# **CIRCULAR DICHROISM**

### **Principles and Applications**

SECOND EDITION

Edited by

**NINA BEROVA** 

KOJI NAKANISHI

**ROBERT W. WOODY** 

## **CONTENTS**

	Pre	face	XV	
	Coı	ntributors	xvii	
1	Cir	cular Dichroism: An Introduction	1	
	Gün	ther Snatzke (edited by Robert W. Woody)		
	1.1	Introduction	1	
	1.2	Principles of UV Spectroscopy	21	
	1.3	Principles of CD Spectroscopy	28	
2	From Pasteur to Parity Nonconservation: Theories of the Origin of Molecular Chirality 3			
	Step	hen F. Mason		
	2.1	Introduction	37	
	2.2	Pasteur on Molecular and Cosmic Dissymmetry	39	
	2.3	Stereoselective Chiral Synthesis	40	
	2.4	Symmetry Principles and Chiral Fields	42	
	2.5	Chance and Necessity in the Evolution of Biochemical Homochirality	44	
	2.6	Parity and Its Nonconservation	47	
	2.7	Summary and Conclusion	50	
3	The	eoretical Approach To Electronic Optical Activity	55	
	Axe	l Koslowski, Narasimha Sreerama, and Robert W. Woody		
	3.1	Introduction	55	
	3.2	Theory of Optical Activity	56	
	3.3	Quantum-Chemical versus Classical Methods for Calculation of		
		Optical Activity	58	
	3.4	Calculation of Optical Properties of Proteins	74	
	3.5	Calculation of Optical Properties of Nucleic Acids	83	
	3.6	Perspectives	86	
4	Vibrational Optical Activity Theory 9			
	Lau	rence A. Nafie and Teresa B. Freedman		
	4.1	Introduction	97	
	4.2	Theory of Vibrational Circular Dichroism	100	
	4.3	Theory of Raman Optical Activity	111	

#### viii CONTENTS

	4.4	Spectral Simulation of VOA Using Ab Initio Methods	114			
	4.5	Recent Technological Advances	124			
5	Cir	cular Dichroism of Oriented Molecules	133			
	Han	Hans-Georg Kuball and Tatiana Höfer				
	5.1	Introduction	133			
	5.2	Molecular Chirality and Chiral Anisotropic Phases	134			
	5.3	ACD Spectroscopy in Chiral Anisotropic Phases without				
		Suprastructural Chirality	137			
	5.4	Description of ACD and Polarized UV Spectroscopy	139			
	5.5	Results and Discussion of ACD Spectroscopy of Phases without Superstructural Chirality	149			
	5.6	ACD Spectroscopy in Chiral Anisotropic Phases with				
		Suprastructural Chirality	152			
	5.7	Summary and Outlook	156			
6	Soli	d-State CD: Application to Inorganic and Organic Chemistry	159			
		o Kuroda				
	6.1	Introduction	159			
	6.2	Uniaxial Single Crystals	160			
	6.3	Decomposition of CD Bands into the $E$ and $A_2$ Components	163			
	6.4	Microcrystalline CD	168			
	6.5	CD Intrinsic to the Solid State	173			
	6.6	Following a Solid-State Reaction by Solid-State CD	178			
	6.7	Interpretation of CD Spectra	179			
	6.8 6.9	Comments and New Developments in Experimental Procedures Conclusion	181 183			
7	Cir	Circularly Polarized Luminescence: A Probe for Chirality in				
		Excited State	185			
	Har	ry P. J. M. Dekkers				
	7.1	Introduction	185			
	7.2	Scope of the CPL Technique	186			
	7.3	Principles of Measurement and Instrumentation	189			
	7.4	Relationship between Experimental and Theoretical Quantities	191			
	7.5	Applications of CPL Spectroscopy: Organic Carbonyl Compounds	201			
	7.6	Conclusion	211			
8		Chiroptical Luminescence Spectroscopy as a Probe of the Chirality-Dependent				
	Electronic State Structure, Stereochemical Dynamics, and Intermolecular Interaction Properties of Dissymmetric Metal					
		mplexes in Solution	217			
		Richardson and David H. Metcalf	,			
	8.1	Introduction	217			
	8.2	Chiroptical Luminescence Measurements	218			
		=				

