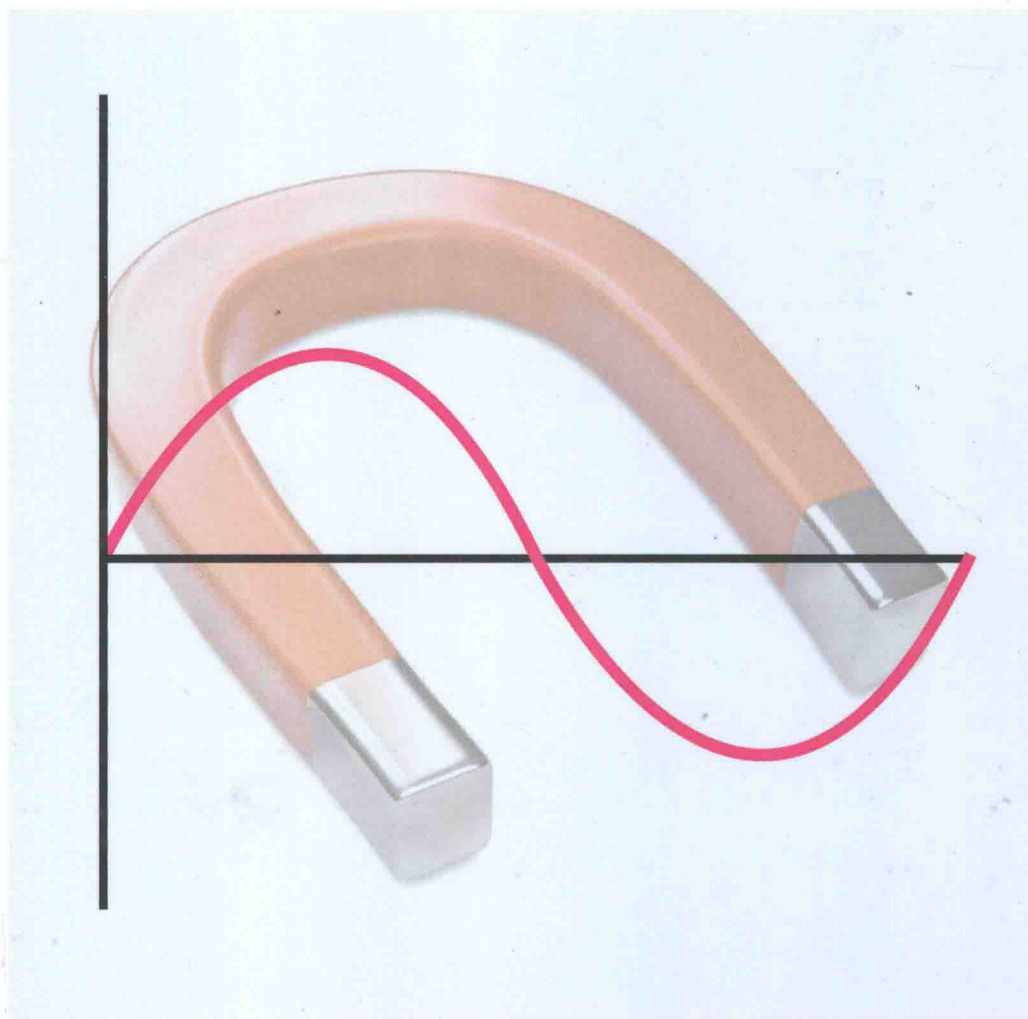


Nagao Kobayashi, Atsuya Muranaka and John Mack

# Circular Dichroism and Magnetic Circular Dichroism Spectroscopy for Organic Chemists



RSC Publishing

# ***Circular Dichroism and Magnetic Circular Dichroism Spectroscopy for Organic Chemists***

**Nagao Kobayashi**

*Department of Chemistry, Graduate School of Science, Tohoku University,  
Sendai, Japan*

