MOLECULAR LIGHT SCATTERING AND OPTICAL ACTIVITY

Using classical and quantum methods with a strong emphasis on symmetry principles, this book develops the theory of a variety of optical activity and related phenomena from the perspective of molecular scattering of polarized light. In addition to the traditional topic of optical rotation and circular dichroism in the visible and ultraviolet region associated with electronic transitions, the newer topic of optical activity associated with vibrational transitions, which may be studied using both infrared and Raman techniques, is also treated. Ranging from the physics of elementary particles to the structure of viruses, the subject matter of the book reflects the importance of optical activity and chirality in much of modern science and will be of interest to a wide range of physical and life scientists.

LAURENCE BARRON worked with Professor Peter Atkins for his doctorate in theoretical chemistry from Oxford University, followed by postdoctoral work with Professor David Buckingham at Cambridge University. He was appointed to a faculty position at Glasgow University in 1975, where he is currently the Gardiner Professor of Chemistry. His research interests are in the electric, magnetic and optical properties of molecules, especially chiral phenomena including Raman optical activity which he pioneered and is developing as a novel probe of the structure and behaviour of proteins, nucleic acids and viruses.

MOLECULAR LIGHT SCATTERING AND OPTICAL ACTIVITY

Second edition, revised and enlarged

LAURENCE D. BARRON, F.R.S.E.
Gardiner Professor of Chemistry, University of Glasgow

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For Sharon

There are some enterprises in which a careful disorderliness is the true method.

Herman Melville, Moby Dick

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Preface to the first edition

Scientists have been fascinated by optical activity ever since its discovery in the early years of the last century, and have been led to make major discoveries in physics, chemistry and biology while trying to grapple with its subtleties. We can think of Fresnel's work on classical optics, Pasteur's discovery of enantiomeric pairs of optically active molecules which took him into biochemistry and then medicine, and Faraday's conclusive demonstration of the intimate connection between electromagnetism and light through his discovery of magnetic optical activity. And of course the whole subject of stereochemistry, or chemistry in space, has its roots in the realization by Fresnel and Pasteur that the molecules which exhibit optical rotation must have an essentially helical structure, so from early on molecules were being thought about in three dimensions.

A system is called 'optically active' if it has the power to rotate the plane of polarization of a linearly polarized light beam, but in fact optical rotation is just one of a number of optical activity phenomena which can all be reduced to the common origin of a different response to right- and left-circularly polarized light. Substances that are optically active in the absence of external influences are said to exhibit 'natural' optical activity. Otherwise, all substances in magnetic fields are optically active, and electric fields can sometimes induce optical activity in special situations.

It might be thought that a subject originating at the start of the nineteenth century would be virtually exhausted by now, but nothing could be further from the truth. The recent dramatic developments in optical and electronic technology have led to large increase in the sensitivity of conventional optical activity measurements, and have enabled completely new optical activity phenomena to be observed and applied. Traditionally, optical activity has been associated almost exclusively with electronic transitions; but one particularly significant advance over the last decade has been the extension of natural optical activity measurements into the vibrational spectrum using both infrared and Raman techniques. It is now becoming clear that vibrational optical activity makes possible a whole new world of fundamental studies and practical applications quite undreamt of in the realm of conventional electronic optical activity.

Optical activity measurements are expected to become increasingly important in chemistry and biochemistry. This is because 'conventional' methods have now laid the groundwork for the determination of gross molecular structure, and emphasis is turning more and more towards the determination of the precise three-dimensional structures of molecules in various environments: in biochemistry it is of course the fine detail in three dimensions that is largely responsible for biological function. Whereas X-ray crystallography, for example, provides such information completely, it is restricted to studies of molecules in crystals in which the three dimensional structures are not necessarily the same as in the environment of interest. Natural optical activity measurements are a uniquely sensitive probe of molecular stereochemistry, both conformation and absolute configuration, but unlike X-ray methods can be applied to liquid and solution samples, and even to biological molecules *in vivo*. The significance of magnetic optical activity measurements, on the other hand, can probably be summarized best by saying that they inject additional structure into atomic and molecular spectra, enabling more information to be extracted.