		CONTENTS	ix
	8.3	Decay Kinetics of Chiral Luminophores	221
	8.4	Emitting-State Populations of Luminophores under Steady-State	
		Excitation/Emission Conditions	224
	8.5	Circularly Polarized Excitation	226
	8.6	Examples of Applications and Experimental Results	229
	8.7	Conclusion	240
9	Fast	Time-Resolved Circular Dichroism Measurements	243
	Davi	d S. Kliger and James W. Lewis	
	9.1	Introduction	243
	9.2	Ellipsometric CD Measurements	244
	9.3	Ellipsometric Magnetic CD Measurements	249
	9.4	Extension of Ellipsometric Approach to Other Polarization Spectroscopies	251
	9.5	Potential Artifacts in Ellipsometric Polarization Spectroscopies	255
	9.6	Applications	257
10	The	Octant Rule	261
	Davi	d A. Lightner	
	10.1	Introduction	261
	10.2	Description of the Octant Rule	262
	10.3	Defining the Boundaries of the Octant Rule	265
	10.4	Theory and Analysis	279
	10.5	Applications of the Octant Rule	287
	10.6	Concluding Comments	299
11	Circ	cular Dichroism and Chirality of Dienes	305
	J. K.	Gawroński	
	11.1	Introduction	305
	11.2	UV Spectra	305
	11.3	Skewed s-cis Dienes	309
	11.4	The 1,3-Cyclohexadiene Chirality Model	316
	11.5	Endocyclic s-Trans Dienes	322
	11.6	Exocyclic s-Trans Dienes	322
	11.7	Strained Dienes	326
	11.8	Interactions with Other Chromophores	328
12	Exc	iton Chirality Method: Principles and Applications	337
	Nina	Berova and Koji Nakanishi	
	12.1	Exciton Chirality Method: Basic Principles	337
	12.2	Additivity Relations in Exciton-Coupled CD Curves	344
	12.3	Unique UV-VIS Absorption and CD Exciton-Split Spectra of Chiral	
		Biscyanine Dye	349
	12.4	CD Chromophores with Favorable Properties for Exciton Coupling and Other Practical Aspects of Exciton Chirality Method	352
	12.5	Application of Exciton Chirality Method to Acyclic Compounds	364
	12.5	Tippitation of English children in regions compounds	201

#### x CONTENTS

	12.6	Sensitivity Enhancement of Exciton-Coupled CD by Fluorescence Detection	376		
13	S-Su	bstituted Aromatics and Exciton Chirality	383		
	Chan	tal Andraud, Chantal García, and André Collet			
	13.1	Introduction	383		
	13.2	Synthesis, Resolution, and Absolute Configuration of Sulfur-Substituted Cyclotriveratrylenes	385		
	13.3	The Exciton Mechanism in $C_3$ -Cyclotriveratrylenes	387		
	13.4	Sulfur-Substituted Cyclotriveratrylenes and Exciton Chirality	389		
	13.5	Conclusion	393		
14		ications of the Benzene Sector and Benzene Chirality Rules	397		
		Introduction	397		
	14.2	Benzene Sector Rule	398		
	14.3	Benzene Chirality Rule	403		
	14.4	Applications to Compounds Related to Phenylcarbinamine and Carbinol	409		
	14.5	Applications to Compounds Related to Benzylcarbinamine			
		and Benzylcarbinol	415		
	14.6	Benzocycloalkenes	426		
15	Theo	ular Dichroism of Twisted π-Electron Systems: oretical Determination of the Absolute Stereochemistry of ral Products and Chiral Synthetic Organic Compounds	431		
	Nobu	yuki Harada			
	15.1	Theoretical Calculation of CD and UV Spectra by the $\pi$ -Electron SCF-CI-DV MO Method	432		
	15.2	Absolute Stereochemistry of (+)-1,8a-Dihydro-3,8-Dimethylazulene, a Labile Biosynthetic Intermediate for 1,4-Dimethylazulene	433		
	15.3	Circular Dichorism and Absolute Stereochemistry of Chiral Troponoid Spiro Compounds	437		
	15.4	Absolute Stereochemistry of the Halenaquinol Family: Marine Natural Products with a Novel Pentacyclic Skeleton, as Determined by Theoretical Calculation of CD Spectra	439		
	15.5	Chiral Spiromatics of 9,9'-Spirobifluorene Skeleton	446		
	15.6	Atropisomerism of Natural Products: CD and Absolute Stereochemistry of the Biflavone, 4,4"',7,7"-Tetra-O-methylcupressuflavone	449		
	15.7	Conclusion	456		
16	Determination of Conformations and Absolute Configurations				
	•	emiempirical Calculation of CD Spectra	459		
		Sandström	450		
	16.1	Introduction	459		
	16.2	Spectroscopic and Computational Methods	460		
	16.3	Studies of Rigid Molecules	467		