**Atsuya Muranaka**

*Institute of Physical and Chemical Research (Riken), Wako-shi, Saitama, Japan*

**John Mack**

*Department of Chemistry, Graduate School of Science, Tohoku University,  
Sendai, Japan*



RSC Publishing

ISBN: 978-1-84755-869-5

A catalogue record for this book is available from the British Library

© Royal Society of Chemistry 2012

*All rights reserved*

*Apart from fair dealing for the purposes of research for non-commercial purposes or for private study, criticism or review, as permitted under the Copyright, Designs and Patents Act 1988 and the Copyright and Related Rights Regulations 2003, this publication may not be reproduced, stored or transmitted, in any form or by any means, without the prior permission in writing of The Royal Society of Chemistry or the copyright owner, or in the case of reproduction in accordance with the terms of licences issued by the Copyright Licensing Agency in the UK, or in accordance with the terms of the licences issued by the appropriate Reproduction Rights Organization outside the UK. Enquiries concerning reproduction outside the terms stated here should be sent to The Royal Society of Chemistry at the address printed on this page.*

The RSC is not responsible for individual opinions expressed in this work.

Published by The Royal Society of Chemistry,  
Thomas Graham House, Science Park, Milton Road,  
Cambridge CB4 0WF, UK

Registered Charity Number 207890

For further information see our web site at [www.rsc.org](http://www.rsc.org)

Printed and bound in Great Britain by CPI Group (UK) Ltd, Croydon, CR0 4YY

# Circular Dichroism and Magnetic Circular Dichroism Spectroscopy for Organic Chemists

# Preface

Circular dichroism (CD) and magnetic circular dichroism (MCD) spectroscopy can often provide key information about the conformations and electronic states of chromophore-containing molecules, which is required for a full understanding of the electronic structures and optical spectroscopy. Unfortunately, the theory that underpins these techniques has been largely inaccessible to many organic chemists and biochemists and only a few researchers have carried out detailed quantitative analyses of their spectral data. Until recently, a key problem that has been encountered is that relatively few molecules have been available that can be used to describe the various methods for analysing the spectral data in a clear and concise manner. This is not surprising because people who excel at spectroscopic theory usually lack the skills required to design and synthesise the molecules that would be most appropriate for describing the theory of CD and MCD spectroscopy. Most of the books that have been written on this subject have, therefore, been based on dense sets of mathematical equations and have been aimed primarily at physical chemists and physicists.

Our aim in writing this book is to try to rectify this situation by summarising the different types of CD and MCD spectra and by describing in detail the qualitative and quantitative methods that can be used to analyse the spectral data. Over the last two decades we have successfully synthesised a series of molecules which are ideal for illustrating key points related to the theory of CD and MCD spectroscopy, and we are confident that the time is finally ripe to write a book which will provide the key practical knowledge required to use the CD and MCD techniques to their full potential. In the first chapter, we will provide an introduction to the most important aspects of the theory of electronic absorption, CD and MCD spectroscopy. The important aspects of electronic absorption spectroscopy are described first, since absorption spectra are usually recorded and analysed during any study of the CD and MCD spectra because the spectral bands in each case arise from the same set of transitions. The content is aimed primarily at a reader who already possesses a

---

Circular Dichroism and Magnetic Circular Dichroism Spectroscopy for Organic Chemists

By Nagao Kobayashi, Atsuya Muranaka and John Mack

© Royal Society of Chemistry 2012

Published by the Royal Society of Chemistry, [www.rsc.org](http://www.rsc.org)

first year undergraduate level of understanding of physical chemistry. In the case of small chromophores, the lowest energy electric dipole allowed transitions are often aligned along the direction of the permanent dipole moment of the molecule. Transitions of this type are often ideally suited for analysis by CD spectroscopy, since both the electric and magnetic dipole transition moments are well defined in terms of their alignment and can play a key role in generating CD intensity based on several different intensity mechanisms, which will be described in detail. MCD spectra are obtained by placing a magnet in the sample compartment of a CD spectrometer. MCD spectroscopy provides key information about the degeneracy of ground and excited states which cannot easily be derived from the electronic absorption spectrum alone.

