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Calibration of photoelastic modulator based dichrometers: maintaining constant phase across the spectrum

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Abstract: Photoelastic modulators can alter the polarization state of a beam of ultraviolet, visible or infrared photons by means of periodic stress-induced differences in the refractive index of a transparent material that forms the optical element of the device and is isotropic in the absence of stress. They have found widespread application in instruments that characterize or alter the polarization state of a beam in fields as diverse as astronomy, structural biology, materials science and ultraviolet lithography for the manufacture of nano-scale integrated circuits. Measurement of circular dichroism, the differential absorption of left- and right circularly polarized light, and of strain-induced birefringence of optical components are major applications. Instruments using synchrotron radiation and photoelastic modulators with CaF₂ optical elements have extended circular dichroism measurements down to wavelengths of about 130 nm in the vacuum ultraviolet.

Maintaining a constant phase shift between two orthogonal polarization states across a spectrum requires that the amplitude of the modulated stress be changed as a function of wavelength. For commercially available photoelastic modulators, the voltage that controls the amplitude of modulation required to produce a specified phase shift, which is a surrogate for the stress modulation amplitude, has been shown to be an approximately linear function of wavelength in the spectral region where the optical element is transparent. But, extrapolations of such straight lines cross zero voltage at a non-zero wavelength, not at zero-wavelength. For modulators with calcium fluoride and fused silica optical elements, the zero-crossing wavelength is always in the spectral region where the optical element of the modulator strongly absorbs the incident radiation, and at a wavelength less than the longest-wavelength apparent resonance deduced from experimental values of the refractive index fit to the Sellmeier equation. Using a model that relates the refractive indices of a stressed optical element to the refractive index of its unstressed state, an expression for the modulator control voltage was derived that closely fits the experimental data. This result provides a theoretical rational for the apparently linear constant-phase programming voltage, and thus provides theoretical backing for the calibration procedure frequently used for these modulators. Other factors that can influence the calibration of a photoelastic modulator, including temperature and atmospheric pressure, are discussed briefly.

Keywords: Spectrometers, Instrumentation for synchrotron radiation accelerators, Polarisation, Spectral responses, Optical detector readout concepts

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1 Introduction

Photoelastic modulators (PEMs) periodically alter the birefringence of a transparent optical element and, therefore, the polarization of an optical beam traversing it. They are key components of dichrometers that measure the differential transmission, reflection, scattering or emission of light by a sample. PEMs are also employed in measurement of stress-induced birefringence in optical components, which has become important in the lithographic manufacture of semiconductors [1]. An important biophysical application of PEMs is the measurement of circular dichroism (CD), the differential absorption of left- and right circularly polarized light, a widely used experimental measurement in studies of the solution structural of proteins. The Protein Circular Dichroism Data Base (PCDDDB) was established to facilitate the systematic collection and distribution of protein CD spectra [2]. CD is also a potential means of verifying the authenticity of biosimilar medicinal proteins, and thus validate their use as therapeutic agents [3]. Such applications challenge the sensitivity and inter-instrumental reproducibility of existing dichrometers. PEMs have been a key component of most dichrometers designed since 1970 to operate in the ultraviolet (UV), visible and infrared (IR) spectral domains. Building a dichrometer is straightforward, but ensuring that different instruments are measuring exactly the intended parameter is challenging. This work explores the functioning of the PEM as a component of a dichrometer, in contrast to previous studies that have focused on the operation and calibration of the PEM as a stand-alone device. A previous publication discussed the accuracy of certain approximations introduced in the analysis of dichrometer spectral data [4].

Polarization dichrometers measure the difference between the responses of a sample to two complementary polarizations of light. The focus here is on the absorption and, in some cases, the subsequent reemission of light involving electronic transitions in the spectral range from roughly 130 nm in the VUV to 1.5 μ in the near IR, and hence, for the most part, involving electronic transitions. PEM based dichrometers are also available for the study of vibrational transitions extending into the IR to almost 60 μ . Observed differences in absorption or fluorescence are frequently small, so dichrometers must be sensitive. Therefore, the difference must be measured directly, as opposed to measuring the absorption or emission of each component separately and then taking the difference. A major application of dichrometers involves biological macromolecules in solution. The most important dichroic experiment, both in terms of frequency of use and impact on science, is circular dichroism (CD), the difference in the absorption of left and right circularly polarized light. CD measurements are used to characterize the structure and interactions of proteins and other macromolecules in solution. Many CD studies of proteins focus on the amide groups, which absorb in the far- and vacuum ultraviolet; the spectral region where synchrotron radiation is particularly advantageous.

An experiment closely related to CD in terms of instrumentation, but completely different in terms of information content, is magnetic circular dichroism (MCD) [5], in which the difference in absorption is induced by an external magnetic field. Two additional measurements used in biophysical spectroscopy involve linearly polarized light. Linear dichroism (LD) measures the difference in absorption of two orthogonal linearly polarized light beams when the absorbing material is rendered dichroic by partial orientation of the relevant chromophores. LD provides information on the absolute orientations of chromophores relative to the direction of orientation. In contrast, fluorescence polarization anisotropy (FPA) measures the difference in intensity of fluorescence emitted with linear polarization parallel and perpendicular to the direction of the polarization of the exciting light. FPA yields information on the motion of the fluorescent species during the brief period – typically measured in nanoseconds – between absorption and emission. Dichrometers are easily adapted to measuring LD [6] and represent one or several approaches for measuring FPA [7, 8]. There are also experiments in which dichroic absorption is monitored by the observation of fluorescence, including fluorescence detected CD [9], MCD [10], and LD [11], or the difference in intensity of the circularly polarized components of the fluorescence of, or the light scattered light by chiral molecules [12, 13].

