Circular Dichroism Spectrometers

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Abbreviations

ACS	ammonium d-10-camphor sulfonate
CD	circular dichroism
CPL	circularly polarized light
ECD	electronic circular dichroism
LPL	linearly polarized light
ORD	optical rotatory dispersion
PEM	photoelastic modulator
PMT	photomultiplier tube
ROA	Raman optical activity
UV	ultraviolet
VCD	vibrational circular dichroism

Historical Perspective

Circular dichroism (CD) is the differential absorption of left and right circularly polarized light (CPL) by a chiral substance. The phenomenon can occur for all wavelengths of light and results in 'vibrational' CD (VCD) in the infrared region and 'electronic' CD (ECD) in the ultraviolet (UV) and visible regions, corresponding to the different excitations induced in a molecule by the light; 'Raman Optical Activity' (ROA) is the analogous phenomenon for Raman scattering. The VCD and ROA techniques are described elsewhere in this encyclopedia; the section here concentrates on the instrumentation for ECD.

Of these different forms of chiroptical spectroscopy, ECD is by far the most commonly employed technique for investigating chiral substances and is, therefore, often referred to simply as 'CD.' Not least this choice is aided by the relatively small sample requirements (typically less than 1 mg) and wide variety of solution conditions that can be accommodated by ECD.

As early as 1811, Arago had discovered that quartz plates cause plane-polarized light to be rotated by different degrees with varying wavelength of light. This wavelength dependence of optical rotation, the basis of optical rotatory dispersion (ORD), was further elucidated by Biot and Fresnel in the following two decades. However, ORD subsequently received little experimental attention, with the primary experimental work being constrained to optical rotations of a single wavelength, the sodium D-line (589.3 nm). Apart from work by Tschugaefi and Rupe (early 1900s), the phenomenon of ORD remained a theoretical concern until the studies of Kuhn, Lowry, Mitchell, Levene, and Rothen in the 1930s.

Nonetheless, the technical difficulties of measuring ORD, primarily through photographic means, hampered the science until the development of photoelectric spectropolarimeters in the mid-1950s. Brand and Rudolph introduced the first photoelectric spectropolarimeter *c.*1956. During the subsequent 10 years various manufacturers, including Roussel-Uclaf, Jasco (1961 onwards, the ORD-UV-5 instrument being notable), and Bellingham and Stanley (otherwise known as Bendix-Ericsson or Bendix-Gillham-King), introduced new designs and automated spectropolarimeters with extended wavelength ranges, often taking advantage of a Faraday cell to electrically generate a compensating optical rotation.

The phenomenon of CD was discovered relatively soon after Arago's initial observations of ORD, with Hidinger reporting differential absorption of CPL by amethyst crystals in 1847. CD of copper and chromium tartrate solutions was later observed by Cotton in 1895–96. Its application to organic molecules awaited the pioneering work of Mitchell, Lowry, and Kuhn in the late 1920s and 1930s. The development of CD instrumentation broadly followed that for ORD and in the late 1950s the Roussel-Juoan dichograph was produced, based around the Pockel cell, a tetragonal crystal of monoammonium phosphate subjected to an electric field to generate circularly polarited light from linearly polarized light (LPL), a forefather of the photoelastic modulators (PEMs) used today. Jasco subsequently made an attachment for its ORD-UV-5 spectropolarimeter in order that it may measure CD; to this day, Jasco CD instruments are described by the company as 'spectropolarimeters' despite their now being designed to primarily measure CD not ORD.

Linearly, Elliptically, and Circularly Polarized Light

The properties of polarized light are of crucial importance to the operation of CD instruments and thus the main features are briefly recapped here.

