Linear & Circular Dichroism

APPLICATION NOTE

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The PEM photoelastic modulator is well suited for experiments which measure linear dichroism (LD) or circular dichroism (CD). The modulator has an RS-232 computer interface which enables the peak retardation level to be varied under computer control in synchronization with a scanning monochromator. The interface allows the computer to monitor the status of the modulator as well.

Linear dichroism is the differential absorption between two orthogonal components of linear polarized light.[1, 2] This phenomenon occurs with certain natural crystals, with stretched polymers and with other non-isotropic samples. The techniques for reflectance difference spectroscopy or reflectance anisotropy spectroscopy are similar to linear dichroism (see PEM Newsletter #9).

Circular dichroism is the differential absorption between left and right circular polarized light components. This occurs naturally with chiral compounds, that is, those molecules which exhibit "mirror isomerism" (left and right-handedness).

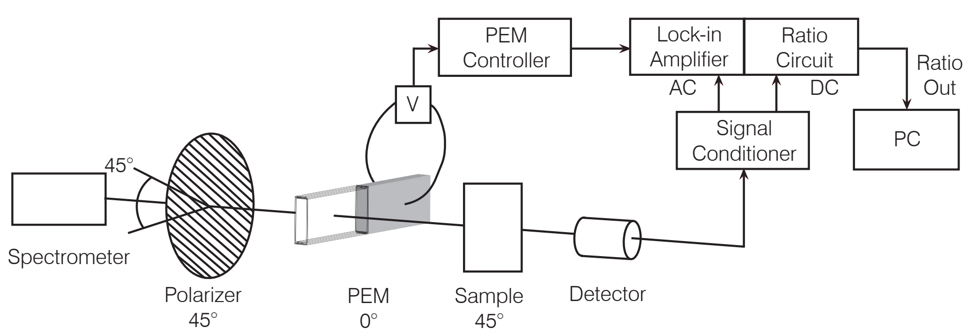
Both LD and CD can be measured with the same apparatus, shown below.

Light from the monochromatic light source is polarized at an angle of 45° with respect to the modulator axis. Light coming from the modulator alternates between two orthogonal linear polarization states, or between the two senses of circular polarized light, depending on the peak retardation of the modulator.

For linear dichroism the sample should be oriented so that a natural dichroic axis is at 45° to the modulator axis. The detector output is an electrical signal whose average (DC) voltage is proportional to the amount of light reaching the detector. The AC portion of the signal (proportional to the LD effect) is at twice the modulator frequency (2f).

No special orientation of the sample is needed for circular dichroism samples. The AC signal (proportional to the CD effect) is at the modulator frequency (f). The average or DC voltage is proportional to the amount of light reaching the detector.

The preamplifier provides current to voltage conversion and buffers the output for wide frequency response. (Hinds provides photodiode detectors which provide proper impedance matching and frequency response, e.g. DC to 1 MHz.) The PEM controller determines the peak retardation of the modulator. This is traditionally chosen to be half-wave retardation for LD experiments and quarter-wave retardation for CD measurement. Use of an intermediate value of retardation (0.383 waves) permits simultaneous measurement of LD and CD.[1]



EXPERIMENTAL SET-UP FOR LINEAR AND CIRCULAR DICHROISM

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The signal conditioner (Hinds Model SCU) provides amplification and derives a broad-band AC signal and a low-pass or DC signal. The AC signal goes to a lock-in amplifier, where detection of the signal is accomplished by phase sensitive detection, using a reference signal (f or 2f) from the modulator controller. The output is an analog voltage proportional to the desired f or 2f signal component.

The electrical signal obtained from the lock-in amplifier is dependent on the intensity of the light used in the experiment. Dividing the lock-in amplifier output by the DC or lowpass signal from the lock-in gives a signal which is directly proportional to the desired LD or CD effect. This may be expressed by the relationship

$$LD \; \alpha \; \frac{V_{2f}}{V_{DC}} \quad \text{or} \quad CD \; \alpha \; \frac{V_{1f}}{V_{DC}}$$

The calculation of the ratio of the AC voltage and the DC voltage may be done using a ratio circuit (such as is provided in many commercial lock-in amplifiers) or may be done in a computer, after the AC and DC signal components have been digitized.

References:

1. Hipps, K.W. and Crosby, G.A., Applications of the Photoelastic Modulator to Polarization Spectroscopy, Journal of Physical Chemistry, 83, 555, 1979.

2. Drake, Alex F., Polarisation modulation the measurement of linear and circular dichroism, J. Phys. E: Sci Instrum. 19, 1986.

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