Moshe Shapiro and Paul Brumer

# **Quantum Control of Molecular Processes**

Second, Revised and Enlarged Edition



WILEY-VCH Verlag GmbH & Co. KGaA

# Contents

Preface to the Second Edition XIII

Preface to the First Edition XV

## 1 Preliminaries of the Interaction of Light with Matter 1

## 2 Weak-Field Photodissociation 5

- 2.1 Photoexcitation of a Molecule with a Pulse of Light 6
- 2.2 State Preparation During the Pulse 8
- 2.3 Photodissociation 13
  - 2.3.1 General Formalism 13
  - 2.3.2 Electronic States 20
  - 2.3.3 Energy-Resolved Quantities 21
- 2.A Appendix: Molecular State Lifetime in Photodissociation 22

## 3 Weak-Field Coherent Control 25

- 3.1 Traditional Excitation 25
- 3.2 Photodissociation from a Superposition State 26
  - 3.2.1 Bichromatic Control 28
  - 3.2.2 Energy Averaging and Satellite Contributions 31
- 3.3 The Principle of Coherent Control 33
- 3.4 Interference between N-Photon and M-Photon Routes 35
  - 3.4.1 Multiphoton Absorption 35
  - 3.4.2 One- vs. Three-Photon Interference 393.4.2.1 One- vs. Three-Photon Interference: Three-Dimensional Formalism 41
  - 3.4.3 One- vs. Two-Photon Interference: Symmetry Breaking 50
- 3.5 Polarization Control of Differential Cross Sections 56
- 3.6 Pump-Dump Control: Few Level Excitation 57
- 3.A Appendix: Mode-Selective Chemistry 68

## 4 Control of Intramolecular Dynamics 71

- 4.1 Intramolecular Dynamics 71
  - 4.1.1 Time Evolution and the Zero-Order Basis 72
  - 4.1.2 Partitioning of the Hilbert Space 73

- 4.1.3 Initial State Control and Overlapping Resonances 75
  - 4.1.3.1 Internal Conversion in Pyrazine 77
  - 4.1.3.2 Intramolecular Vibrational Redistribution: OCS 78

## 5 Optimal Control Theory 83

- 5.1 Pump-Dump Excitation with Many Levels: the Tannor–Rice Scheme 83
- 5.2 Optimal Control Theory 895.2.1 General Principles of Optimal Control Theory 89

#### 6 Decoherence and its Effects on Control 95

- 6.1 Decoherence 95
  - 6.1.1 Master Equations 98
- 6.2 Sample Computational Results on Decoherence 100
  - 6.2.1 Electronic Decoherence 100
  - 6.2.2 Vibrational Decoherence in Condensed Phases 102
  - 6.2.3 Decoherence: Towards the Classical Limit 106
- 6.3 Environmental Effects on Control: Some Theorems 109
  - 6.3.1 Environment Can Limit Control 109
  - 6.3.2 Environment Can Enhance Control 112 6.3.2.1 Environmentally Assisted Transport 112
  - 6.3.3 Environmentally Assisted One-Photon Phase Control 114
  - 6.3.4 Isolated Molecules 116
  - 6.3.5 Nonisolated Systems 117
- 6.4 Decoherence and Control 119
  - 6.4.1 The Optical Bloch Equation 1206.4.1.1 Decoherence Effects in One-Photon vs. Three-Photon Absorption 121
  - 6.4.2 Countering Collisional Effects 126
  - 6.4.3 Additional Control Studies 129
  - 6.4.4 State Stability against Decoherence 133
  - 6.4.5 Overlapping Resonances and Decoherence Control: Qualitative Motivation 135
  - 6.4.6 Control of Dephasing 139
- 6.5 Countering Partially Coherent Laser Effects in Pump-Dump Control 142
- 6.6 Countering CW Laser Jitter 149
  - 6.6.1 Laser Phase Additivity 150
  - 6.6.2 Incoherent Interference Control 151

## 7 Case Studies in Coherent Control 153

- 7.1 Two-Photon vs. Two-Photon Control 153
  - 7.1.1 Experimental Implementation 160
- 7.2 Control over the Refractive Index 169
  - 7.2.1 Bichromatic Control 171
- 7.3 The Molecular Phase in the Presence of Resonances 176