		CONTENTS	хi	
	16.4	Flexible Molecules: Planar Groups with Attached Chiral Rotors	469	
	16.5	Concluding Remarks	486	
17	A M	odel for How Polymers Amplify Chirality	491	
	Mark	M. Green		
	17.1	Introduction	491	
	17.2	The Uniform Chiral Field	492	
	17.3	The Quenched Random Chiral Field	500	
	17.4	Final Remarks	517	
18	Indu	ced CD or Polymers	521	
	Eiji Y	Yashima and Yoshio Okamoto		
	18.1	Introduction	521	
	18.2	Helix Formation and Induced CD of Polyacetylenes	522	
	18.3	Induced CD of Polyisocyanates	540	
	18.4	Induced CD of Other $\pi$ -Conjugated Polymers: Polyaniline and Polypyrrole	542	
19	Appl	lication of CD to the Study of Some Cholesteric Mesophase	547	
	Giova	anni Gottarelli and Gian Piero Spada		
	19.1	Introduction	547	
	19.2	Validity of CD Measurements on Cholesteric Samples	550	
	19.3	CD Study of Some Lyotropic Cholesterics	550	
20	Circ	ular Dichroism of Inorganic Complexes: Interpretation		
	and	Applications	563	
	Reiko	Kuroda and Yoshihiko Saito		
	20.1	Introduction	563	
	20.2	Trisbidentate Complexes	564	
	20.3	Complexes Involving Multidentate Ligands	575	
	20.4	Chiral Tetrahedral Coordination	580	
	20.5	Investigation of Formation Reaction and Thermodynamic Stability	585	
	20.6	Lanthanide Complexes	585	
	20.7	Application to Life Sciences	586	
	20.8	Concluding Remarks	594	
21	Circ	ular Dichroism of Peptides and Proteins	601	
	Narasimha Sreerama and Robert W. Woody			
	21.1	Introduction	601	
	21.2	Peptide Backbone and Far-UV CD	602	
	21.3	CD of Model Polypeptides	604	
	21.4	Structural Analysis of Proteins	608	
	21.5	Aromatic Side Chains and Disulfides	612	
	21.6	Extrinsic Chromophores	615	

22	Pept	tide and Protein Conformational Studies with Vibrational		
	Circ	ular Dichroism and Related Spectroscopies	621	
	Timo	thy A. Keiderling		
	22.1	Introduction	621	
	22.2	Experimental Techniques	626	
	22.3	Peptide VCD Studies	633	
	22.4	Protein VCD Spectral Results	644	
	22.5	Quantitative Protein VCD Studies in Terms of Structure	651	
	22.6	Conclusions	656	
23	Vibrational Raman Optical Activity: From Fundamentals to			
	Biochemical Applications		667	
	Laur	ence D. Barron and Lutz Hecht		
	23.1	Introduction	667	
	23.2	Basic Theory of ROA	669	
	23.3	ROA Instrumentation	683	
	23.4	1	687	
	23.5	Concluding Remarks	695	
24	CD (	of Nucleic Acids	703	
	W. Cı	urtis Johnson		
	24.1	Introduction	703	
	24.2	Right-Handed Nucleic Acids	707	
	24.3	Left-Handed DNA	709	
	24.4	Applications of CD to Study Secondary Structure	712	
25	Circ	ular Dichroism of Nucleic Acids: Nonclassical Conformations		
	and	Modified Oligonucleotides	719	
	Jean	Claude Maurizot		
	25.1	Introduction	719	
	25.2	Nonclassical Nucleic Acid Structures	720	
	25.3	CD of Chemically Modified Oligonucleotides	728	
	25.4	Concluding Remarks	736	
26	DNA	A-Drug Interactions	741	
	Mali	n Ardhammar, Tomas Kurucsev, and Bengt Nordén		
	26.1	Introduction	741	
	26.2	Background	742	
	26.3	Intercalation	746	
	26.4	Groove Binding	749	
	26.5	Illustrative Examples	751	
	26.6	Additional Systems Studied	755	
	26.7	Triplex and Z-Form DNA	756	
	26.8	Metal Complexes	757	

		CONTENTS	xiii
	26.9	Peptide Nucleic Acid Drugs	762
	26.10	Other Nucleic Acid Complexes	765
27	CD (	of Protein–Nucleic Acid Interactions	769
	Dona	ld M. Gray	
	27.1	Introduction	769
	27.2	Complexes Dominated by CD Changes of Protein Secondary Structure	770
	27.3	Complexes that Involve CD Changes of Nucleic Acids	778
	27.4	Complexes with Nucleotides	791
	27.5,	Summary	792
28	HPL	C-CD: Stereochemical Analysis at Work	797
	Piero	Salvadori, Lorenzo Di Bari, and Gennaro Pescitelli	
	28.1	Introduction	797
	28.2	HPLC-CD Device	798
	28.3	Applications and Interpretation Methods	800
	28.4	Related Techniques and Perspectives	813
	28.5	Conclusions	814
29	Appl	ications of Chiroptical Spectroscopy in the Characterization	
	of C	ompounds Having Pharmaceutical Importance	819
	Harry	G. Brittain	
	29.1	Introduction	819
	29.2	Applications of Circular Birefringence (Polarimetry)	820
	29.3	Applications of Circular Dichroism	822
	29.4	Concluding Remarks	841
Ind	Index		845