 27 |
| 1.4.2 Molecular Dynamics : Spin Evolution in RP Systems | 31 |
| 1.4.3 Qualitative Description: Vector Model of S and T States | 32 |
| 1.4.4 S-T Transition in RP | 33 |
| 1.4.5 Magnetic Field Dependent (MFD) Chemical Yield | 37 |
| 1.4.6 Diffusion Dynamics and Chemical Reactions | 37 |

| | | |
|-------|---|--------------|
| 1.4.7 | Examples of MFE Studies | 38 |
| | <i>References</i> | 55 |
| | Chapter II : Scope of the Thesis | 70-72 |
| | Chapter III : Experimental Techniques | 73-85 |
| 3.1 | Introduction | 73 |
| 3.2 | An Overview of Instruments | 74 |
| 3.2.1 | Absorption Spectrophotometer | 74 |
| 3.2.2 | Fluorescence Spectrophotometer | 74 |
| 3.2.3 | Laser Flash Photolysis | 74 |
| 3.2.4 | MFE Measurement | 75 |
| 3.3 | Laser Flash Photolysis Technique | 75 |
| 3.4 | TCSPC Technique | 76 |
| 3.5 | PSD System | 79 |
| 3.6 | Measurement of Fluorescence Quantum Yield | 79 |
| 3.7 | Fluorescence Polarization (P) and Anisotropy (A) | 80 |
| 3.8 | Measurement of Triplet Extinction Coefficients in Different Solvents | 81 |
| 3.9 | Preparation of Grafted Film | 82 |
| 3.10 | Materials | 83 |
| | <i>References</i> | 85 |

| | |
|---|---------------|
| Chapter IV: Identification of Charge Transfer Intermediates of a Series of Four D-A Pairs: Elucidation of Mechanistic Pathways by Laser Flash Photolysis and Magnetic Field Effect Studies | 86-127 |
| 4.1 Introduction | 86 |
| 4.2 Results and Discussion | 91 |
| 4.2.1 Characterization of Exciplex | 91 |
| 4.2.2 Marcus Analysis: Evidence of ET from Theoretical Viewpoint | 95 |
| 4.2.3 Fluorescence Studies on ECZ-TCNB and PMC-TCNB | 98 |
| 4.2.4 Temperature Dependence of ET with Four D-A Pairs | 99 |
| 4.2.5 Laser Flash Photolysis (LFP) Studies | 101 |
| 4.2.6 Magnetic Field Effect (MFE) Studies | 106 |
| MFE on the RIP of the Four Pairs in Micellar Medium by Laser Flash Photolysis Technique | 106 |
| MFE on Exciplex Luminescence using PSD System | 108 |
| Dielectric Constant Dependence of MFE on Exciplex Luminescence | 108 |
| MFE on the Triplet Free Ions in Non-viscous Medium | 118 |
| 4.3 Conclusion | 120 |
| <i>References</i> | 122 |

| | | |
|-------------------|--|----------------|
| Chapter V: | Fluorescence Polarization of N-vinyl carbazole Grafted on Cellulose Acetate Film and its Electron Transfer Reaction with 1,4-dicyanobenzene | 128-139 |
| 5.1 | Introduction | 128 |
| 5.2 | Results and Discussion | 131 |
| | 5.2.1 Fluorescence Polarization with GVCZ Film | 131 |
| | 5.2.2 Evidence of Electron Transfer from GVCZ to DCB in THF through the Formation of an Exciplex | 132 |
| 5.3 | Conclusion | 137 |
| | <i>References</i> | 138 |

| | | |
|--------------------|--|----------------|
| Chapter VI: | Characterization of Triplet Charge Transfer State of 4-amino N-Methyl Phthalimide in Aprotic and Protic Media by Laser Flash Photolysis | 140-158 |
| 6.1 | Introduction | 140 |
| 6.2 | Results and Discussion | 143 |
| | 4-AMP in Aprotic Media | 143 |
| | 4-AMP in Protic Media | 148 |
| | Magnetic Field Effect on the Semiquinone radical of 4-AMP in SDS Micellar Medium | 152 |
| 6.3 | Conclusion | 154 |
| | <i>References</i> | 155 |

Chapter VII Future Prospects

159-162

List of Publications

163