In Chapters 2 and 3, we present key information about two of the most widely used analytical approaches that have been reported to date, which could probably be viewed as core knowledge for organic chemists and biochemists who want to become active in this field. Our hope is that in many instances researchers who are new to the field will find that the examples provided can serve as a useful template for analysing their own data. In Chapter 2, the most well known empirical rules for analysing CD spectra, which have been developed over the past 50 years, are described. Although theoreticians have described detailed mathematical rationales for these, there is usually no need to study their research in detail to be able to derive key information about the conformation or configuration of certain specific types of chiral system, such as ketones and substituted benzene rings. The key is to learn how the empirical rules have been applied successfully by earlier researchers and to be fully aware of any exceptions to the rules which have been reported. In Chapter 3, we describe a wide range of examples of the use of exciton coupling theory in the conformational analysis of natural and synthetic dimers, oligomers and polymers. The sign sequence observed in the CD spectra of excitation couplets has been found to be related to the relative alignments of the interacting chromophores in space.

In Chapters 4 to 8 more specialised types of analysis are examined. In chapter 4, the use of cyclodextrin inclusion compounds to study the CD spectra of guest molecules trapped in the central cavity is described in detail. Host-guest complexes with clearly defined geometries are readily formed in solution, which enables the analysis of the alignment of band polarisations at wavelengths as short as 200 nm even in the absence of single crystals. The focus in Chapter 5 shifts over to the CD spectroscopy of inorganic complexes based either on the  $\pi$ -system transitions of the ligand or on the  $d \rightarrow d$  transitions of the central metal. In recent years the incorporation of 1,1'-binaphthyl (BINAP) moieties has been used to study the asymmetric synthesis of porphyrinoids, since BINAP provides a well defined asymmetric field, which interacts with the porphyrinoid  $\pi$ -system in a manner that can be readily predicted. This research is described in detail in Chapter 6. Although CD spectra can often be readily analysed in conceptual terms based on the theory which describes various intensity mechanisms, in some cases this is not possible and the analysis of the

system has to depend almost entirely on theoretical calculations. Molecules with intrinsic chirality are best suited to this approach. Several examples are described in detail in Chapter 7. The results of these calculations have to be treated with caution, however, for reasons that are described in detail. In Chapter 8, the CD spectroscopy of biomolecules will be described. Since large proteins contain many chromophores, which lie at various distances from each other in a wide range of alignments, the quantitative analysis of these spectra is usually not possible, but the CD technique can still be used to derive qualitative information and has been widely applied on this basis.

In Chapter 9, representative examples of the use of MCD spectroscopy are described. Many of the examples revolve around the study of porphyrin complexes, since the technique has been particularly widely utilised in this context. The theory of MCD spectroscopy can be challenging for many organic chemists, because it revolves around the application of molecular orbital theory to conceptualise the structure and bonding of chromophores, rather than the valence bond theory approach that tends to be used in organic chemistry. In Chapter 10, we describe how Michl's perimeter model, a molecular bonding theory approach, can be used a molecular bonding theory approach can be used to analyse the MCD spectra of aromatic and antiaromatic  $\pi$ -systems.

# Abbreviations

|           |  |
|-----------|--|
| [3,3]PCP  | [3,3]paracyclophane  |
| acac      | acetylacetonate  |
| Ara       | arabinose  |
| BINAP     | 1,1'-binaphthyl  |
| bipy      | 2,2'-bipyridyl   |
| B3LYP     | Becke 3-parameter (exchange), Lee, Yang and Parr (correlation) |
| CAM-B3LYP | Coulomb attenuated method B3LYP                                |
| CBD       | cyclobutadiene   |
| CD        | circular dichroism   |
| CI        | configuration interaction                                      |
| con.      | consignate   |
| Cp        | cyclopentadiene  |
| CyD       | cyclodextrin   |
| dis.      | dissignate   |
| DFT       | density functional theory                                      |
| DNA       | deoxyribonucleic acid  |
| edtm      | electric dipole transition moment                              |
| en        | ethylenediamine  |
| EPR       | electron paramagnetic resonance                                |
| Fc        | ferrocene  |
| Gal       | galactose  |
| Glu       | glucose  |
| HPLC      | high-performance liquid chromatography                         |
| ICD       | induced circular dichroism                                     |
| LCAO      | linear combination of atomic orbitals                          |
| lcp       | left circularly polarised                                      |
| LMCT      | ligand to metal charge transfer                                |
| Lys       | lysine   |