LPL of a given wavelength λ and frequency ν is defined as having its electric field vector transverse to the direction of propagation, lying in a single plane and varying sinusoidally with time and space as depicted in **Figure 1**(**a**). The equation for the electric field vector at a particular position z along the direction of propagation at time t can be written as follows:

$$A(z,t) = A_{\mathrm{o}} \sin\left(\frac{\omega z}{c_{\mathrm{m}}} - \omega t\right) i$$

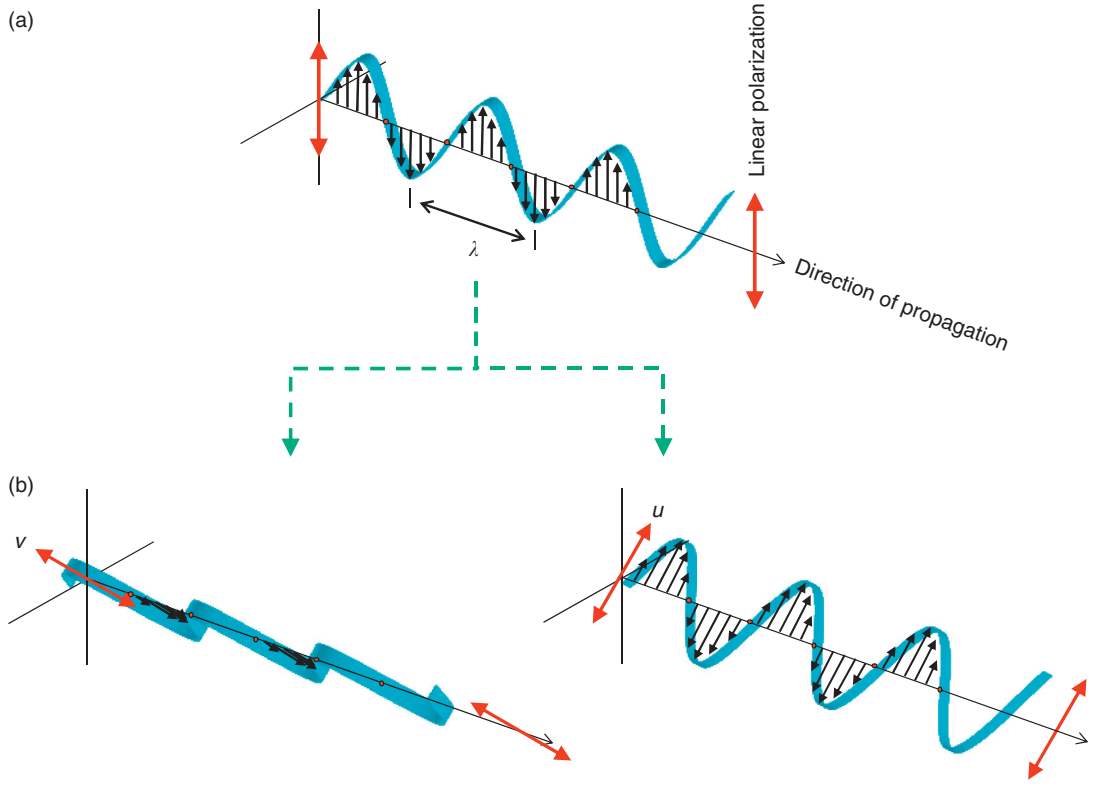

Figure 1 (a) (*Top*) linearly polarized light of wavelength λ, polarized in the vertical plane, showing the electric field vectors perpendicular to the direction of propagation through space; (b) (*bottom*) the light decomposed into two in-phase components with mutually orthogonal plane polarizations at $\pm 45^\circ$ to the original polarization. From Chiralabs Ltd., with permission.

where i is the unit vector in the direction of polarization, ω is the angular frequency ($2\pi v$), and c_m is the velocity of light in the medium, with the scalar amplitude being A_o.

This LPL can be considered as composed of either two mutually orthogonal linearly polarized components, as in **Figure 1(b)**, or two oppositely handed circularly polarized components, as in **Figure 5(b)**. Both descriptions are equally valid and by modifying these components in various ways, a range of possible polarization states of light can be obtained.

Linearly Polarized Components

First (LPL), can be considered as being composed of two mutually orthogonal, in-phase, equal magnitude linearly polarized components with planes of polarization lying at -45° and $+45^\circ$ to the original plane, as in **Figure 1(b)**. In this figure, the directions of the component polarizations are denoted as u and v.

