INTRODUCTION TO NONLINEAR OPTICAL EFFECTS IN MOLECULES AND POLYMERS

PARAS N. PRASAD

Photonics Research Laboratory Department of Chemistry State University of New York Buffalo, New York

and

DAVID J. WILLIAMS

Corporate Research Laboratories Eastman Kodak Company Rochester, New York



A Wiley-Interscience Publication JOHN WILEY & SONS, Inc. New York · Chichester · Brisbane · Toronto · Singapore

CONTENTS

1. Introduction

- 1.1 Nonlinear Optics and Photonics, 1
- 1.2 Nonlinear Optical Materials, 2
- 1.3 Basic Research Opportunities, 5
- 1.4 Multidisciplinary Research, 5
- 1.5 Scope of This Book, 6

2. Basis and Formulation of Nonlinear Optics

- 2.1 Interaction of Light with a Medium, 8
- 2.2 Light Propagation through an Optical Medium, 10
- 2.3 The Harmonic Oscillator Model for Linear Optical Processes, 12
- 2.4 Nonlinear Optical Media, 15
- 2.5 The Anharmonic Oscillator Model for Nonlinear Optical Effects, 19
- 2.6 Anisotropic Media, 21
- 2.7 Tensors, 24
- 2.8 Symmetry, 27 Appendix, 29 References, 33

3. Origin of Microscopic Nonlinearity in Organic Systems

- 3.1 Microscopic Nonlinearity, 35
- 3.2 Brief Review of σ and π Electrons and Bonding, 36
- 3.3 Equivalent Internal Field Model, 39

vii

35

1

8

- 3.4 Additivity Model for Molecular Hyperpolarizabilities, 40
- 3.5 Quantum-Chemical Approaches,, 42
 - 3.5.1 Derivative versus Sum-over-States Method, 42
 - 3.5.2 Derivative Methods, 44
 - 3.5.3 Sum-over-States Approach, 52
 - 3.5.4 Two-Level Model, 53
 - 3.5.5 The Free-Electron Model, 54
- 3.6 Orientational Nonlnearity, 56 References, 57

4. Bulk Nonlinear Optical Susceptibility

- 4.1 Induced Polarization, 59
- 4.2 Relationship between Microscopic and Macroscopic Nonlinearities in Crystals, 60
- 4.3 Poled Polymers, 66
- 4.4 Langmuir-Blodgett Films, 73
- 4.5 Third-Order Susceptibilities in Crystals, Polymers, and Langmuir-Blodgett Films, 77
- 4.6 Relation of $\chi^{(3)}$ between Film-Based and Laboratory-Based Coordinate Systems, 80 References, 80

5. Second-Order Nonlinear Optical Processes

- 5.1 General Considerations, 82
- 5.2 Second-Harmonic Generation, 85
- 5.3 Parametric Processes, 96
 - 5.3.1 Sum-Frequency Generation, 96
 - 5.3.2 Parametric Up-conversion, 98
 - 5.3.3 Difference-Frequency Generation, 99
 - 5.3.4 Parametric Oscillator, 100
- 5.4 Low-Frequency Effects, 102
 - 5.4.1 Electrooptic Effect, 102
 - 5.4.2 Optical Rectification, 104
 - References, 104

6. Measurement Techniques for Second-Order Nonlinear Optical Effects

- 6.1 Electric Field-Induced Second-Harmonic Generation Method, 106
- 6.2 Solvatochromic Measurements, 114
- 6.3 Methods for Measuring $\chi^{(2)}$, 117
- 6.4 Kurtz Powder Technique, 121
- 6.5 Electrooptic Measurements, 122 References, 131

82

59

106

7. A Survey of Second-Order Nonlinear Optical Materials 132 7.1 Perspective, 132 7.2 Structural Requirements for Second-Order Optical Nonlinearity, 134 7.3 Crystals and Inclusion Complexes, 143 7.4 Poled Polymers, 152 7.5 Langmuir-Blodgett Films, 160 References, 170 8. Third-Order Nonlinear Optical Processes 175 8.1 The Various Third-Order Processes and Resulting Polarizations, 175 8.1.1 Third-Harmonic Generation, 176 8.1.2 Self-Action, 177 8.1.3 Two-Photon Absorption, 178 8.1.4 Degenerate Four-Wave Mixing, 178 8.1.5 Coherent Raman Effects, 178 8.2 Third-Harmonic Generation, 180 8.3 Electric Field-Induced Second-Harmonic Generation, 184 8.4 Degenerate Four-Wave Mixing, 184 8.5 Resonant Nonlinearity, 188 8.6 Other Mechanisms Contributing to the Intensity Dependence of the Refractive Index, 194 8.7 Intensity-Dependent Phase Shift, 195 8.8 Cascading Effect, 196 References, 197 9. Measurement Techniques for Third-Order Nonlinear Optical Effects 199 9.1 A General Discussion of the Measurement of $\chi^{(3)}$, 199 9.2 Selective Measurement Techniques, 201 9.2.1 Third-Harmonic Generation, 201 9.2.2 Electric Field-Induced Second-Harmonic Generation, 205 9.2.3 Degenerate Four-Wave Mixing, 205 9.2.4 Optical Kerr Gate, 209 9.2.5 Self-Focusing Methods, 211 9.2.6 Surface Plasmon Nonlinear Optics, 214 9.2.7 Nonlinear Fabry-Perot Method, 216 9.3 Measurement of Microscopic Nonlinearities, y, 218 References, 220 10. A Survey of Third-Order Nonlinear Optical Materials 222

- 10.1 Perspective, 222
- 10.2 Structural Requirements for Third-Order Optical Nonlinearity, 224

- 10.3 Liquid Materials and Solutions, 225
- 10.4 Conjugated Polymers, 231
 - 10.4.1 Polydiacetylenes, 231
 - 10.4.2 Poly-p-phenylene Vinylenes and Analogues, 235
 - 10.4.3 Polyacetylene, 238
 - 10.4.4 Polythiophene, 239
 - 10.4.5 Other Conjugated Polymers, 241
- 10.5 Macrocycles, 243
- 10.6 Polysilanes, 245
- 10.7 Organometallic Structures, 246 References, 248

11. Nonlinear Optics in Optical Waveguides and Fibers

- 11.1 Basic Concepts of Guided Waves, 252
- 11.2 Nonlinear Optics with Guided Waves, 256
- 11.3 Second-Order Nonlinear Optical Processes, 25811.3.1 Second-Harmonic Generation in a Planar Waveguide, 258
 - 11.3.2 Phase Matching in a Periodically Poled Waveguide, 261
 - 11.3.3 Second-Harmonic Generation in Organic Crystal Cored Fibers, 263
- 11.4 Third-Order Nonlinear Optical Processes, 264
- 11.5 Material Requirements for Waveguides, 268 References, 270

12. Device Concepts

- 12.1 Introduction, 272
- 12.2 Frequency Conversion, 274
- 12.3 Light Modulation, 27712.3.1 Spatial Light Modulators, 27912.3.2 Mach–Zehnder Interferometer, 281
- 12.4 Optical Switching, 282
- 12.5 Optical Bistability, 285
- 12.6 Sensor Protection, 290
- 12.7 Optical Phase Conjugation, 292 References, 293

13. Issues and Future Directions

- 13.1 Microscopic Processes, 296
- 13.2 Local Fields, 297
- 13.3 Materials for Second-Order Nonlinear Optics, 297
- 13.4 Materials for Third-Order Nonlinear Optics, 300 References, 302

Appendix: Units Index 303 305

272

295

252