|            |  |
|------------|--|
| Man        | mannose  |
| MCD        | magnetic circular dichroism  |
| mdtm       | magnetic dipole transition moment                                  |
| MO         | molecular orbital  |
| MORD       | magnetic optical rotatory dispersion                               |
| MLCT       | metal to ligand charge transfer                                    |
| MW         | molecular weight   |
| NMR        | nuclear magnetic resonance   |
| OAM        | orbital angular momentum   |
| OBz        | benzoate   |
| ORD        | optical rotatory dispersion  |
| Pc         | phthalocyanine   |
| phen       | <i>o</i> -phenanthroline   |
| rcp        | right circularly polarised   |
| RNA        | ribonucleic acid   |
| SCF-CI-DV  | self consistent field–configuration interaction–dipole velocity    |
| SCF-PPP-CI | self-consistent field Pariser-Parr-Pople configuration interaction |
| SM         | spectroscopic moment   |
| TD-DFT     | time dependent–density functional theory                           |
| TFA        | trifluoroacetic acid   |
| TZVP       | triple zeta valence plus polarisation                              |
| VTVF       | variable temperature variable field                                |
| x–c        | exchange–correlation   |
| Xyl        | xylose   |
| ZFS        | zero field splitting   |

# Contents

|  |           |
|--|-----------|
| <b>Abbreviations</b>   | <b>xv</b> |
| <b>Chapter 1 Theory of Optical Spectroscopy</b>  | <b>1</b>  |
| 1.1 Electronic Absorption Spectroscopy   | 1         |
| 1.1.1 Exciton Coupling Theory  | 6         |
| 1.2 CD Spectroscopy  | 11        |
| 1.2.1 Units used for CD Spectroscopy   | 14        |
| 1.2.2 Analysis of CD Spectra   | 17        |
| 1.3 MCD Spectroscopy   | 21        |
| 1.3.1 Zeeman Splitting of States   | 23        |
| 1.3.2 MCD Intensity Mechanism, Sign Conventions and Intensity Units                    | 26        |
| 1.3.3 Quantitative Analysis of Groundstate and Excited State Magnetic Dipole Moments   | 31        |
| 1.3.4 MCD Spectroscopy of Transition Metal Complexes                                   | 34        |
| 1.3.5 Qualitative Analysis of MCD Spectra  | 39        |
| References   | 40        |
| <b>Chapter 2 Empirical Rules in CD Spectra and Absolute Configuration of Molecules</b> | <b>42</b> |
| 2.1 The Octant Rule  | 42        |
| 2.2 Benzene Sector and Benzene Chirality Rules   | 47        |
| 2.2.1 Benzene Sector Rule  | 47        |
| 2.2.2 Benzene Chirality Rule   | 50        |
| References   | 52        |