If the v component were to be retarded relative to the u component by a distance $\delta = \lambda/2$ and the components recombined, as depicted in **Figure 2**, then LPL would be regained, but the plane of polarization would be rotated through 90°. A similar result is obtained if the u component is retarded instead. This is the basis of a 'half-wave plate' for rotating plane-polarized light and applies for all retardations that are odd integer multiples of $\lambda/2$, the even integer multiples simply retaining the linear polarization at its initial state.

Alternatively, if the v component were to be retarded relative to the u component by a distance of $\delta = \lambda/4$ and the components recombined, then left CPL would be generated, as depicted in **Figure 3**. (By convention, a viewer looking at the oncoming light, back along the direction of propagation toward the source, sees the electric field describe an anticlockwise motion with time for left CPL and, correspondingly, a clockwise motion for right CPL; thus, at any point in time, left CPL spatially describes a left-handed helix and right CPL spatially describes a right helix.) An analogous result but generating right CPL occurs if the u component is retarded instead (which can alternatively be described as a negative retardation), as depicted in **Figure 4**. This is the basis of a 'quarter-wave plate' for converting plane-polarized light to circular polarization.

For retardations that are not integer multiples of $\lambda/4$ or $\lambda/2$, the situation is rather more complex and generally ellipsoidally-polarized light results. The degree of ellipticity can be described by the ratio of its minor to major axes, P_{minor} and P_{major}, respectively (as electric

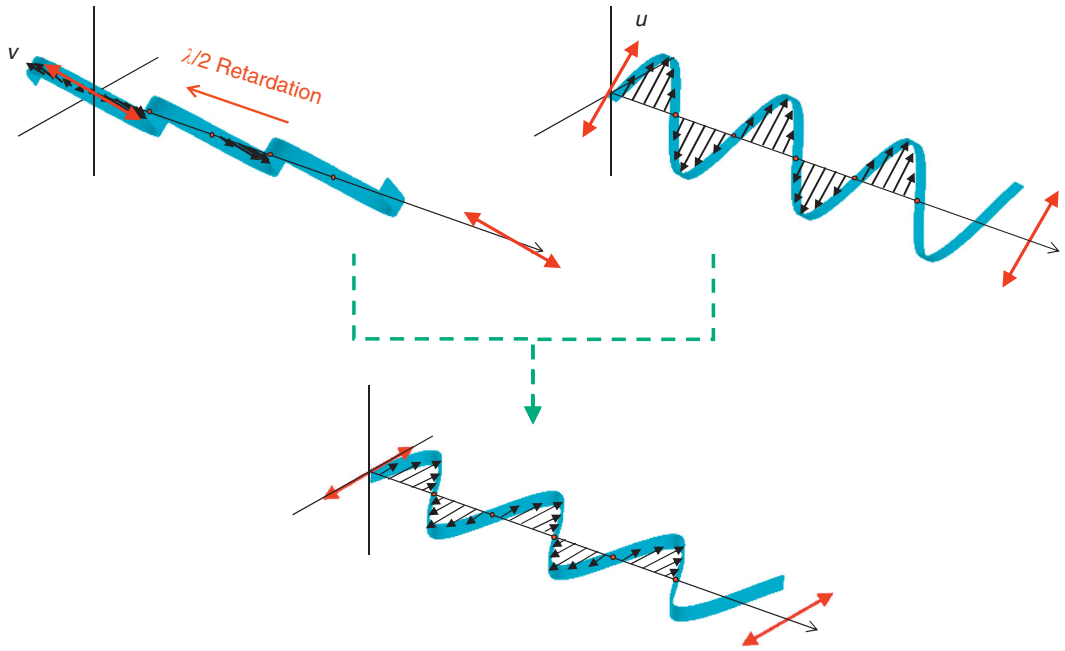

Figure 2 Retardation of one component by $\lambda/2$ gives plane-polarized light with its plane of polarization rotated through 90°. From Chiralabs Ltd., with permission.

