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Real-Time Circular Dichroism Spectrograph Based on a Single Liquid Crystal Diffractive Element

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A simple spectrograph based on a polarization grating has been developed for real time measurements of circular dichroism. The main and unique element is a liquid crystal replica of a polarization grating recorded by means of holographic techniques in thin films of organic materials. This gratings offer long time stability and high diffraction efficiency. Due to the peculiar features of the grating, the circular dichroism of any system can be easily evaluated measuring only the intensities of the first order diffracted beams, just locating the grating after the investigated system. The spectral selectivity of the grating allows simultaneous measurements for all wavelengths of the spectra by using two linear Charged-Coupled devices.

Keywords Circular dichroism; polarisation grating; real-time spectrograph

Introduction

The systems conventionally used to measure circular dichroism (CD) generally require an intense source of light with a wide spectrum, a monochromator, modulators of polarisation, and use phase sensitive detectors (lock-in amplifiers) tuned to the frequency and the phase of the modulator [1–7].

They are generally constituted by several optical elements placed before and after the sample to be analysed, and some of these elements are used to alternatively select the right and left circular polarisation (CP) of the incoming wave, while others are dispersive elements (prisms or gratings) necessary to select the various wavelengths, etc.

All the systems based on conventional methods have parts that move or modulate the signal, therefore limiting their use for dynamic processes studies to the characteristic time of the moving or modulated parts. The object of the present paper proposes a method that allows overcoming the difficulties and disadvantages present in the state of the art.

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The main aim of the work is to show a method for measuring the CD that uses a polarization hologram (PH) recorded in a liquid crystal (LC) cell, in which the nematic molecular director has a spatially modulated linear optical anisotropy. The diffracted beams from the holographic grating are detected, and these signals are sent to a computer where dedicated software calculates the CD spectrum.

The real time measurement of the CD permits both dynamic processes and kinetics studies of chiral molecules.

The Liquid Crystal Cell

The diffracting grating, on whose properties the proposed method is based, is a LC film having spatially modulated linear optical anisotropy (dichroism or linear birefringence) [8].

The LC diffraction grating is obtained recording a polarization grating on each of the photosensitive aligning substrates, by using two beams having opposite CP. Azo-dye-doped layers are used, which provide planar alignment of the LC perpendicular to the light polarization, [9] through anisotropic van der Waals interaction between partially conjugated LC molecules and strongly conjugated dye molecules. For proper values of the cell thickness and spatial periodicity ratio d/L (d is the thickness of the sample and L the grating periodicity), the LC director follows the modulation of the anchoring conditions, creating a perfect bulk replica of the polarization gratings at the aligning substrates. Only first order diffracted beams occur, as expected for this configuration. Very high diffraction efficiency (DE$\sim$98%) with low scattering can be obtained in thin grating regime at the proper cell thickness. In order to minimise the losses, the experiment the polarization holograms where recorded on the aligning substrates of a wedge cell with a thickness ranging from 1 to about 2 μm. In this way, carefully selecting the proper cell thickness, it was possible to fulfil the condition to approach 100% diffraction efficiency.

In the experiment, the 20 nm thick polarization sensitive layers of azo-dye-doped polyimide were prepared by spin coating on glass plates. These substrates were used to assemble the wedge LC cell. The empty cell was exposed to a polarization pattern obtained by interference of two opposite CP beams of an Ar-Ion laser, $\lambda = 458$ nm (Innova 90 by Coherent). Finally the cell was filled by capillary action with LC E7 (BL001 of Merck).

A perfect replica of the polarization grating recorded on the substrates was obtained in the LC director bulk distribution. A diffraction efficiency of about 90% has been obtained.

Operating Principles

Transmission and diffraction properties of the grating are below explained in order to illustrate the proposed method [10].

Let us consider a plane monochromatic wave with an arbitrary polarisation that impinges along the normal (axis z, Figure 1) on the grating.