The need to measure tiny differences in absorption or fluorescence dictates the use of modulation techniques in which the polarization of a light beam is switched between the two extremes and the difference is measured directly. Initial CD spectrometers converted a linearly polarized beam into alternately left- and right circularly polarized beams using Pockels cells [14]. Within a decade, the limitations of these devices in this application resulted in the development of PEMs [15-18]. The bar-type design described by Kemp was commercialized and evolved into the line of modulators presently available from Hinds Instruments Inc., Hillsboro, Oregon, USA. These modulators are found in many commercial and laboratory built dichrometers that operate in the ultraviolet, visible and near-infrared spectral. Hinds Instruments also sells a line of octagonal photoelastic modulators that are optimized for longer wavelength.

Dichrometers require more intense, near-monochromatic beams to measure small differences in beam intensities than are needed for the measurement of unpolarized absorption. Essentially all laboratory-based instruments rely on high-pressure xenon arcs as the light source. However, xenon arcs approximate black bodies with color temperatures typically just above 6,000 C. Therefore, their emission spectrum peaks between 400 and 500 nm in the visible region, and decreases rapidly with decreasing wavelength through the ultraviolet. The amorphous quartz envelopes or windows required to contain the high-pressure xenon gas become opaque around 165 nm. Although the short wavelength performance of some dichrometers with xenon light sources has improved over the past several decades, they are less than optimal for wavelengths throughout much of the vacuum-ultraviolet (VUV) spectral region – wavelengths less than about 200 nm – and useless below 160 nm.

The performance of bespoke dichrometers in the VUV improves significantly when the light source is a beam of relativistic electrons or positrons circulating in a synchrotron storage ring [19-21]. Unlike xenon arcs, synchrotron radiation (SR) light sources increase in intensity with decreasing wavelength throughout the VUV. SR dichrometers use bar-shaped PEMs, also from Hinds Instruments, in which a CaF_2 or LiF crystal replaces the typically fused silica optical element, hence extending the spectral range to below 130 nm. Presently, there are roughly a dozen SR dichrometer beamlines in operation around the world.

Enhanced UV performance combined with ubiquitous digitization of recorded CD spectra and multiple protocols for extracting information on protein secondary structure from CD spectra lead to a systematic protocol for storing and analyzing spectra in the form of the Protein CD Data Bank [22]. The conversion of CD into a rigorous method for extraction conformational data from proteins and other macromolecules is predicated on the accurate

and reproducible calibration of multiple dichromators and accessory equipment, such as sample cells. Such calibrations tend to be more challenging in the VUV, where wavelength standards are scarce and cell path lengths are frequently measured in microns instead of centimeters.[4, 21, 23] Two additional challenges are properly calibrating the amplitude of the detected dichroic signal and operating the PEM so that the polarization phase-shift remains constant across the spectrum of interest. The latter issue is addressed in this article, which combines data from previous reports and extends the previous analysis.

2 Methods

The manuscript, including all figures, was prepared using an Apple MacBook Pro computer (Apple Inc., Cupertino, CA, USA) running under the OS-X operating system (v.10.10.3; *ibid.*). Figure 1 was created using Microsoft PowerPoint for Mac 2011 Version 14.5.2 (Microsoft Corp. Redmond, Washington, USA). All other figures were created using Mathematica 10 (v. 10.0.2.0; Wolfram Research, Champaign, Illinois, USA). Digital values of data points in published charts were obtained using the Draw module of Apache OpenOffice.org 4.1.2. In addition to standard mathematical conventions, square brackets are used exclusively to enclose function arguments, braces indicate lists or collections, and parentheses are reserved for grouping terms. Multiple mathematical expressions are connected by right arrows, which can be read as “which implies”. For expressions containing multiple steps, the arrows are numbered to facilitate referencing in the text. All angles are expressed in radians unless otherwise indicated.

3 Discussion

3.1 Background

The frequency, and thus the period, of a monochromatic beam of light do not change when it enters a transparent material, such as the optical element of a PEM, but the phase velocity of the radiation, and thus the wavelength, decrease. The wavelength inside the modulator element is given by λ/n , where λ is the wavelength of the light *in vacuo*, and n is the refractive index of the material at that wavelength. The definition of n as the ratio of the magnitude of the phase velocity of the radiation in vacuum to the corresponding value in the medium applies only to regions that are transparent. If absorption cannot be ignored, the refractive index must be treated as a complex function. Stress applied along the long axis of the modulator element, the p axis in Figure 1, causes the refractive index for light polarized parallel to that axis to differ from the refractive index for light polarized in the perpendicular orientation, *i.e.* parallel to the q axis. Applied stress results in a relative rearrangement of the atomic components of a transparent material, thus changing the way the material interacts with an electromagnetic wave. Presumably, it is this atomic-level rearrangement, *i.e.*, the resulting strain, that is responsible for altering the optical properties of the material. For the low stresses considered here, the material can be considered strictly elastic and so effects can be described as due to stress, even when they actually are a consequence of the resulting strain. In a dichrometer the light incident on the PEM is linearly polarized, so the projection of the electric vector on the p and q axes will be in phase when the light enters the PEM. Inside the PEM, the wavelengths of these components are λ/n_p and λ/n_q respectively, and the relative retardation of the q component relative to the p component per unit (vacuum) wavelength is $\Delta n x_m/\lambda$, where $\Delta n = n_p - n_q$ is the stress induced birefringence, x_m is the thickness of the modulator, and λ and x_m are expressed in the same units of length. The resultant angular phase shift, δ (radians), between the p and q polarized components is $2\pi \Delta n x_m/\lambda$. The stress applied to the optical element, and therefore the birefringence and phase shift between the two polarization components of the emerging beam, is modulated sinusoidally, so the time-dependent phase

shift is as shown in (1), where $\omega = 2\pi f$, with f being the frequency of the PEM. For the bar-type PEMs employed in the visible and UV, the frequency is typically near 50 kHz. The phase shift amplitude, δ_o , between the p and q polarized components exiting the modulator is $2\pi \Delta n_o x_m / \lambda$, where Δn_o is the amplitude of the sinusoidal modulation of the refractive index (assuming the maximum retardation is $< \lambda$).