Following the recent triumph of theoretical physics in unifying the weak and electromagnetic forces into a single 'electroweak' force, the world of physics has also started to look at optical activity afresh. Since weak and electromagnetic forces have turned out to be different aspects of the same, more fundamental, unified force, the absolute parity violation associated with the weak force is now thought to infiltrate to a tiny extent into all electromagnetic phenomena, and this can be studied in the realm of atoms and molecules by means of delicate optical activity experiments. So just as optical activity acted as a catalyst in the progress of science in the last century, in our own time it appears set to contribute to further fundamental advances. One could say that optical activity provides a peephole into the fabric of the universe!

In order to deal with the optical properties of optically active substances in a unified fashion, and to understand the relationship between the conventional 'birefringence' phenomena of optical rotation and circular dichroism and the newer 'scattering' phenomena of Rayleigh and Raman optical activity, the theory is developed in this book from the viewpoint of the scattering of polarized light by molecules. In so doing, a general theory of molecular optics is obtained and is applied to the basic phenomena of refraction, birefringence and Rayleigh and Raman scattering. Optical activity experiments are then regarded as applications of these phenomena in ways that probe the asymmetry in the response of the optically active system to right- and left-circularly polarized light. As well as using the results of the general theory to obtain expressions for the observables in each particular optical activity phenomenon, where possible the expressions are also derived separately in as simple a fashion as possible for the benefit of the reader who is interested in one topic in isolation.

There are several important topics within the general area of optical activity that I have either omitted or mentioned only briefly, mainly because they are outwith the theme of molecular scattering of polarized light, and also because of my lack of familiarity with them. These include circular polarization of luminescence, and chiral discrimination. I have also not treated helical polymers: to do justice to this very important topic would divert us too far from the fundamental theory. Where I have discussed specific atomic or molecular systems, this has been to illuminate the theory rather than to give an exhaustive explanation of the optical activity of any particular system. For a much broader view of *natural* optical activity, including experimental aspects and a detailed account of a number of specific systems, the reader is referred to S. F. Mason's new book 'Molecular Optical Activity and the Chiral Discriminations' (Mason, 1982).

So this is not a comprehensive treatise on optical activity. Rather, it is a personal view of the theory of optical activity and related polarized light scattering effects that reflects my own research interests over the last 14 years or so. During the earlier part of this period I was fortunate to work with, and learn from, two outstanding physical chemists: Dr P. W. Atkins in Oxford and Professor A. D. Buckingham in Cambridge; and their influence extends throughout the book.

I wish to thank the many colleagues who have helped to clarify much of the material in this book through discussion and correspondence over the years. I am particularly grateful to Dr J. Vrbancich for working through the entire manuscript and pointing out many errors and obscure passages.

Glasgow
May 1982

Preface to the second edition

Interest in optical activity has burgeoned since the first edition of this book was published in 1982. The book anticipated a number of new developments and helped to fuel this interest, but has become increasingly hard to find since going out of print in 1990. Numerous requests about where a copy might be found, often accompanied by 'our library copy has been stolen' and the suggestion that a second edition would be well-received, have encouraged me to prepare this new edition. The book has been considerably revised and enlarged, but the general plan and style remain as before.