|                  |  |           |
|------------------|--|-----------|
| <b>Chapter 3</b> | <b>Representative Systems Analysed by the Exciton Coupling Method</b>  | <b>53</b> |
| 3.1              | Exciton Coupling among Fewer than Four Identical Chromophores  | 54        |
| 3.1.1            | Spectra of 5 $\alpha$ -Cholestane-2 $\beta$ ,3 $\beta$ - and 3 $\beta$ ,6 $\beta$ -diol <i>Bis</i> ( <i>p</i> -dimethylamino-benzoate) | 54        |
| 3.1.2            | Spectra of (6 <i>R</i> ,15 <i>R</i> )-(+)-6,15-Dihydro-6,15-ethanonaphtho[2,3- <i>c</i> ]pentaphene                                    | 55        |
| 3.1.3            | Additivity Relationship in the Amplitudes of Exciton-Split CD Curves of Sugar Benzoates  | 57        |
| 3.1.4            | Determination of the Absolute Configuration of Oligonaphthalenes   | 62        |
| 3.1.5            | Determination of the Absolute Configuration of a Natural Catechol Product, Haematoxylin, using the Phthalocyanine Chromophore          | 65        |
| 3.1.6            | Supramolecular Chirality in a Bisporphyrin System Axially Coordinated by a Chiral Guest  | 69        |
| 3.1.7            | A Chiral Biscyanine Dye exhibiting an Exciton Couplet with Well-resolved Absorption Bands  | 72        |
| 3.1.8            | CD and Absolute Configuration of C <sub>3</sub> Symmetry Chiral Cyclotrimeratrylenes   | 75        |
| 3.2              | Polymer Systems (Systems Consisting of more than Four Chromophores)  | 78        |
| 3.2.1            | Helical Structures of N-Alkylated Poly( <i>p</i> -benzamide)s  | 78        |
| 3.2.2            | Conformation of Helical Poly(2,3-quinoxaline)s   | 83        |
| 3.3              | Exciton Coupling between Non-Identical Chromophores  | 83        |
| 3.3.1            | Determination of the Absolute Configuration of Allylic Alcohols: Systems Containing a C=C Double Bond and a Benzoate                   | 86        |
| 3.3.2            | Application of the Exciton Chirality Method to Conjugated Enones, Esters and Lactones  | 88        |
|                  | References   | 91        |
| <b>Chapter 4</b> | <b>Cyclodextrin Inclusion Compounds</b>  | <b>93</b> |
| 4.1              | Induced Circular Dichroism of CyDs   | 94        |
| 4.1.1            | Inclusion of Pyrene in $\beta$ -CyD at Room Temperature and in $\gamma$ -CyD at 70°  | 95        |
| 4.1.2            | Inclusion of 2,3-Diaminonaphthalene and 1,8-Diaminonaphthalene in $\beta$ -CyD   | 96        |

|                  |  |            |
|------------------|--|------------|
| 4.1.3            | Lid-type Inclusion of Pyrene-1,3,6,8-tetrasulphonate Anion by $\beta$ -CyD   | 97         |
| 4.1.4            | Inclusion of 4,4'-Substituted Biphenyls by $\beta$ -CyD  | 98         |
| 4.1.5            | Inclusion of Bipyridyls by $\beta$ -CyD  | 99         |
| 4.1.6            | Disposition of Ferrocene in $\beta$ - or $\gamma$ -CyD   | 99         |
| 4.1.7            | Chirality of Two Pyrene Molecules in $\gamma$ -CyD   | 102        |
|                  | References   | 103        |
| <b>Chapter 5</b> | <b>Metal Complexes</b>   | <b>104</b> |
| 5.1              | Systems which can be Analysed by Excitation Coupling Theory: Absolute Configurations of Metal Complexes Containing <i>o</i> -Phenanthroline, 2,2'-Bipyridyl or Acetylacetonate | 104        |
| 5.2              | CD spectra in the $d \rightarrow d$ Transition Region  | 110        |
| 5.2.1            | $[\text{Co}(\text{en})_3]^{3+}$ and $[\text{Cr}(\text{en})_3]^{3+}$  | 110        |
| 5.2.2            | Near-IR Absorption and CD Spectra of Ferrocyclochrome <i>c</i> : $d \rightarrow d$ Transitions   | 112        |
|                  | References   | 115        |
| <b>Chapter 6</b> | <b>Circular Dichroism Induced by Optically Active Binaphthyl</b>   | <b>116</b> |
| 6.1              | Chiral Binaphthyl-Induced CD in Phthalocyanines  | 116        |
|                  | References   | 128        |
| <b>Chapter 7</b> | <b>Analysis of Chiral Systems by Theoretical Calculations</b>  | <b>130</b> |
| 7.1              | Semi-empirical Calculations  | 131        |
| 7.1.1            | Absolute Stereochemistry of (+)-1,8a-Dihydro-3,8-Dimethylazulene   | 131        |
| 7.1.2            | Analysis of Naphthalene-diene Derivatives  | 132        |
| 7.2              | TD-DFT Calculations  | 133        |
| 7.2.1            | Correlation between CD Sign and Conformation in Optically Active Oxo(phthalocyaninato)vanadium(IV)   | 133        |
| 7.2.2            | Optically Active Porphyrin Dimers  | 135        |
| 7.2.3            | Absolute Configuration and Chiroptical Properties of Three-layered [3,3]Paracyclophane   | 137        |
|                  | References   | 141        |