$$\delta[t] = 2\pi x_m \Delta n[t] / \lambda \rightarrow \delta_o \sin[\omega t] \quad (1)$$

The stress induced birefringence is the product of the stress tensor and the stress-optical tensors, but for the simple geometry of the PEM system this can be reduced to the produce of the uniaxial stress along the p axis, σ (expressed in Pa) and a scalar stress-optical coefficient, C , (Pa^{-1}). The stress is produced by a standing acoustic wave generated in the optical element of the PEM by a crystalline piezoelectric transducer bonded to one end of the element. Therefore, the stress is modulated sinusoidally at the frequency of the transducer, which is chosen to be near the lowest resonate frequency of the element. As a result, the retardation and phase shift are also modulated at this frequency. The maximum amplitude of the stress, and therefore the maximum amplitude of the retardation and phase shift, is determined by a voltage, V , applied to the electronic circuit that controls the operation of the PEM.¹ This is a static voltage for a particular wavelength; it is not modulated at the frequency of the PEM. Oakberg reported that at a given wavelength, the phase shift amplitude is directly proportional to V [24, 25]. Therefore, the control voltage required to produce a phase shift amplitude of δ_o is simply related to the voltage that produces a phase shift amplitude of π by the expression in (2). An experimental method for determining V_π at a given wavelength is described below. In addition to providing the foundation for programming the PEM to achieve a given phase shift, this result demonstrated that the wavelength dependence of the control voltage required to achieve a given phase shift is an inherent property of the modulator, and not an artifact of the control circuitry [24].

$$V_{\delta_o}[\lambda] = \frac{\delta_o}{\pi} V_\pi[\lambda] \quad (2)$$

A useful implication of the linear dependence of the phase shift on the applied voltage is that the amplitude of the applied stress, can be replaced by gV where g is the effective gain in the control circuit (Pa/volt), which is not a function of wavelength. Combining these expressions with (1), replacing the change in refractive index with the product of the stress and the stress-optical coefficient, and rearranging results in (3). In CD and most other applications, it is desirable to keep the phase shift amplitude, δ_o (radians) constant across the spectrum. Thus to achieve a constant phase shift across the spectrum, the PEM amplitude control voltage must be changed as a function of wavelength.

$$V_{\delta_o}[\lambda] = \frac{\delta_o}{2\pi g x_m} \frac{\lambda}{C[\lambda]} \quad (3)$$

In their descriptions of the PEM, the inventors indicated that achieving a constant value of δ_o across the spectrum requires that V_c should be directly proportional to wavelength [16, 17], an assertion repeated in subsequent product literature for commercially available modulators [26]. While programming the PEM as strictly proportional to wavelength might have been an acceptable approximation for some applications in the visible region of the spectrum, it assumes that the photo-elastic coefficient is independent of wavelength. But the dependence of stress-optical coefficients as a function of wavelength, which had been

¹ Some commercial PEM control units may not have an external control voltage input. Instead, they generate this voltage internally based on a digital value of wavelength supplied by a user's computer system.

reported for a variety of materials dating to the early part of the twentieth century [27], becomes significant at lower wavelength near the limits of transparency of the material.

Figure 1. The geometry of the optical element of a PEM is shown in the upper panel relative to the coordinate system of a typical instrument. Light is assumed to be traveling in the positive x direction. The x and y axes define the horizontal plane, the z axis is vertical, and the Cartesian coordinate system is right handed so $\mathbf{i} \times \mathbf{j} = \mathbf{k}$, where $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ are the unit vectors for the x , y , and z axes, respectively. The optical element of the PEM is aligned parallel to the y - z plane and centered on the x axis with the long (p) and short (q) axes of the PEM optical element, of lengths L and W respectively, oriented at angles of $\pi/4$ with respect to the y and z axes. One end of the optical element is bonded to a quartz piezoelectric crystal, indicated by the gray line along the end of the optical element on the negative p axis. The coordinates of the uppermost corner of the optical element as expressed in the p - q coordinate system are shown in the figure. The incident light is assumed to be linearly polarized along either the y or the z axis. Rotation of the optical element about the x axis in steps of $\pi/2$ leaves a perfectly aligned system essentially invariant. The dotted circle represents the outline or “foot print” of a circular beam of light of radius r passing through and centered on the optical element. The lower panel shows the experimental configuration used to obtain the values of control voltage that produce half wave retardation for each wavelength. The reference signal from the PEM control triggers the horizontal scan of an oscilloscope, which displays the temporal profile of the light signal as a function of time.

The wavelength dependence of stress-induced birefringence is referred to as the dispersion of the photo-elastic effect. Thus, to achieve a constant phase shift, the wavelength dependence of the programming voltage must go as λ/C , where C is a function of wavelength, as indicated in (3). It is not surprising that stress-induced birefringence should be wavelength dependent considering that the refractive index of the unstressed material, n , and therefore the individual values of n_p and n_q , are wavelength dependent, with the rate of change increasing at shorter wavelengths – see, e.g., the upper panel of Figure 2. The curve through the refractive index experimental data in this figure is from the empirical Sellmeier equation, shown in (4), using the parameters shown in Table 1. These data show an apparent singularity at about 94 nm, which is indicated by the dashed line in both panels of. The Sellmeier equation represents the refractive index only in spectral regions where the sample is transparent. It has singularities for all wavelengths equal to one of the values of λ_i , but such wavelengths always fall in regions where the material absorbs and thus the Sellmeier equation does not apply. In such regions, the refractive index must be represented by a complex expression.

$$n[\lambda] = \sqrt{1 + \sum_i \frac{b_i}{1 - \frac{\lambda_i^2}{\lambda^2}}} \quad (4)$$

Table 1. The values of the parameters used in the Sellmeier equation describing the refractive index of crystalline CaF_2 in the UV, visible and infrared [28]. The values of b_i , which are dimensionless, depend on the oscillator strengths of effective transition dipoles located at the corresponding wavelengths. Other authors, working with different samples of CaF_2 and over different spectral domains have reported somewhat different parameters.