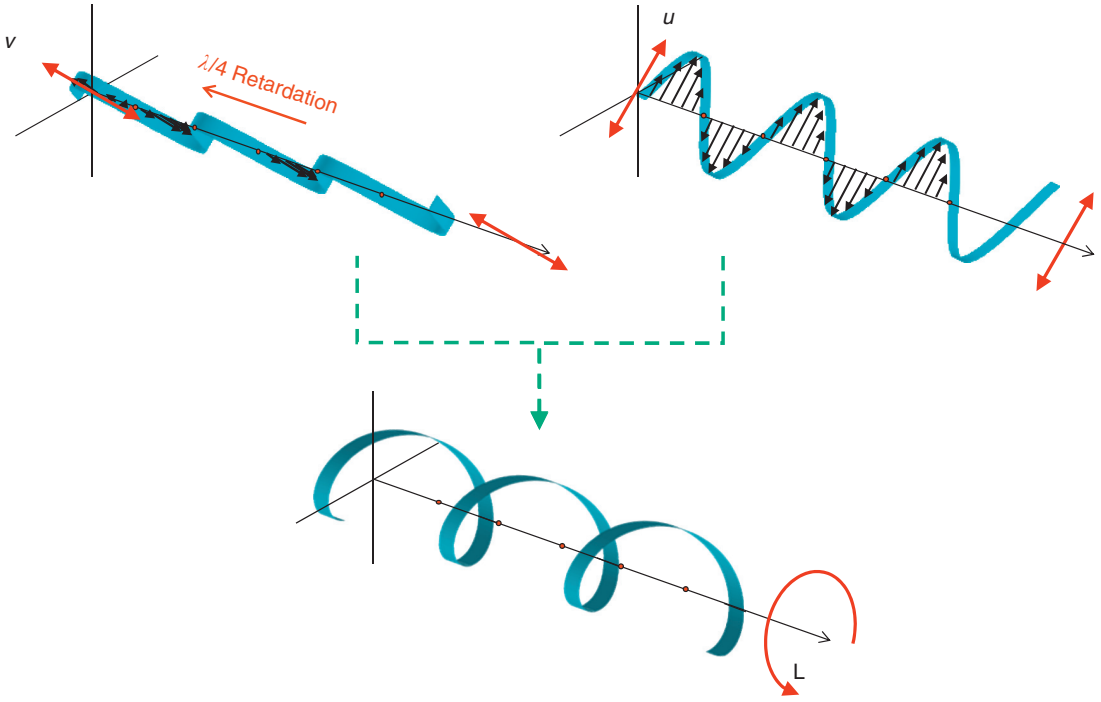

Figure 3 Retardation of *v* component by $\lambda/4$ relative to *u* component gives left circularly polarized light. From Chiralabs Ltd., with permission.

field vector amplitudes), to give an angular ellipticity of θ:

$$\tan\theta = \frac{P_{\text{minor}}}{P_{\text{major}}}$$

Now suppose, instead of retardation, the v polarized component underwent a reduction in magnitude (such as when it is absorbed). In this case, on combining back with its u polarized complement, plane-polarized light is regained albeit with a loss in amplitude, but with the plane rotated clockwise (following the viewing convention