|                   |   |            |
|-------------------|---|------------|
| <b>Chapter 8</b>  | <b>Circular Dichroism of Biomolecules</b>   | <b>142</b> |
| 8.1               | Protein Chromophores and Electronic Absorption Spectroscopy   | 143        |
| 8.2               | CD Spectroscopy of Peptides   | 147        |
| 8.2.1             | $\alpha$ -Helix CD  | 147        |
| 8.2.2             | $\beta$ -Sheet and random coil CD   | 148        |
| 8.2.3             | $\beta$ -Turn CD  | 149        |
|                   | References  | 149        |
| <br>              |   |            |
| <b>Chapter 9</b>  | <b>Analysis of MCD Spectra</b>  | <b>150</b> |
| 9.1               | Examples of the Analysis of Faraday $\mathcal{A}_1$ Terms   | 150        |
| 9.1.1             | Cyclononatetraenide Anion   | 151        |
| 9.1.2             | Cycloheptatrienyl (Tropylium) Cation  | 152        |
| 9.1.3             | C <sub>60</sub> Fullerene   | 152        |
| 9.1.4             | Identification of the Electronic Origin of the S1 State of Zinc Tetraphenyltetraacenaphthoporphyrin | 153        |
| 9.2               | Examples of the Analysis of Faraday $\mathcal{B}_0$ Terms   | 155        |
| 9.2.1             | Analysis of the Symmetry-split Excited States of Azaporphyrins                                      | 155        |
| 9.2.2             | Analysis of Data Recorded at Cryogenic Temperature: Phthalocyanine Anion Radicals                   | 157        |
| 9.3               | Examples of Analysis of Faraday $\mathcal{C}_0$ MCD Terms   | 161        |
| 9.3.1             | The "Fingerprint" Approach  | 161        |
| 9.3.2             | Analysis of Data Recorded at Cryogenic Temperatures   | 163        |
| 9.3.3             | The Quantitative Analysis of Magnetisation Curves   | 167        |
| 9.4               | Analysis of MCD Spectra based on Molecular Orbital Calculations                                     | 168        |
|                   | References  | 169        |
| <br>              |   |            |
| <b>Chapter 10</b> | <b>Michl's Perimeter Model in MCD Spectroscopy</b>  | <b>172</b> |
| 10.1              | Michl's 4N+2-Perimeter Model for Aromatic $\pi$ -Systems  | 175        |
| 10.2              | Michl's 4N-Perimeter Model for Antiaromatic $\pi$ -Systems  | 179        |
| 10.3              | Applications of Michl's Perimeter Model   | 180        |
| 10.3.1            | Negative Faraday $\mathcal{A}_1$ MCD Term in a Cyclobutadiene Dianion                               | 180        |