Traditionally, the field of optical activity and chirality has been largely the preserve of synthetic and structural chemistry due to the inherent chirality of many molecules, especially natural products. It has also been important in biomolecular science since proteins, nucleic acids and oligosaccharides are constructed from chiral molecular building blocks, namely the L-amino acids and the D-sugars, and the chemistry of life is exquisitely stereospecific. The field is becoming increasingly important in these traditional areas. For example, chirality and enantioselective chemistry are now central to the pharmaceutical industry since many drugs are chiral and it has been recognized that they should be manufactured as single enantiomers; and chiroptical spectroscopies are used ever more widely for studying the solution structure and behaviour of biomolecules, a subject at the forefront of biomedical science. But in recent years optical activity and chirality have also been embraced enthusiastically by several other disciplines. Physicists, for example, are becoming increasingly interested in the field due to the subtle new optical phenomena, linear and nonlinear, supported by chiral fluids, crystals and surfaces. Furthermore, since homochiral chemistry is the signature of life, and considerable effort is being devoted to searches for evidence of life, or at least of prebiotic chemistry, elsewhere in the cosmos including interstellar dust clouds, cometary material and the surfaces of extrasolar planets, chirality has captured the interest of some astrophysicists and space scientists. It has even caught the attention of applied mathematicians and electrical engineers on account of the novel and potentially useful electromagnetic properties of chiral media.

Although containing a significant amount of new material the second edition, like the first, is not a comprehensive treatise on optical activity and remains a personal view of the theory of optical activity and related polarized light scattering effects that reflects my own research interests. The material on symmetry and chirality has been expanded to include motion-dependent enantiomorphism and the associated concepts of ‘true’ and ‘false’ chirality, and to expose productive analogies between the physics of chiral molecules and that of elementary particles which are further emphasized by considering the violation of parity and time reversal invariance. Another significant addition is a detailed treatment of *magnetochiral* phenomena, which are generated by a subtle interplay of chirality and magnetism and which were unknown at the time of writing the first edition. Since vibrational optical activity has now ‘come of age’ thanks to new developments in instrumentation and theory in the 1980s and 1990s, the treatment of this topic has been considerably revised and expanded. Of particular importance is a new treatment of vibrational circular dichroism in Chapter 7; serious problems in the quantum chemical theory, now resolved, were unsolved at the time of writing the first edition, which contains an error in the way in which the Born–Oppenheimer approximation was applied. The revised material on natural Raman optical activity now reflects the fact that it has become an incisive chiroptical technique giving information on a vast range of chiral molecular structures, from the smallest such as CHFClBr to the largest such as intact viruses. New developments in magnetic Raman optical activity are also described which illustrate how it may be used as a novel probe of magnetic structure.

Another subject to come of age in recent years is nonlinear optical activity, manifest as a host of different optical phenomena generated by intense laser beams incident on both bulk and surface chiral samples. However the subject has become too large and important, and too specialized with respect to its theoretical development, to do it justice within this volume which is therefore confined to linear optical activity phenomena.

I have benefited greatly from interactions with many colleagues who have helped directly and indirectly with the identification and correction of errors in the first edition, and with the preparation of new material. I am especially grateful in this respect to E. W. Blanch, I. H. McColl, A. D. Buckingham, J. H. Cloete, R. N. Compton, J. D. Dunitz, K.-H. Ernst, R. A. Harris, L. Hecht, W. Hug, T. A. Keiderling, L. A.

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I hope that workers in many different areas of pure and applied science will find something of value in this second edition.

Glasgow
2004

Symbols

The symbols below are grouped according to context. In some cases the same symbol has more than one meaning, but it is usually clear from the context which meaning is to be taken. A tilde above a symbol, for example $\tilde{A}$, denotes a complex quantity, the complex conjugate being denoted by an asterisk, for example $\tilde{A}^*$. A dot over a symbol, for example $\dot{A}$, denotes the time derivative of the corresponding quantity. An asterisk is also used to denote an antiparticle or an antiatom, for example ν^* and Co*.