i	1	2	3	4
b_i	0.3397	0.6991	0.1199	4.3518
λ_i (nm)	0	93.74	21,180	38,460

An experimental measurement can determine the control voltage that produces the stress amplitude resulting in a retardation of π radians at each wavelength [16, 24, 25]. The light incident on the PEM optical element is presumed to be polarized at an angle of $\pi/4$ with respect to the p axis of the modulator; *i.e.*, along either the y or z axes in the upper panel of Figure 1. A polarizer, functioning as an analyzer, is placed after the PEM, with its transmission direction orthogonal to the initial polarization, as shown in the lower panel of Figure 1. Thus, when the PEM is not operating, or when the phase shift passes through zero, minimal light will reach the detector (assuming that the optical element of the PEM is free of residual stress.) When the PEM is operating and the instantaneous applied stress is non-zero, however, the stress-induced phase shift between the p and q axis polarized components cause the plane of polarization of the incident light to be rotated out of the original plane, so some fraction of the light will pass the second polarizer. When the output of the detector, usually a photomultiplier or photodiode, is viewed on an oscilloscope, a double peaked pattern can be observed, the zero's of which represent the transient passage of the PEM through zero stress, as shown in Figure 3. The value of the control voltage that produces the "flat-topped" pattern – the solid curve in Figure 3– is V_π , the control voltage that produces a maximum phase shift of π radians for the selected wavelength. Values of V_π obtained for various wavelengths for four different experimental systems are shown in the lower panel of Figure 2. The three multi-wavelength instruments provided data that were fit by straight lines, which can be written as shown in (5), where $V_{\pi,0}$ is the magnitude of the intersection of the extrapolated line with the voltage axis at $\lambda = 0$, and λ_o is the intersection

of the extrapolated lines with the wavelength axis, *i.e.*, at $V = 0$. The values of these parameters reported for three CaF_2 PEMS are shown in Table 2.

Figure 2. Upper panel: Refractive index ($\bullet$) and transmission ($\circ$) of calcium fluoride as a function of wavelength. Refractive index data are from Dalman and Masumura [29]. Transmission data are for a 5 mm thickness reported by Korth Kristalle GMBH and cover the spectral domain from 122.5 to 240 nm. For longer wavelengths, the transmission is approximately constant to about 7 μm . The solid line is calculated from the Sellmeier equation (3) using the parameters in Table 1. The vertical dotted line marks the location of λ_z , the longest wavelength singularity in the Sellmeier expression. Lower panel: PEM amplitude control voltages required to produce half-wave retardation for three PEMS with calcium fluoride optical elements mounted in three different instruments: ($\diamond$) a xenon-arc source instrument [25], ($\square$) beamline U9b at the National Synchrotron Light Source (NSLS) [24], and ($\circ$) beamline U11, also at the NSLS [24]. The remaining symbol, ($\odot$), denotes the voltage required to produce a half-wave retardation for the PEM used in the xenon-arc experiment at 632.8 nm using a HeNe laser [25]. The use of the HeNe laser was described as a standard part of the factory calibration of PEMS. The dashed line is the linear PEM calibration fit to the experimental data for the xenon-arc system. The vertical dotted line is extended from the upper panel. Note that the refractive index and transmission data were obtained from different samples of CaF_2 and they were not the materials used in construction of any of the PEMS.

$$V_\pi[\lambda] = V_{\pi,0} \left(\frac{\lambda}{\lambda_0} - 1 \right) \quad (5)$$

Setting $\delta_o = \pi$ in (3), equating the right hand sides of (3) and (5), and solving for C results in (6), where the subscript *lin* indicates that this is the expression for C resulting from the assumption that the control voltage necessary to produce half-wave retardation is a linear function of wavelength. In the second expression on the right-hand-side of (6), the value of C at a reference wavelength λ_{ref} is introduced, where λ_{ref} is the wavelength used to calibrate a PEM, typically the HeNe laser emission at 632.8 nm. Oakberg [25] presented a similar expression in which the value of the photo-elastic coefficients at various wavelength is expressed relative to its value at 632.8 nm, but did not indicate how they it was derived. Expressions with the same wavelength dependence, *i.e.*, $1/(1 - \lambda_0/\lambda)$, were reported for the photoelastic constants of various glasses early in the twentieth century [27].

$$C_{\text{lin}}[\lambda] = \frac{\lambda}{2 g x_m V_{\pi,0} \left(\frac{\lambda}{\lambda_0} - 1 \right)} \xrightarrow{1} C[\lambda_{\text{ref}}] \frac{\lambda}{\lambda_{\text{ref}}} \left(\frac{\lambda_{\text{ref}} - \lambda_0}{\lambda - \lambda_0} \right) \xrightarrow{2} C[\lambda_{\text{ref}}] \left(\frac{1 - \frac{\lambda_0}{\lambda_{\text{ref}}}}{1 - \frac{\lambda_0}{\lambda}} \right) \quad (6)$$

Table 2. Parameters for the straight lines fit to the data for the control voltage that results in a phase difference of π radians as a function of wavelength, as shown in the lower panel of Figure 2. The values were obtained from experimental data to which the Oakberg multiplicative alignment correction [25], which causes each extrapolated line to pass through the laser calibration point at 632.8 nm, had been applied.