- 7.3.1 Theory of Scattering Resonances 178
- 7.3.2 Three-Photon vs. One-Photon Coherent Control in the Presence of Resonances 182
  7.3.2.1 Case (a): an Indirect Transition to an Isolated Resonance 184
  7.3.2.2 Case (b): a Purely Direct Transition to the Continuum 184
  7.3.2.3 Case (c): an Indirect Transition to a Set of Overlapping Resonances 185
  7.3.2.4 Case (d): a Sum of Direct and Indirect Transition to an Isolated Resonance 185
- 7.4 Control of Chaotic Dynamics 186

#### 8 Coherent Control of Bimolecular Processes 191

- 8.1 Fixed Energy Scattering: Entangled Initial States 191
  - 8.1.1 Issues in the Preparation of the Scattering Superposition 193
  - 8.1.2 Identical Particle Collisions 195
  - 8.1.3 Sample Control Results 198
    - 8.1.3.1 *m* Superpositions 198

8.1.3.2 Control in Cold Atoms: Penning vs. Dissociative Ionization 201

- 8.1.3.3 Control in Electron Impact Dissociation 207
- 8.1.4 Experimental Implementation: Fixed Total Energy 211
- 8.1.5 Optimal Control of Bimolecular Scattering 212
  8.1.5.1 Optimized Bimolecular Scattering: the Total Suppression of a Reactive Event 214
- 8.1.6 Sculpted Imploding Waves 216
- 8.2 Time Domain: Fast Timed Collisions 217
  - 8.2.1 Nonentangled Wave Packet Superpositions: Time-Dependent Scattering 217
  - 8.2.2 Entangled or Wave Packets? 220

#### 9 The Interaction of Light with Matter: a Closer Look 223

- 9.1 Classical Electrodynamics of a Pulse of Light 223
  - 9.1.1 The Classical Hamiltonian 223
  - 9.1.2 The Free Light Field 226
- 9.2 The Dynamics of Quantized Particles and Classical Light Fields 228

#### 10 Coherent Control with Quantum Light 233

- 10.1 The Quantization of the Electromagnetic Field 233 10.1.1 Light-Matter Interactions 235
- 10.2 Quantum Light and Quantum Interference 236
  - 10.2.1 One-Photon vs. Two-Photon Quantum Field Control 238
    - 10.2.1.1 Use of Number States 238
    - 10.2.1.2 Use of Coherent States 239
  - 10.2.2 Pump-Dump Coherent Control 240

X | Contents

- 10.2.2.1 Results with Quantized Light 240
- 10.2.2.2 Results with Classical Fields 242
- 10.2.3 Phase-Independent Control 243
- 10.3 Quantum Field Control of Entanglement 245
  - 10.3.1 Light-Matter Entanglement 245
  - 10.3.2 Creating Entanglement between a Chain of Molecules and a Radiation Field 247
- 10.4 Control of Entanglement in Quantum Field Chiral Separation 250
- 11 Coherent Control beyond the Weak-Field Regime: Bound States and Resonances 253
  - 11.1 Adiabatic Population Transfer 253
    - 11.1.1 Adiabatic States, Trapping, and Adiabatic Following 254
    - 11.1.2 The Multistate Extension of STIRAP 260
  - 11.2 An Analytic Solution of the Nondegenerate Quantum Control Problem 261
  - 11.3 The Degenerate Quantum Control Problem 266
  - 11.4 Adiabatic Encoding and Decoding of Quantum Information 271
  - 11.5 Multistate Piecewise Adiabatic Passage 275
    - 11.5.1 Multistate Piecewise Adiabatic Passage Experiments 280 11.5.1.1 Chirped Adiabatic Passage 281 11.5.1.2 Rabi Flopping 283
  - 11.6 Electromagnetically Induced Transparency 290
    - 11.6.1 EIT: a Resonance Perspective 291
    - 11.6.2 EIT as Emerging from the Interference between Resonances 293
      - 11.6.2.1 Unstructured Continua 300
      - 11.6.2.2 Structured Continua 300
    - 11.6.3 Photoabsorption 301
    - 11.6.4 The Resonance Description of Slowing Down of Light by EIT 306

#### 12 Photodissociation Beyond the Weak-Field Regime 315

- 12.1 One-Photon Dissociation with Laser Pulses 315
  - 12.1.1 Slowly Varying Continuum 318
  - 12.1.2 Bichromatic Control 319
  - 12.1.3 Resonance 319
- 12.2 Computational Examples 325