Historical review

α	optical rotation angle
$[\alpha]$	specific rotation
ψ	ellipticity
$[\psi]$	specific ellipticity
ϵ	decadic molar extinction coefficient
g	dissymmetry factor
V	Verdet constant
Δ	dimensionless Rayleigh or Raman circular intensity difference
R, S	absolute configuration in the Cahn–Ingold–Prelog notation. (R)-$(+)$ etc. specifies the sense of optical rotation associated with a particular absolute configuration
P, M	helicity designation of the absolute configuration of helical molecules

Electric and magnetic fields and electromagnetic waves

λ	wavelength
c	velocity of light
v	wave velocity
ω	angular frequency, magnitude $2\pi v/\lambda$ ($2\pi c/\lambda$ in free space)
n	refractive index, magnitude c/v
n'	absorption index

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$\tilde{n}$	complex refractive index $n + \mathrm{i}n'$
$\mathbf{n}$	propagation vector, magnitude n
$\boldsymbol{\kappa}$	wavevector, magnitude ω/v (may be written $\omega\mathbf{n}/c$)
$\mathbf{E}$	electric field vector in free space
$\mathbf{B}$	magnetic field vector in free space
$\mathbf{D}$	electric field vector within a medium
$\mathbf{H}$	magnetic field vector within a medium
ρ	electric charge density
$\mathbf{J}$	electric current density
$\mathbf{N}$	Poynting vector
I	intensity (time average of $\lvert\mathbf{N}\rvert$)
ϕ	scalar potential
$\mathbf{A}$	vector potential
$\mathbf{P}$	bulk polarization
$\mathbf{M}$	bulk magnetization
$\mathbf{Q}$	bulk quadrupole polarization
ϵ	dielectric constant
μ	magnetic permeability
ϵ_0	permittivity of free space
μ_0	permeability of free space

Polarized light

η	ellipticity of the polarization ellipse
θ	azimuth of the polarization ellipse
S_0, S_1, S_2, S_3	Stokes parameters
P	degree of polarization
$\tilde{\boldsymbol{\Pi}}$	complex polarization vector
$\tilde{\rho}_{\alpha\beta}$	complex polarization tensor

Geometry and symmetry

$\mathbf{i},\mathbf{j},\mathbf{k}$	unit vectors along space-fixed axes x,y,z.
$\mathbf{I},\mathbf{J},\mathbf{K}$	unit vectors along molecule-fixed axes X,Y,Z.
$\mathbf{r}$	position vector
$l_{\lambda'\alpha}$	direction cosine between the λ' and α axes ($\cos^{-1} l_{\lambda'\alpha}$ is the angle between the λ' and α axes)
$\delta_{\alpha\beta}$	Kronecker delta
$\varepsilon_{\alpha\beta\gamma}$	alternating tensor
$T_{\alpha\beta\ldots}$	$\nabla_\alpha \nabla_\beta \ldots R^{-1}$
P	parity operation
T	classical time reversal operation

C	charge conjugation operation
p	eigenvalue of P
$2\pi b$	helix pitch
a	helix radius
$[\Gamma^2]$	symmetric part of the direct product of the representation Γ with itself
$\{\Gamma^2\}$	antisymmetric part of the direct product of the representation Γ with itself
$D^{(j)}$	irreducible representation of the proper rotation group R_3^+
T_q^k	irreducible spherical tensor operator

Classical mechanics

$\mathbf{v}$	velocity vector
$\mathbf{p}$	linear momentum vector
$\mathbf{L}$	angular momentum vector
$\mathbf{F}$	Lorentz force vector
W	total energy
T	kinetic energy
V	potential energy
L	Lagrangian function
H	Hamiltonian function
$\mathbf{p}'$	generalized momentum vector
Q_p	normal coordinate for the pth normal mode of vibration
P	momentum conjugate to Q_p, namely $\dot{Q}_p$
s_q	qth internal vibrational coordinate
$\mathbf{L}$	vibrational $\mathbf{L}$-matrix