System (symbol)	$V_{\pi,0}$ (volts)	λ_0 (nm)	$V_{\pi,0}/\lambda_0$ (volts/nm)	Correlation Coefficient	Wavelength Span (nm)	Reference
Xe-arc ($\diamond$)	0.2571	47.56	$5.406 \cdot 10^{-3}$	0.99998	250 - 800	[25]
U9b ($\square$)	0.3715	66.02	$5.627 \cdot 10^{-3}$	0.99969	180 - 600	[24]
U11 ($\circ$)	0.4608	79.87	$5.769 \cdot 10^{-3}$	0.9994	134 - 307

Figure 3. Calculated time-dependent light signals from a detector when a PEM is placed between crossed polarizers with its major (p) axis at an angle of $\pi/4$ with respect to the transmission axes of

each polarizes. One of the two major peaks in each trace corresponds to compression of the optical element, the other to extension. The time period of 20 ms corresponds to one complete cycle of the PEM operating at a frequency of 50 kHz. When the control voltage is set to give half-wave retardation ($\delta_0 = \pi$, solid curve), both peaks exhibit a flat top. Slightly lower values ($\delta_0 = 0.9 \pi$ shown) of the control voltage result in both branches having a single peak (dashed curve: the retardation never gets to half-wave), while higher values of the control voltage ($\delta_0 = 1.1 \pi$) gives double-peaked tops (dotted curve: the retardation goes past half-wave and the signal dips, but returns to the maximum value as the retardation goes back through half-wave on the return portion of the curve). The value of the control voltage corresponding to half-wave retardation (V_π) measured at each wavelength is the value of V_c that results in the flat-topped trace. Residual stress in the optical element of a PEM results in an asymmetric pattern. For example, the control voltage that results in a flat-topped trace on the right-hand portion of the trace might result in a single peak on the left-hand portion. In this case, the control voltage producing a flat-top on the right will show a double peak on the left. If such patterns were observed, Oakberg [24, 25] calculated the effective half-wave retardation voltage by averaging the voltages producing the flat-topped traces on the right and left portions of the trace. Such static stress induced phase shifts are capable of mixing the 50 and 100 kHz signals, which can result in the linear dichroism of a sample appearing as apparent CD in experimental spectra [21].

3.2 Wavelength dependence of PEM induced phase shifts

The singularities in the stress-optical coefficient at λ_0 , the wavelength where the extrapolated modulator calibration line crosses the wavelength axis, might appear to be related to the singularity in the refractive index, but they occur at wavelengths that differ by more than experimental error in the linear extrapolations of the experimentally determined half-wave retardation line presented in Figure 2. The data on PEM performance also show small differences between the slope and intercepts for the different modulators. In addition to the data for CaF_2 PEMs reviewed here, apparently linear relationships between the control voltage required for half-wave retardation as a function of wavelength and a negative voltage-axis intercept have been reported for PEMs with quartz [25], lithium fluoride [24], and zinc selenide [30] optical elements.

In evaluating the differences in the data for the three PEMs summarized in Table 2 there are three relevant factors: 1) the data were collected using three different PEMs; 2) the PEMs were in different optical instruments; and 3) the four data sets cover different spectral ranges. All three PEMs were manufactured by Hinds Instruments and had CaF_2 optical elements. The PEM in the U9B dichrometer was built in the late 1970s and was mounted inside a vacuum housing. The PEM in the U11 dichrometer was built in the early 1990s and was mounted in a non-vacuum housing purged with dry nitrogen gas. The PEM used in the xenon-arc instrument and in the HeNe laser source configuration was presumably manufactured in the late 1990s. Even if all of the differences observed in the data in Figure 2 and Table 2 were due to differences inherent in the PEM systems – including both the optical units and their associated electronic components – the similarity of results would speak well for the robustness of these devices. All show apparently linear control voltages curves with extrapolated negative voltage intercepts, which imply expressions for the photoelastic coefficient as shown in (6). This result leads to a conundrum: it would seem that the photoelastic coefficient of a material should be related to the average refractive index of the material. But the empirical expression for the photoelastic coefficient depends of an odd power of reciprocal wavelength, as shown in (6), while the empirical expression for the refractive index involves only even powers of reciprocal wavelength, as shown in (4). In addition, the singularity in the expression for C_π occurs at wavelength λ_0 , which is clearly distinct from the singularity in the refractive index, indicated by the dotted line Figure 2. Thus, it is not possible to directly relate the performance of the PEM with the optical properties of the material from which it is constructed. The question therefore arises whether it is possible to relate the photoelastic coefficients to the refractive index of a

material in such a way as to retain the apparent linear relationship of the PEM control voltage necessary to maintain a given fractional retardation as a function of wavelength.

My approach to this question is related to the analysis of Sinha[31], who was interested in the stress-induced and natural birefringence of quartz and the stress-induced birefringence of fused silica and various silica-based glasses. The approach is to assume that the properties of the optical element are represented by the parameters in the Sellmeier expression and that the corresponding parameters of the material when under stress are a perturbation of those of the unstressed material. The difference between the properties of the stressed and unstressed materials are, therefore, responsible for observed changes in optical properties. Therefore, the objective is to express the refractive index for light polarized along the p and q axes of the modulator element experiencing a uniaxial stress along the p axis, σ_p , as the sum of the refractive index of the unstrained material plus the stress-induced changes associated with the corresponding axis. The formal expansion shows the changes associated with the strain induce changes of each of the values of b_i and λ_i in the Sellmeier equation, as shown in (7). Calculating the birefringence eliminates the unperturbed value of the refractive index, as shown in (8), where the differences between the changes in the refractive indices for the p and q axes have been combined using the expressions shown in (9).

$$n_j[\lambda, \sigma_p] = n_o[\lambda] + \left(\sum_i \frac{\partial n_j}{\partial b_i} \frac{db_i}{d\sigma_p} + \sum_i \frac{\partial n_j}{\partial \lambda_i} \frac{d\lambda_i}{d\sigma_p} \right) \sigma_p, \quad j \in \{p, q\} \quad (7)$$

$$n_p - n_q \equiv \Delta n[\lambda, \sigma_p] = \left(\sum_i \frac{\partial n}{\partial b_i} \frac{db_i}{d\sigma_p} + \sum_i \frac{\partial n}{\partial \lambda_i} \frac{d\lambda_i}{d\sigma_p} \right) \sigma_p \quad (8)$$

$$\frac{\partial n}{\partial b_i} = \frac{\partial n_p}{\partial b_i} - \frac{\partial n_q}{\partial b_i}, \quad \frac{\partial n}{\partial \lambda_i} = \frac{\partial n_p}{\partial \lambda_i} - \frac{\partial n_q}{\partial \lambda_i} \quad (9)$$