|        |  |     |
|--------|--|-----|
| 10.3.2 | The Effect of Ligand Non-planarity on the Alignment of the Excited State Magnetic Moments of Zinc<br>Tetraphenyltetraacenaphthoporphyrin | 182 |
| 10.3.3 | The Application of the $4N$ and $4N+2$ Perimeter Model to the Spectra of Hexaphyrin(1.1.1.1.1.1)s  | 183 |
| 10.3.4 | Using Michl's Perimeter Model to Conceptualise the Optical Properties of Low Symmetry Aromatic $\pi$ -Systems                            | 185 |
| 10.3.5 | Analysis of the MCD Spectra of Benzofuran Derivatives Substituted with Group 16 Heteroatoms  | 187 |
|        | References   | 190 |

|                      |            |
|----------------------|------------|
| <b>Subject Index</b> | <b>192</b> |
|----------------------|------------|

## CHAPTER 1

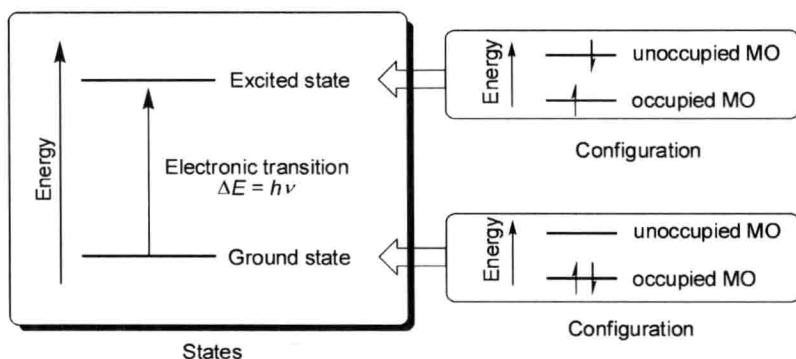
# *Theory of Optical Spectroscopy*

### 1.1 Electronic Absorption Spectroscopy

Optical spectroscopy is based ultimately on the interaction between atoms or molecules and incident electromagnetic radiation. In the 1860s, a Scottish physicist called James Clerk Maxwell first postulated that an oscillating electric field generates an oscillating magnetic field and *vice versa*. A propagating sinusoidal electromagnetic wave can be formed on this basis, with electric and magnetic fields oscillating perpendicular to one another and to the direction of propagation. Electromagnetic radiation exhibits both wave properties and particle properties and was described successfully by Albert Einstein in quantum mechanical terms as a particle, referred to as a photon ( $h\nu$ ), which has no mass or charge. At longer wavelengths in the IR region ( $>1000$  nm) the interaction between the atomic nuclei and the oscillating electric and magnetic fields typically results in molecular vibrations, which can be studied by infrared spectroscopy. At shorter wavelengths the heavier nuclei can no longer oscillate significantly, but the surrounding cloud of electron density can still be polarised in the direction of the oscillating electric field, resulting in an electronic transition from a groundstate electron configuration to an excited state. UV-visible absorption spectroscopy can be used to derive key information about the electronic structures of molecules on this basis, while techniques such as fluorescence spectroscopy can be used to derive information from the manner in which the molecule returns to its groundstate configuration.

As shown in Figure 1.1, molecular orbital theory can be used to describe this electronic excitation on the basis of the transfer of an electron from an occupied molecular orbital to an unoccupied molecular orbital. The energy difference between the ground and excited states ( $\Delta E$ ) is proportional to the frequency of the absorbed electromagnetic radiation ( $\nu$ ):