Quantum mechanics

h	Planck constant
$\hbar$	$h/2\pi$
ψ	wavefunction
H	Hamiltonian operator
e_j, v_j, r_j	electronic, vibrational, rotational parts of the jth quantum state
j, m	general angular momentum quantum number, associated magnetic quantum number, of a particle
l, m_l	orbital angular momentum quantum number, associated magnetic quantum number, of a particle
s, m_s	spin angular momentum quantum number, associated magnetic quantum number, of a particle
J, M	total angular momentum quantum number, associated magnetic quantum number, of an atom or molecule

K	quantum number specifying the projection of the total angular momentum onto the principal axis of a symmetric top
g_i	g-value of the ith particle spin
Θ	quantum mechanical time reversal operator
ϵ	eigenvalue of Θ^2
A^T	transpose of operator A
$A^\dagger = A^{T*}$	Hermitian conjugate of operator A
Y_{lm}	spherical harmonic function
2δ	tunnelling splitting
2ϵ	parity-violating energy difference between chiral enantiomers
G	Fermi weak coupling constant
α	fine structure constant
g	weak charge
Q_W	effective weak charge
θ_W	Weinberg electroweak mixing angle
$\boldsymbol{\sigma}$	Pauli spin operator
Z	proton number
$[a, b]$	commutator $ab - ba$
$\{a, b\}$	anticommutator $ab + ba$

Molecular properties

e_i	electric charge of the ith particle ($+e$ for the proton, $-e$ for the electron)
q	net charge or electric monopole moment
$\boldsymbol{\mu}$	electric dipole moment vector
$\mathbf{m}$	magnetic dipole moment vector
$\Theta_{\alpha\beta}$	traceless electric quadrupole moment tensor
$\alpha_{\alpha\beta}$	real part of the electric dipole–electric dipole polarizability tensor
$\alpha'_{\alpha\beta}$	imaginary part of the electric dipole–electric dipole polarizability tensor
$G_{\alpha\beta}$	real part of the electric dipole–magnetic dipole optical activity tensor
$G'_{\alpha\beta}$	imaginary part of the electric dipole–magnetic dipole optical activity tensor
$A_{\alpha,\beta\gamma}$	real part of the electric dipole–electric quadrupole optical activity tensor
$A'_{\alpha,\beta\gamma}$	imaginary part of the electric dipole–electric quadrupole optical activity tensor
$\mathcal{G}_{\alpha\beta}$	real part of the magnetic dipole–electric dipole optical activity tensor
$\mathcal{G}'_{\alpha\beta}$	imaginary part of the magnetic dipole–electric dipole optical activity tensor

$\mathscr{A}_{\alpha,\beta\gamma}$	real part of the electric quadrupole–electric dipole optical activity tensor
$\mathscr{A}'_{\alpha,\beta\gamma}$	imaginary part of the electric quadrupole–electric dipole optical activity tensor
$\tilde{\alpha}_{\alpha\beta}$, etc.	complex polarizability $\alpha_{\alpha\beta} - \mathrm{i}\alpha'_{\alpha\beta}$, etc. (the minus sign arises from the choice of sign in the exponents of the complex dynamic electric and magnetic fields)
α	isotropic invariant of $\alpha_{\alpha\beta}$
G'	isotropic invariant of $G'_{\alpha\beta}$
$\beta(\alpha)^2$	anisotropic invariant of $\alpha_{\alpha\beta}$
$\beta(G')^2$	anisotropic invariant of $G'_{\alpha\beta}$
$\beta(A)^2$	anisotropic invariant of $A_{\alpha,\beta\gamma}$
κ	dimensionless polarizability anisotropy

Spectroscopy

$[\Delta\theta]$	specific rotation
η	ellipticity
$I^{\mathrm{R}}, I^{\mathrm{L}}$	Rayleigh or Raman scattered intensity in right (R)- or left (L)-circularly polarized incident light
$D(j \leftarrow n)$	dipole strength for the $j \leftarrow n$ transition
$R(j \leftarrow n)$	rotational strength for the $j \leftarrow n$ transition
$\hbar\delta$	Zeeman splitting
A, B, C	Faraday A-, B- and C-terms