The next step is to apply what can be called the *nearest resonance approximation*, which is to consider only the stress-induced changes in the refractive index associated with the effective transition located closest to the wavelength (energy) of interest, as shown in (10). For the data shown in Table 1, this would be for $i = 2$, but in the following discussion the value of i associated with the nearest transition is designated by the symbol i^* , because the number and distributions of the effective transitions can vary for Sellmeier expressions obtained from different data sets for the same material, and may differ significantly for different materials. The Sellmeier parameters presented by Li [28], *i.e.*, the values shown in Table 1, are well suited for an analysis based on the nearest effective resonance approximation because there is only one effective transition in the ultraviolet, the other transitions being either at high energy ($\lambda_1 = 0$) or in the infrared.

$$\Delta n[\lambda, \sigma_p] \approx \left(\frac{\partial n}{\partial b_{i^*}} \frac{db_{i^*}}{d\sigma_p} + \frac{\partial n}{\partial \lambda_{i^*}} \frac{d\lambda_{i^*}}{d\sigma_p} \right) \sigma_p \rightarrow C_{i^*}[\lambda] \sigma_p \quad (10)$$

The component of the stress optical coefficient associated with the nearest transition is denoted by C_{i^*} . Differentiating the Sellmeier expression, (3), with respect to b_{i^*} and λ_{i^*} results in (11), showing two terms, which can be described as the contributions to the stress optical coefficient due to strain induced changes to the amplitude (b_{i^*}) and wavelength (λ_{i^*}) of the nearest effective transition. Dividing the expression for the PEM control voltage required to

achieve half-wave retardation at any wavelength, λ , as shown in (3), by the corresponding expression for this voltage at wavelength λ_{ref} and substituting the corresponding expressions for C_{i*} gives results in the expression shown in (12), where α is as shown in (13). The approximately-equal symbol in (12) indicates application of the nearest resonance approximation.

$$C_{i*}[\lambda] = \frac{1}{n[\lambda]} \left(\frac{1}{2} \left(1 - \frac{\lambda_{i*}^2}{\lambda^2} \right)^{-1} \frac{db_{i*}}{d\sigma_p} + \frac{b_{i*} \lambda_{i*}}{\lambda^2} \left(1 - \frac{\lambda_{i*}^2}{\lambda^2} \right)^{-2} \frac{d\lambda_{i*}}{d\sigma_p} \right) \quad (11)$$

$$\begin{aligned} \frac{V_\pi[\lambda]}{V_\pi[\lambda_{ref}]} &= \frac{\lambda}{\lambda_{ref}} \frac{C[\lambda_{ref}]}{C[\lambda]} \approx \frac{\lambda}{\lambda_{ref}} \frac{C_{i*}[\lambda_{ref}]}{C_{i*}[\lambda]} \\ &\rightarrow \frac{\lambda}{\lambda_{ref}} \frac{n[\lambda]}{n[\lambda_{ref}]} \left(\frac{\frac{1}{2} \left(1 - \frac{\lambda_{i*}^2}{\lambda_{ref}^2} \right)^{-1} + \alpha \frac{b_{i*} \lambda_{i*}}{\lambda_{ref}^2} \left(1 - \frac{\lambda_{i*}^2}{\lambda_{ref}^2} \right)^{-2}}{\frac{1}{2} \left(1 - \frac{\lambda_{i*}^2}{\lambda^2} \right)^{-1} + \alpha \frac{b_{i*} \lambda_{i*}}{\lambda^2} \left(1 - \frac{\lambda_{i*}^2}{\lambda^2} \right)^{-2}} \right) \end{aligned} \quad (12)$$

$$\alpha = \frac{d\lambda_{i*}}{d\sigma_p} / \frac{db_{i*}}{d\sigma_p} \quad (13)$$

Equation (12) results in an expression for the control voltage required to produce a maximum phase shift of π , which depends only on parameters derived from the measured refractive index of CaF_2 and the voltage required to produce half-wave retardation at the reference wavelength, λ_{ref} , with the singular exception of α . This result differs from the work of Sinha, who ignored the contributions of what might be called the effective-resonance wavelength-shift terms, i.e., effectively setting α to zero. He also allowed the values of the effective resonant wavelength, λ_{i*} to be an adjustable parameters, rather than being determined from the refractive index data *via* the Sellmeier expression. This is, however, the approach employed here in the case of PEMs with LiF optical elements (*vide infra*).

Calculated values of the half-wavelength control voltage versus wavelength are compared with the experimental values obtained by Oakberg [24, 25] in Figure 4. The solid curve was computed with α set to zero, so all of the parameters in the calculation are from the values for the refractive index of CaF_2 shown in Figure 2, plus the wavelength and control voltage for the HeNe calibration laser experiment. For wavelengths greater than about 150 nm, the computed curve is very close to the linear fit to the experimental data, which is shown as the dashed line. Using Mathematica to determine the value of α that provides the best fit to the experimental data resulted in the dot-dashed curve and a value of α of 25.88. Including the data obtained from beamline U9B returned a value of α of 32.15 (data not shown). In both cases, the calculated curve dropped further below the experimental line for wavelengths less than about 200 nm. While these values of α may seem large, the small magnitude of the term it multiplies means that the wavelength-shift term plays only a minor role in determining the shape of the control-voltage function.