Using the Jones' formalism to describe the polarised light propagation through the above-mentioned grating, the Jones' vector of a light beam with arbitrary polarisation can be written as follows: [11]

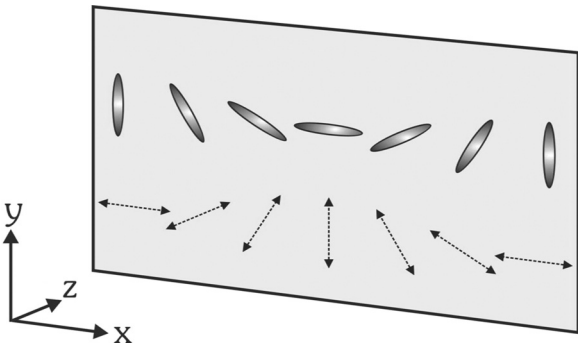

Figure 1. Diffraction grating. Representation of the spatial modulation of the optical axis in the material.

$$\begin{pmatrix} \mathrm{E_x} \\ \mathrm{E_y}\exp(i\theta) \end{pmatrix}, \tag{1}$$

where $\mathrm{E_x}$ e $\mathrm{E_y}$ are the field components along x- and y-axis, while θ represents the phase difference between the two components.

The transmission matrix of the grating can be written in the following way: [12]

$$T_r = \begin{vmatrix} a + 2b\cos qx & 2b\mathrm{sinqx} \\ 2b\sin q\mathrm{x} & a - 2b\cos qx \end{vmatrix} \tag{2}$$

In the case of a material with induced linear dichroism a is the average transmission of the grating, and $b = \Delta\mathrm{T}/2$, where $\Delta\mathrm{T}$ is the linear dichroism. In the case of a material with induced linear birefringence $a = \cos(\Delta\phi)$ and $b = \mathrm{i}(\sin(\Delta\phi))/2$ with $\Delta\phi = \pi\Delta n\, d/\lambda$, $\Delta\mathrm{n}$ is the birefringence, d is the layer thickness of the material and λ is the wavelength of the incoming wave.

Only the first order diffracted beams and the zero order are transmitted by this grating, and the three waves fields $\mathrm{E_0}$ (zero order-transmitted beam), $\mathrm{E_{+1}}$ and $\mathrm{E_{-1}}$ can be written in the following way:

$$\mathbf{E}_0 = a\begin{pmatrix} \mathrm{E_x} \\ \mathrm{E_y}\exp(\mathrm{i}\theta) \end{pmatrix} \tag{3}$$

$$\mathbf{E}_{+1} = b(\mathrm{E_x} - \mathrm{iE_y}\exp(\mathrm{i}\theta))\begin{pmatrix} 1 \\ -\mathrm{i} \end{pmatrix} \tag{4}$$

$$\mathbf{E}_{-1} = b(\mathrm{E_x} + \mathrm{iE_y}\exp(\mathrm{i}\theta))\begin{pmatrix} 1 \\ \mathrm{i} \end{pmatrix} \tag{5}$$

The diffraction occurs only onto the first orders $+1$ and/or -1.

The transmitted wave, zero order (Eq. 3), has the same polarisation state of the incident wave, but its amplitude is reduced by the factor a. The first order diffracted beam $+1$ (Eq. 4) is a wave having left CP but its amplitude is proportional to the one of the right component of the incident wave. The diffracted beam of the -1 order has

a right CP but its amplitude is proportional to the one of the left component of the incident wave (Eq. 5).

On the basis of the grating properties just described, the method that we propose for measuring CD can be thus explained.

CD is generally calculated by measuring the transmitted intensity when a beam with right or left CP impinges the sample by using the following expression:

$$\Delta A = \log \frac{I_{0L}}{I_{TL}} - \log \frac{I_{0R}}{I_{TR}} \tag{6}$$

where I_{0L} e I_{0R} are the intensities of right and left polarised beams that alternatively hit a system (sample), while I_{TL} e I_{TR} are, respectively, the intensities of the left and right CP transmitted light.

In the method proposed the beam of light that hit the sample to be analysed can have a linear polarisation or a random linear polarisation or with a non-polarised light, when analysing isotropic systems, liquids, solutions, etc.