#### 13 Coherent Control Beyond the Weak-Field Regime: the Continuum 329

- 13.1 Control over Population Transfer to the Continuum by Two-Photon Processes 329
  - 13.1.1 The Adiabatic Approximation for a Final Continuum Manifold 330
- 13.2 Pulsed Incoherent Interference Control 335
- 13.3 Resonantly Enhanced Photoassociation 345

- 13.3.1 Theory of Photoassociation of a Coherent Wave Packet 346
- 13.3.2 Photoassociation by the Consecutive Application of APC and STIRAP 353
- 13.3.3 Interference between Different Pathways 357
- 13.3.4 Experimental Realizations 359
- 13.4 Laser Catalysis 363
  - 13.4.1 The Coupling of a Bound State to Two Continua by a Laser Pulse 364

# 14 Coherent Control of the Synthesis and Purification of Chiral Molecules 373

- 14.1 Principles of Electric Dipole Allowed Enantiomeric Control 374
- 14.2 Symmetry Breaking in the Two-Photon Dissociation of Pure States 376
- 14.3 Purification of Racemic Mixtures by "Laser Distillation" 381
- 14.4 Enantiomer Control: Oriented Molecules 395
- 14.5 Adiabatic Purification of Mixtures of Right-Handed and Left-Handed Chiral Molecules 397
  - 14.5.1 Vibrational State Discrimination of Chiral Molecules 399
  - 14.5.2 Spatial Separation of Enantiomers 404
  - 14.5.3 Internal Hamiltonian and Dressed States 405
  - 14.5.4 Laser Configuration 408
  - 14.5.5 Spatial Separation Using a Cold Molecular Trap 409
- 14.A Appendix: Computation of B-A-B' Enantiomer Selectivity 413

#### 15 Strong-Field Coherent Control 415

- 15.1 Strong-Field Photodissociation with Continuous Wave Quantized Fields 415
  - 15.1.1 The Coupled-Channels Expansion 419
  - 15.1.2 Number States vs. Classical Light 423
- 15.2 Strong-Field Photodissociation with Pulsed Quantized Fields 425
   15.2.1 Light-Induced Potentials 426
- 15.3 Controlled Focusing, Deposition, and Alignment of Molecules 429
  15.3.1 Focusing and Deposition 429
  15.3.2 Strong-Field Molecular Alignment 435

#### 16 Coherent Control with Few-Cycle Pulses 443

- 16.1 The Carrier Envelope Phase 443
- 16.2 Coherent Control and the CEO Frequency Measurement 445
- 16.3 The Recollision Model 446
  - 16.3.1 Step 1: Tunnel Ionization 447
  - 16.3.2 Step 2: Classical "Swing" Motion 448
  - 16.3.3 Step 3: Recollision 448
  - 16.3.4 Step 4: Emission of a Photon 450
- 16.4 CEP Stabilization and Control 451
  - 16.4.1 The Attosecond Streak Camera 452
- 16.5 Coherent Control of Sample Molecular Systems 453

- XII Contents
- 16.5.1 One-Photon vs. Two-Photon Control with Few-Cycle Pulses 453 16.5.1.1 Backward-Forward Asymmetry in the Dissociative Photoionization of D<sub>2</sub>. 453
- 16.5.2 Control of the Generation of High-Harmonics 455
- 16.5.3 Control of Electron Transfer Processes 456
- 16.5.4 Electron Transfer in Alkali Halides 457

#### 17 Case Studies in Optimal Control 463

- 17.1 Creating Excited States 463 17.1.1 Using Prepared States 467
- 17.2 Optimal Control in the Perturbative Domain 468
- 17.3 Adaptive Feedback Control 471
- 17.4 Analysis of Adaptive Feedback Experiments 480
  - 17.4.1 trans-cis Isomerization in 3,3'-Diethyl-2,2'-thiacyanine Iodide 480
  - 17.4.2 Controlled Stokes Emission vs. Vibrational Excitation in Methanol 486
- 17.5 Interference and Optimal Control 487

#### 18 Coherent Control in the Classical Limit 491

- 18.1 The One-Photon vs. Two-Photon Scenario Revisited 491
  - 18.1.1 Resonant Regime 491
  - 18.1.2 Off-Resonant Extension 492
  - 18.1.3 A Three-State Example 494
  - 18.1.4 Quantum Features 495
- 18.2 The Quartic Oscillator 496
- 18.3 Control in an Optical Lattice 499
  - 18.3.1 Equivalence with Dipole Driving 501
  - 18.3.2 Computational Results 502

#### Appendix Common Notation Used in the Book (in Order of Appearance) 507

References 513

Subject Index 537