$$\Delta E = h\nu = hc/\lambda \quad (1.1)$$

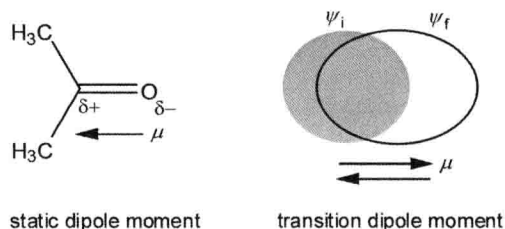


**Figure 1.1** Energy diagram showing an electronic transition.

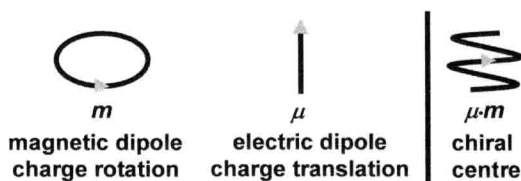
where  $h$  is the Planck constant ( $h = 6.626 \times 10^{-34}$  J s), and  $c$  and  $\lambda$  denote the velocity of light ( $c = 2.998 \times 10^8$  m s $^{-1}$ ) and the wavelength, respectively. Especially in the context of organic molecules, absorption in a particular region of the spectrum is often characteristic of a transition that is associated primarily with a particular type of bond or structural unit within a molecule. These structural units are usually referred to as chromophores. In the context of saturated organic molecules, wavelengths much shorter than 200 nm are required to cause electronic transitions. Since the conventional use of UV-visible absorption spectrometers under an air atmosphere tends to be limited to 200 nm, owing to strong absorption by oxygen and ozone formation at shorter wavelengths, electronic absorption spectroscopy is applied primarily to the  $\pi$ -systems of organic molecules and inorganic metal complexes, which absorb strongly at wavelengths  $> 200$  nm, with a particularly strong focus on aromatic and heteroaromatic cyclic compounds.

The interaction of UV or visible region light (typically 200–750 nm) with a molecule or complex can result in an electronic excitation from one molecular orbital to another, resulting in a transition from the groundstate electronic configuration to an excited state, Figure 1.1. This inherently results in a rearrangement of the electron density of a molecule. Since the size of molecules and complexes will typically be a few orders of magnitude smaller than the wavelength of UV-visible light, the electric field induces an oscillating electric dipole moment upon absorption of a photon. An electric dipole transition moment (edtm),  $\mu$ , can be defined for each transition, which describes the net linear displacement of charge during a transition. The initial point of this vector is set to the centre of gravity of the molecule, and the square of the transition dipole moment is proportional to the intensity of the electronic transition. If a transition is dipole forbidden,  $\mu = 0$ , while a transition is said to be allowed if  $\mu > 0$ . The direction in which  $\mu$  is aligned determines the polarisation of the associated spectral band with respect to the  $x$ -,  $y$ - and  $z$ -axes. It should be noted that edtm's are different from static electric dipole moments (also known as permanent dipole moments), which describe the polarisation of charge in a





**Figure 1.2** An illustration of a static dipole moment (left) and an electric transition dipole moment (right). The grey and white circles indicate electron distributions of the groundstate and an excited state.



**Figure 1.3** The origin of chirality, based on the combined effect of electronic and magnetic transition moments.

molecule in the groundstate, Figure 1.2. The direction of a static dipole moment can be determined definitively on the basis of the molecular structure. In contrast, since a transition dipole has an oscillating property, the choice of the sense of a transition dipole moment is arbitrary and depends on the phase of the wavefunctions. A magnetic dipole transition moment (mdtm),  $m$ , can also be defined for each electronic transition, which describes the net circulation of charge during a transition, Figure 1.3. The edtms are usually the dominant factor in coupling the groundstate with excited states within UV-visible absorption spectroscopy, since they tend to be *ca.* five orders of magnitude stronger than magnetic dipole moments. It should be noted that this is not the case during the quantitative analysis of CD spectral data, since the intensity mechanism is based on an interaction between electric and magnetic dipole transition moments. Sections 2.2 and 5.2 describe the analyses of carbonyl  $n \rightarrow \pi^*$  transitions in organic molecules and the  $d \rightarrow d$  transitions of transition metal complexes, which are magnetic dipole allowed but electric dipole forbidden.

Group theory can be used to determine whether transitions are electric dipole and magnetic dipole allowed or forbidden and the polarisation of the spectral bands, which arise in the UV-visible absorption spectrum based on the value of the transition moment integral:

$$\int \psi_1 \mu \psi_2 d\tau \quad (1.2)$$