Analysing systems that present linear birefringence (crystals, oriented polymers, LC, etc.) the method requires the use of non-polarised light or random linear polarisation.

The discussion will be limited to the use of linearly polarised light; however the extension to non-polarised light will be therefore considered.

For a linearly polarised wave the incoming beam can be considered as composed of two opposed CP waves (one right and another left) of equal amplitude. This allows us to write the Jones' vector of this wave in terms of opposite CP states, right and left:

$$\mathbf{E}_0 = \frac{E_x}{2}\begin{pmatrix} 1 \\ -i \end{pmatrix} + \frac{E_x}{2}\begin{pmatrix} 1 \\ i \end{pmatrix} \tag{7}$$

If the system (or in our case the sample to be analysed) that is passed through by this wave possess CD, then the right CP component is absorbed differently respect to the left component, according to the CD sign. As a consequence, the wave transmitted by the sample will have an elliptic polarisation whose Jones' vector

$$\mathbf{E}_\mathrm{T} = \begin{pmatrix} \mathrm{E_x} \\ \mathrm{E_y}\exp(\mathrm{i}\theta) \end{pmatrix}, \tag{8}$$

can be expressed in terms of right and left circular components as follows:

$$\mathbf{E}_\mathrm{T} = \frac{1}{2}(\mathrm{E_x} - \mathrm{iE_y}\exp(\mathrm{i}\theta))\begin{pmatrix} 1 \\ -i \end{pmatrix} + \frac{1}{2}(\mathrm{E_x} + \mathrm{iE_y}\exp(\mathrm{i}\theta))\begin{pmatrix} 1 \\ i \end{pmatrix} \tag{9}$$

If the grating is placed immediately after the sample the wave (transmitted or reflected) coming from it and impinging onto the grating will be diffracted in the way described above.

Using, therefore, the expressions (4) and (5) it is possible to write the beams intensities diffracted from the grating in the following way:

$$\mathrm{I_{+1}} = 2\mathrm{b}^2\mathrm{I_{TR}} \quad \text{and} \quad \mathrm{I_{-1}} = 2\mathrm{b}^2\mathrm{I_{TL}}. \tag{10}$$

In the case of linear polarisation of the beam hitting onto the sample, the intensity of the left CP component, I_{0L} is equal to the intensity of the right CP component, I_{0R}, therefore $I_{0L} = I_0/2$ and $I_{0R} = I_0/2$, can be expressed both in terms of the total intensity, I_0; while by using expression (7), I_{TL} e I_{TR} can be written in terms of the intensities of the beams diffracted by the grating, I_{+1} e I_{-1}.

The expression (6) becomes

$$\Delta A = \log \frac{I_0 2b^2}{2I_{-1}} - \log \frac{I_0 2b^2}{2I_{+1}} = \log \frac{I_{+1}}{I_{-1}} \tag{11}$$

Equation (11) demonstrates that CD can be easily calculated by the logarithm of the intensities ratio of the beams diffracted by the grating.

The described method does not necessarily require the use of linearly polarised light to be sent onto the sample, and it is, in fact, possible to use a light source having random variable linear polarisation or non-polarised. This is necessary for the analysis of ordered samples that present linear birefringence.

The grating preserves the same diffraction properties also for non-polarised and for random linearly polarized light [14].

The only optical element necessary to the described method is a diffraction grating that has an intrinsically spectral selectivity, intending that waves with different wavelengths incident onto the grating are diffracted at diverse angles. By using two multi-channel detectors, as photodiodes array or Charged-Coupled device (CCD), the simultaneous diffracted beams intensity acquisition at different wavelengths is possible, and at the same time the CD measurement throughout the spectral range of the light source used.

The proposed method does not require any particular procedure for the grating characterisation, such as for example diffraction efficiency measurement and its determination at each wavelength, since it is simply based on the ratio of the diffracted beams intensities.

No calibration procedure of the device in the wavelength range of interest is necessary, except the existence of an optical anisotropy in that interval.