The results shown in Figure 4 demonstrate that the apparently linearly half-wave retardation control voltage observed in the wavelength domain where the optical element is transparent, is consistent with the known properties of the refractive index of the PEM's CaF_2 optical element. Note, however, that CD spectra recorded using a CaF_2 PEM and a synchrotron light source have been reported to 130 nm [23] and thus into the range where there appears to be some difference between the extrapolated experimental data line and the curves computed from refractive index data. However, the measurement of the CD of macromolecules in aqueous solution is presently limited to wavelengths longer than 165 to

170 nm. In addition, small deviations in phase shift result in relatively small errors in the measurement of CD because the phase shift appears in the argument of a J_1 Bessel function that changes quite slowly for changes in δ_o for the values of this parameter typically chosen for the measurement of CD. This argument does not hold for the measurement of LD or FPA, which involve J_2 Bessel functions and different values of δ_o , [8, 21] but such measurements rarely involve wavelengths less than 200 nm. It is tempting to correlate the slopes of the control voltage lines, which decrease monotonically as the range of wavelengths used to determine them increase, (Table 2) with the decreasing slope of the calculated curves shown in Figure 4. However, the fact that the experimental data were recorded with three different PEMs mounted in different spectrometers argues for caution in interpreting these data.

Figure 4. Control voltage required for half-wave retardation as a function of wavelength for CaF_2 PEMs. The experimental data are for Oakberg's xenon-source system and for the laser, which was used to calibrate it. The blue dashed line was determined from these data by least-squares fitting [25]. The solid curve was obtained from (12) using only the oscillator-strength dependent terms, *i.e.*, with $\alpha = 0$. The red dotted curve was obtained from (12) with $\alpha = 25.88$, a value obtained by fitting (12) to the experimental data using Mathematica.

Refractive index and absorption data for fused silica (SiO_2) and LiF, and the half-wave retardation control voltages for PEMs with optical elements made from these materials are shown in Figure 5. The results for fused silica are similar to those for calcium fluoride; the experimental values of the half-wave control voltage are close to the predictions of the theory presented in (12), depending only on the refractive index and the calibration wavelength and voltage. However, this does not hold for the LiF modulator, where λ_0 is greater than λ_{i^*} , and the slope of the control voltage line is much steeper than that for the other modulators. A reasonable fit to the experimental data was obtained by letting λ_{i^*} become a variable, which returned a value greater than λ_0 , as shown in the figure. The curvature of the control voltage curve for the LiF PEM is greater than for the CaF_2 and fused silica systems. Oakberg et al. [24] noted some curvature in the experimental data, with the low and high wavelength data points being slightly lower than the intermediate data.

3.3 Other Factors that Affect PEM Calibration

The major focus of this publication is on calibrating a PEM to maintain a constant value of δ_0 across the spectral domain of a dichrometer. However, several other factors can affect the value of δ_0 . These include temperature, atmospheric pressure, the alignment of the optical element of the PEM with respect to the optical beam and the footprint of the beam on the optical element. For all such effects, the short-wavelength region of the spectral domain in which a PEM is operated is of particular importance. Errors in the amplitude control voltage in this spectral region have a much greater proportional impact on the operation of the modulator than at longer wavelengths.

Figure 5. Refractive index for fused silica (upper left) and LiF (upper right) and control voltage required for half-wave retardation as a function of wavelength for a fused silica PEM (lower left) and a LiF PEM (lower right). The dotted lines indicate the wavelength of the longest wavelength UV resonance obtained from the Sellmeier equation. The dashed lines were the control voltages obtained by Oakberg [24, 25] using the method outlined in Figure 3, and the solid lines were obtained using (6), as described in the text.

Figure 6. The refractive index of crystalline CaF_2 at 20°C (●, right scale) and the difference between

the refractive indices of this material at 25 C and 20 C ($\circ$, left scale). Data are from Daimon and Masumura [29]. Between 1 and 2.3 μ , the refractive index and the refractive index difference remains essentially constant with values near 1.42 and -5×10^{-5} , respectively (data not shown).

The temperature of the optical element affects its refractive index and photoelastic coefficient. While a potentially formidable problem from a theoretical perspective, there is a simple experimental approach to avoiding complications due to variations in temperature, which is to calibrate and always operate a PEM at a single constant temperature. Indeed, at least one vendor of commercial dichrometers has for some time equipped the PEM in their instruments with a heater and control circuit to maintain the PEM at slightly above normal room temperatures. Hinds Instruments has also introduced an accessory to maintain a PEM at a constant temperature of 32 C. While variations in temperature are easily prevented, it is worthwhile to explore the situation using available data. Daimon and Masumura[29] reported the refractive index of calcium fluoride from the vacuum ultraviolet to above 2.3 μ in the infrared at both 20 and 25 C. Their data for the refractive index at 20 C and the difference between the values at 25 and 20 C are shown in Figure 6. From about 300 nm, in the UV, to the long wavelength extent of their data, both the refractive index and the refractive index difference are close to constant. The differences, which are less than five parts in 10^4 in this range, are negative, presumably reflecting the decrease in the density of CaF_2 at the elevated temperature. But for wavelengths deeper into the UV, where the refractive index begins to increase rapidly, the refractive index difference first changes sign and then begins a rapid increase in magnitude. The more rapid increase of the refractive index at 25 C compared to 20 C presumably reflects absorption due to electronic transitions originating in higher vibrational modes of the ground state of the material. Such “hot bands” will shift the absorption edge in the VUV to slightly longer wavelengths, thus reducing the spectral range available for CD and related measurements. Therefore, heating a PEM to achieve a constant photoelastic coefficient profile may not be the optimum strategy in those dichrometers designed for operation in the VUV. While, active cooling to achieve a constant temperature might be considered, it would be more expensive than a temperature control system that maintains the PEM at an elevated temperature. In addition, cooling the PEM to below ambient temperatures may make it vulnerable to condensation if the optical system is neither evacuated nor purged with a dry gas, and may lead to an increased probability of shattering the optical element. Hinds Instruments strongly advises against operating, or even storing CaF_2 PEMs at reduced temperatures.

