

Contents

Part I Ultrafast Photochemistry

| | | |
|----------|--|----|
| 1 | Introduction | 3 |
| 1.1 | Motivation: Molecular Conformation and Photochemistry | 3 |
| | References | 5 |
| 2 | Aspects and Investigation of Photochemical Dynamics | 7 |
| 2.1 | Photochemical Reaction Mechanisms | 7 |
| 2.1.1 | The Photochemical Funnel | 7 |
| 2.1.2 | Non-Adiabatic Dynamics | 9 |
| 2.1.3 | Intersystem Crossing. | 11 |
| 2.1.4 | Ultrafast Reactivity. | 11 |
| 2.2 | Probing Ultrafast Dynamics: The Pump–Probe Principle | 13 |
| 2.2.1 | Coherence | 14 |
| 2.2.2 | Pump: Creation of a Wave Packet | 15 |
| 2.2.3 | Probe: Projection onto a Final State | 17 |
| 2.2.4 | Experimental Techniques | 18 |
| 2.3 | What is Probed? | 19 |
| 2.3.1 | The Final State | 19 |
| 2.3.2 | Sample Averaging | 19 |
| | References | 20 |
| 3 | A Time-Resolved Probing Method: Photoionization | 23 |
| 3.1 | Fundamentals | 23 |
| 3.1.1 | The Final State | 23 |
| 3.1.2 | Ionization Correlations | 24 |
| 3.2 | Probing Non-Adiabatic Dynamics Through Photoionization. . . | 24 |
| 3.2.1 | Choosing a Pump–Probe Scheme | 26 |

| | | |
|------------|---|----|
| 3.3 | Analyzing and Interpreting Experimental Results | 28 |
| 3.3.1 | Ultrafast Dynamics Modeled by First Order Kinetics | 28 |
| 3.3.2 | Time-Resolved Mass Spectrometry. | 29 |
| 3.3.3 | Time-Resolved Photoelectron Spectroscopy. | 30 |
| References | | 32 |

Part II Theory

| | | |
|------------|---|----|
| 4 | Simulation of Time-Resolved Photoionization Signals. | 37 |
| 4.1 | Quantum Molecular Dynamics: The AIMS Method | 37 |
| 4.1.1 | Electronic Structure | 38 |
| 4.1.2 | The Nuclear Wave Function and Equations of Motion | 39 |
| 4.1.3 | Non-Adiabatic Dynamics: Spawning New Basis Functions | 41 |
| 4.1.4 | Conducting an AIMS Simulation | 43 |
| 4.2 | Theoretical Framework for Signal Simulation | 44 |
| 4.2.1 | The Electronic Photoionization Matrix Element | 44 |
| 4.2.2 | Dyson Orbitals. | 46 |
| 4.2.3 | Simulation of Time-Resolved Photoelectron Spectra | 47 |
| References | | 49 |
| 5 | Simulation: The Norrish Type-I Reaction in Acetone. | 53 |
| 5.1 | Motivation. | 53 |
| 5.2 | Computational Details. | 54 |
| 5.3 | Results and Discussion | 55 |
| 5.3.1 | Electronic State Populations | 55 |
| 5.3.2 | Nuclear Dynamics | 55 |
| 5.3.3 | Simulation of TRMS and TRPES Signals | 57 |
| 5.4 | Conclusion. | 61 |
| References | | 62 |

Part III Experiments

| | | |
|----------|---------------------------------------|----|
| 6 | Experimental Setups. | 65 |
| 6.1 | Femtolab Copenhagen. | 65 |
| 6.1.1 | Laser System. | 65 |

| | | |
|----------|--|------------|
| 6.1.2 | The Time-of-Flight Spectrometer and Continuous Inlet System | 66 |
| 6.2 | Molecular Photonics Group | 69 |
| 6.2.1 | Laser System | 70 |
| 6.2.2 | The Magnetic Bottle and Pulsed Inlet System | 71 |
| | References | 73 |
| 7 | Paracyclophanes I: [2+2]cycloaddition of Ethylenes. | 75 |
| 7.1 | Studying Bimolecular Reaction Dynamics with Femtosecond Time-Resolution | 75 |
| 7.2 | Motivation | 76 |
| 7.3 | Results | 76 |
| 7.3.1 | Ab Initio Calculations | 76 |
| 7.3.2 | Time-Resolved Photoelectron Spectra | 81 |
| 7.4 | Discussion | 83 |
| 7.4.1 | Pseudo- <i>para</i> -divinyl[2.2]paracyclophane (PARA-V) | 83 |
| 7.4.2 | Pseudo- <i>gem</i> -divinyl[2.2]paracyclophane (GEM-V) | 84 |
| 7.5 | Conclusion | 86 |
| | References | 87 |
| 8 | Paracyclophanes II: The Paternò-Büchi Reaction | 89 |
| 8.1 | Motivation | 89 |
| 8.2 | Results | 91 |
| 8.2.1 | Computational Results | 91 |
| 8.2.2 | Time-Resolved Photoelectron Spectra | 95 |
| 8.3 | Discussion | 98 |
| 8.3.1 | Pseudo- <i>para</i> -vinylformyl[2.2]paracyclophane (PARA-VF) | 98 |
| 8.3.2 | Pseudo- <i>gem</i> -vinylformyl[2.2]paracyclophane (GEM-VF) | 99 |
| 8.4 | Conclusion | 101 |
| | References | 102 |
| 9 | Probing Structural Dynamics by Interaction Between Chromophores | 103 |
| 9.1 | Time-Resolved Ion Photofragmentation Spectroscopy | 103 |
| 9.2 | Motivation | 105 |
| 9.3 | Results and Discussion | 106 |
| 9.3.1 | Ground State Structural Aspects | 106 |
| 9.3.2 | Photoelectron Spectroscopy | 107 |
| 9.3.3 | Mass Spectrometry | 108 |
| 9.3.4 | The Unifying Picture | 111 |
| 9.4 | Conclusion | 113 |
| | References | 113 |

Part IV Conclusion

10 Summarizing Discussion 117
 10.1 Future Research 119
 References 120

Index 121

Molecular Conformation and Organic Photochemistry

Time-resolved Photoionization Studies

Brogaard, R.Y.

2012, XVI, 124 p., Hardcover

ISBN: 978-3-642-29380-1