Figure 2 schematically illustrates the spectrograph. A beam of light L passes through the sample S and the diffracting grating PH, which has a spatially modulated linear optical anisotropy. The beams diffracted to the first order I_{+1} e I_{-1}

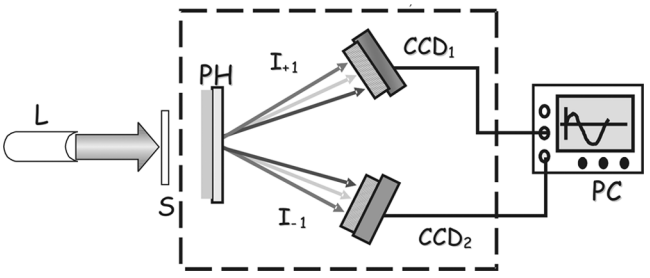

Figure 2. Scheme of the CD spectrometer. The two circular polarization components of the beam incoming onto the grating are diffracted in the two different first-diffraction orders. L light source; S sample; PH polarization hologram; I_{+1}, I_{-1} diffracted beams; CCD Charge-Coupled devices; PC personal computer.

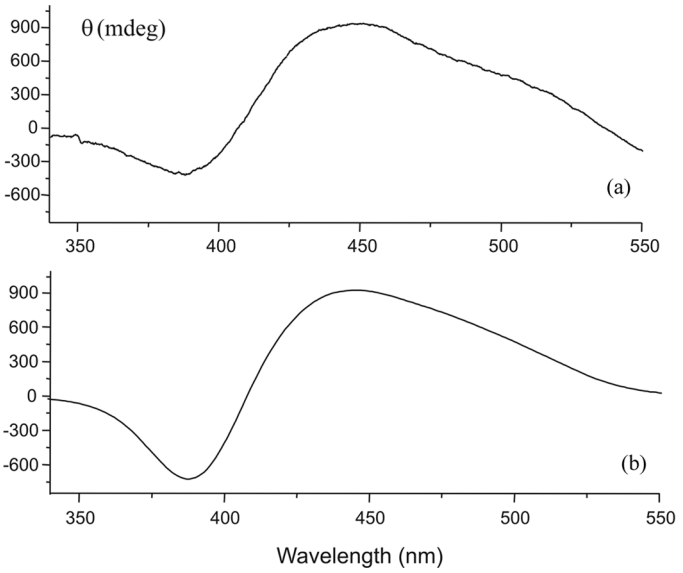

Figure 3. Spectrum of the sample {poly[(*S*)-**MAP-C**]} performed with our device (a), and with the conventional dichrograph 810-A by Jasco Inc. (b).

are collected by the multi-channel light sensors CCD1 and CCD2 that convey the relative signals to the computer PC which, through an appropriate software calculates the CD measure, carrying out the logarithm of the diffracted beams intensities ratio.

In Figure 3 the CD spectrum of the polymer sample {poly[(*S*)-**MAP-C**]}, synthesized and described in reference [13], has been measured by our device in 1 second time (a) and compared with the reference spectrum (b) measured with a conventional dichrograph (Jasco Inc. 810A) in 260 seconds time, with scanning speed of 50 nm/min. The curves show qualitative agreement in the region where the sample exhibits CD. The discrepancy in the low wavelength range (350–400 nm), where the CD signal changes faster versus wavelength, is due to the limited collimating and focusing performance of the optical elements which reduces the resolution in the adopted refractive scheme [14].

Conclusions

The CD spectrograph described in this paper successfully employs as main element a highly efficient LC based diffraction grating. The grating is obtained by means of planar periodic boundary condition at both aligning layers, achieved by means of polarization holographic techniques on photosensitive guest-host polymers. Proper values of the cell thickness and spatial periodicity ratio yield a perfect replica of the surface alignment in the bulk nematic director configuration. High diffraction efficiency has been found, even in the thin grating regime. Diffraction properties of these pure polarization gratings are preserved, allowing a high reliable operation of the CD spectrograph having an extreme simplicity, being free of modulating or moving parts, and does not require complex calibration procedure.

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