The operation of a PEM is also affected by the ambient pressure in which it operates [24]. This was observed on beamline U9B, where the PEM was mounted in an evaluable chamber. Results were reported for a PEM with a CaF_2 optical element, and for one with an LiF optical element. In both cases, evacuating the system resulted in the V_π vs. λ line moving down slightly, reflecting larger values of both $V_{\pi,0}$ and λ_0 , but with little change in the slope, i.e., the ratio of these parameters. As shown in Figure 7, changes are greater for the LiF PEM than for the CaF_2 device. The impact on the performance of a PEM in vacuum compared to atmospheric pressure will be tiny in terms of the measurement of CD over most of the spectrum, but with the largest fractional change in the control voltage, and thus the largest change in phase shift, occurring in the VUV, just the spectral range where evacuating the spectrometer is most desirable from the perspective of optical throughput. While inconsequential in many cases, these data reinforces the desirability of calibrating a PEM in the environment in which it is used.

Figure 7. Half-wave control voltages is the vacuum UV for PEMs with LiF and CaF₂ optical elements at room temperature (≈ 21 C) in gaseous nitrogen at atmospheric pressure (—) and under vacuum (- - - -). Data are plotted using parameters from Oakberg *et al.* [24].

The performance of a PEM also depends on how it is aligned with the optical beam and on the footprint of the beam on the optical element. All of the analysis presented above assumes perfect alignment of the PEM with respect to a beam it is modulating. The plane of the optical element, as shown in Figure 1, is assumed exactly perpendicular to the axis of the beam, the stress axis is presumed to be at exactly an angle of $\pi/4$ with respect to the direction of polarization of the radiation incident on it, and the beam is presumed on the exact center of the optical element. The design and calibration of a dichrometer should reflect the importance of achieving appropriate alignment precision. The footprint of the beam on the optical element, represented schematically by the dotted circle in the upper panel of Figure 1, is a more complex issue because it cannot be obviated by careful alignment of the PEM with respect to the optical beam. The footprint becomes an issue because calculations of the phase shifts imparted by the PEM, as discussed above, are applicable only to the exact center of the optical element. The magnitude of the phase shift imparted to rays entering the optical element for both positive and negative distances on the p axis away from the exact center will decrease because the strain induced birefringence is due to a standing acoustic wave, which is a maximum in the center and decreases sinusoidally to zero at the ends, i.e., at $\pm L/2$ [16]. Experimental measurements are in excellent agreement with the theoretical predictions [32]. In addition, the phase shift imparted to rays incident on the optical element moving away from the origin along the q axis are also found to decrease monotonically with distance from the origin [32]. The impact in reduction in the ray-specific phase shift or measured parameters such as CD will be specific to individual dichrometers. However, synchrotron-source dichrometers may tend to reduce such effects because the radiation is usually less divergent compared to xenon-arc and other conventional light sources and thus will tend to traverse a PEM with a smaller cross sectional area.

3.4 Comparisons of PEM Spectral Domains

The optical elements of PEMs designed to operate in the far- and vacuum ultraviolet can be fabricated from fused silica, calcium fluoride and lithium fluoride. The dependence of the control voltages of PEMs with each type of optical elements are shown in the lower panel of Figure 2 for CaF₂ and in the lower panels of Figure 5 for fused silica and LiF. Transmission spectra for samples of these materials roughly the same thickness as the optical element of a PEM are shown in Figure 8. The transmission data show that PEMs with fused silica (Suprasil 311/312) optical elements are adequate for ultraviolet wavelengths greater than about 170 nm, and the slope of the control voltage indicates that approximately quarter-wave retardation can be achieved without damage to the modulator to at least 1 μm . This is adequate for most experiments in which a sample is in an aqueous environment, and all present instruments that do not use a synchrotron radiation light source. Calcium fluoride optical elements extend the spectral domain of PEM experiments about 50 nm further into

the UV, and the control voltage curve shown in Figure 2 means that such modulators can cover the entire visible spectrum in addition to the ultraviolet to about 125 nm. Lithium fluoride is transparent to shorter wavelengths than any other material suitable as a window or the optical element of a PEM, and should extend the short wavelength limit by about 10 nm compared to CaF_2 . As shown in Figure 8, however, LiF is no more transparent than CaF_2 above about 125 nm, and the much steeper control voltage line increases the risk of shattering the optical element when operating in the visible. In addition, the possibility that the control voltage curve is a nonlinear function of wavelength and the very small values of this voltage required to achieve a given phase shift in the very region where LiF PEMs would offer the advantage of greater transmission, suggest that their use is problematic. They may also be more difficult to fabricate (T. Oakberg, personal communication.) The LiF PEM used to produce the data reported by Oakberg *et al.* was manufactured by Hinds Instruments, but that company is not offering LiF PEMs at the time this paper was written.

Figure 8. Transmission spectra of the three principal materials used for the optical elements used in PEMs designed to operate in the far- and vacuum ultraviolet spectral region: 10 mm thick superasil 311/312 fused silica ($\bullet$), 5 mm CaF_2 ($\circ$), and 5 mm LiF ($\square$, $\blacksquare$). The values for the LiF sample for wavelengths less than 120 nm, shown as the filled squares, were read from a published chart on which the wavelength scale is logarithmic and thus may be less certain than for the other data points.

4 Conclusions

It is relatively easy to construct sensitive dichrometers that measure circular- and linear dichroism and fluorescence polarization anisotropy. Assuring that such instruments are properly calibrated in terms of the maximum phase shifts induced is more demanding, particularly at the shortest accessible wavelengths. Determining predictable and reproducible calibrations of dichrometers is becoming more important as CD becomes widely used in demanding applications such as supplying spectra for the PCDDDB and its potential for use as an assurance tool for the validation of biosimilar proteins with medicinal properties. Such measurements of CD focus on the far- and vacuum UV, where errors associated with the magnitude of the control voltage, from whatever cause, result in a proportionally larger effect on the resulting phase shift. This is the spectral region that is critical for the measurement of CD and where synchrotron radiation source dichrometers have the greatest impact.

PEMS with calcium fluoride optical elements offer significantly better short wavelength penetration compared to fused silica. Their UV penetration is almost as good as lithium fluoride, but without the complications associated with those modulators.

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