

Circular Dichroism and Linear Dichroism

ALISON RODGER

University of Warwick

and

BENGT NORDÉN

Chalmers University of Technology, Gothenburg

Oxford New York Tokyo

OXFORD UNIVERSITY PRESS

1997

Contents

1 Spectroscopy, chirality, and oriented systems

1.1 Introduction	1
1.2 Electromagnetic radiation and spectroscopy	2
1.3 Measuring a <i>CD</i> spectrum	6
1.4 Design and implementation of an <i>LD</i> experiment	8
References	14

2 Circular dichroism of biomolecules

2.1 Introduction	15
2.2 <i>CD</i> of polypeptides and proteins	17
2.3 <i>CD</i> of polynucleotides: DNA and RNA	24
2.4. DNA-ligand interactions	30
References	31

3 Linear dichroism of biomolecules

3.1 Introduction	33
3.2 Proteins	34
3.3 Nucleic acids	36
References	44

4 Linear dichroism of small molecules

4.1 Introduction	45
4.2 Orientation distribution	45
4.3 Some <i>LD</i> definitions	47
4.4 Determination of molecular orientation	50
4.5 Determination of transition polarization	54
4.6 <i>LD</i> of flow-oriented polymers	64
References	65

5 Analysis of circular dichroism: electric dipole allowed transitions

5.1 Introduction	66
5.2 Pictorial description of <i>CD</i> spectroscopy	66
5.3 Ways of analysing <i>CD</i>	67
5.4 Degenerate coupled-oscillator <i>CD</i> : general case	70

5.5 Degenerate coupled-oscillator <i>CD</i> : some examples	73
5.6 Non-degenerate coupled-oscillator <i>CD</i> : general case	80
5.7 Non-degenerate coupled-oscillator <i>CD</i> : some examples	82
References	89

6 Analysis of circular dichroism: magnetic dipole allowed transitions and magnetic *CD*

6.1 Introduction	90
6.2 Magnetic dipole allowed transitions	90
6.3 $n \rightarrow \pi^*$ carbonyl transition and the octant rule	91
6.4 $n \rightarrow \pi^*$ carbonyl transition and the dynamic coupling model: justification of the octant rule	95
6.5 <i>d-d</i> transitions of metal complexes: symmetry dependence of the <i>CD</i> of mda transitions	98
6.6 Magnetic circular dichroism	103
References	106

7 Circular dichroism formalism

7.1 Introduction	107
7.2 Polarized light and spectropolarimeters	107
7.3 Interaction of radiation with matter	110
7.4 <i>CD</i> , transition moment operators, and transition moments	114
7.5 <i>CD</i> from the coupling of degenerate electric dipole transition moments in identical distinct chromophores: the degenerate coupled-oscillator model	117
7.6 <i>CD</i> from the coupling of electric dipole transition moments in non-identical chromophores: the non-degenerate coupled-oscillator model	119
7.7 Qualitative approach to exciton <i>CD</i>	122
7.8 Magnetic dipole allowed transitions: the dynamic coupling model	123
7.9 Magnetic circular dichroism	127
References	131

Appendices

A1 Vectors	132
A2 Determination of equilibrium binding constants	135
A3 Momentum-dipole equivalence	141
A4 Definitions and units	143

Index

148