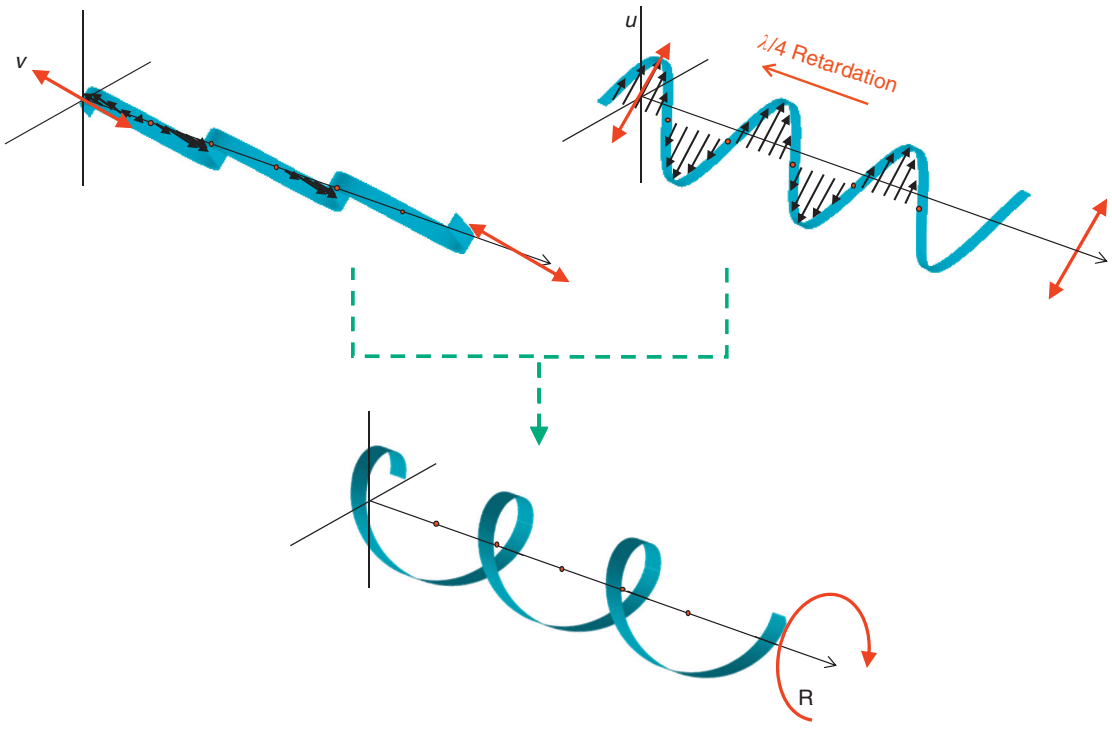

Figure 4 Retardation of *u* component by $\lambda/4$ relative to *v* component gives right circularly polarized light. From Chiralabs Ltd., with permission.

described earlier). Correspondingly, a reduction in magnitude of the *u* polarized component gives rise to an anticlockwise rotation. This forms the basis of linear dichroism spectroscopy, details of which can be found elsewhere in this encyclopedia.

Circularly Polarized Components

LPL can also be considered as being composed of two in-phase equal magnitude CPL components, with their electric field vectors describing left- and right-handed helices, respectively, as in **Figure 5**.

If the left circularly polarized component were to be retarded relative to the right by a distance δ and then the components recombined, LPL would be regained but with a rotated plane of polarization; the angle or rotation (φ) being given by the relationship:

$$\varphi = \frac{\delta \cdot \pi}{\lambda}$$

Similarly, if the right CPL were to be retarded (a negative δ) a rotation of the plane in the opposite direction would be apparent, corresponding to an inversion in the sign of rotation. This is the basis of optical rotation, more of which can be found in the related sections in the encyclopedia, the retardation distance being given by the differential refractive indices of a chiral sample to CPL ($n_L - n_R$). Likewise, it is the basis of 'half-wave plates' that rotate plane-polarized light by 90°, but simply described from a different perspective.

However, suppose instead of retardation, the left circularly polarized component underwent a reduction in magnitude (such as when it is absorbed). Combining back with its right circular polarized complement, *elliptically polarized light* is obtained instead of the original linearly polarization. In terms of the amplitudes of the two circularly polarized components (P_L and P_R, respectively), the ellipticity defined earlier in the text is now given by

$$\tan\theta = \frac{P_R - P_L}{P_R + P_L}$$

and, in terms of their intensities I_L and I_R:

$$\tan\theta = \frac{I_R^{1/2} - {I_L}^{1/2}}{I_R^{1/2} + {I_L}^{1/2}}$$

Differential Absorption and Light Intensities

To measure CD, a CD spectrometer invariably generates both hands of CPL from plane-polarized light and, in some way, measures the difference in absorption of each by a sample. By scanning or delineating the wavelengths of light, a CD spectrum is acquired, that is,

$$\Delta A_\lambda = A_{L\lambda} - A_{R\lambda}$$