

# Time-Resolved Profiles in Modulated Polarization Spectroscopy

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The absorption of a modulated light beam in which the state of the polarization is continuously variable is discussed. It is now possible to measure the average time-dependent profile for the polarization cycle of such a beam, and corresponding theoretical descriptions are needed in order to extract the information contained in it. This work generates such a description. Based on a semiclassical treatment of light/matter interactions, a three-parameter fit function is derived that permits the simultaneous extraction of absorbance, linear dichroism, and circular dichroism from the profile for various types of uniformly oriented, partially oriented, and isotropic materials and combinations of them. The theoretical expressions are used to analyze data for (+)-3-methylcyclopentanone, the results being (1) an increase of the *S/N* ratio, (2) the simultaneous generation of absorption and dichroism spectra of identical quality, and (3) a description of window adsorbates of the cyclopentanone material. The Jones parameters for the macroscopic description of polarized light interactions with matter are reformulated at the microscopic (i.e., transition moment) level, and an alternative derivation of the Jones matrix is given.

## I. INTRODUCTION

A new instrument for the measurement of modulated polarization spectra has been described recently.<sup>1,2</sup> This instrument is referred to as a selective digital integrator or, for short, SDI. The advantage of the instrument is its ability to record the intensity of light transmitted by a sample as a continuous function of polarization. Alternatively, if the SDI is regarded as a data-acquisition device, it may be said to generate an average time-resolved profile of a modulation cycle. The SDI, as far as we know, is the first instrument capable of providing such profiles.

Given that these profiles are new observables, a means of analyzing them must be generated. Indeed, that is the main goal of this work. However, in order to do so, a brief overview of modulated polarization spectroscopy is prerequisite. In particular, considerable attention must be devoted to that subset of experiments that measure the various dichroisms.<sup>3</sup>

An experimental apparatus for modulated polarization spectroscopy consists of five parts: a monochromatic light source,<sup>4</sup> a polarizer, a sample cell, a detector, and a data-acquisition system. The unpolarized light emitted by the source is first polarized. It then passes through the sample cell where it is absorbed. The intensity of the transmitted light is transformed into a current signal by a detector, usually a photomultiplier tube or semiconductor diode. Finally, the data-acquisition system measures the current and extracts the polarization-dependent information.

When polarizations other than linear are required over any extensive wavelength range, a photoelastic modulator (PEM) must be used as the polarizer. As a result, instead of the one or two polarizations required by experiment, light with a

periodic time-dependent pattern of polarizations ( $\vec{\Pi}(t)$ ) is generated:<sup>5,6</sup>

$$\vec{\Pi}(t) = \frac{1}{\sqrt{2}}[\hat{x} + \hat{y}e^{i\delta\sin(\Omega t)}] \quad (\text{I.1})$$

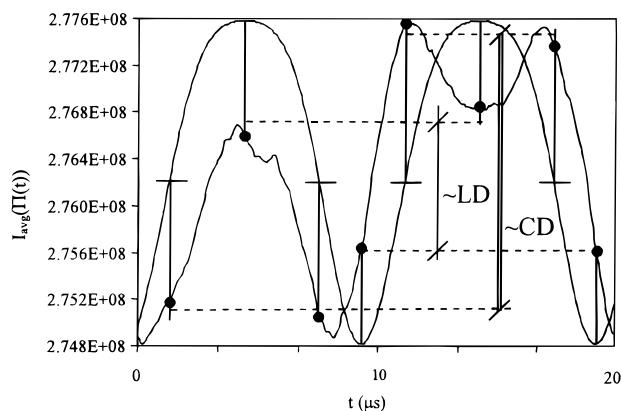
Equation I.1 uses a complex representation of the light polarization:<sup>7</sup>  $\hat{x}$  and  $\hat{y}$  denote unit vectors in the *x* and *y* directions, respectively; *z* is the direction of light propagation;  $\delta$  is the retardation amplitude;  $\Omega$  is the PEM angular frequency; and  $\hat{x} + i\hat{y}$  and  $\hat{x} - i\hat{y}$  denote right and left circular polarizations, respectively. Unfortunately, when the source is of low intensity and/or the sample exhibits a high absorbance, the polarization-dependent differences of transmitted light intensities cannot be recorded in a single period  $T = 2\pi/\Omega$ . Instead, one of the following two approaches is used:

(1) A lock-in amplifier is used to measure the absorbance difference of two polarizations separated by a time  $t = T/2$ . For example, when  $\delta = \pi/2$ , the CD can be measured since, according to eq I.1, right circularly polarized light (RCP) occurs at  $t = T/4 + nT$ , *n* being an integer, and left circularly polarized light (LCP) occurs at  $t = 3T/4 + nT$ . However, this approach has problems that we will refer to later, one of them being disregard of all the other useful information contained in the polarization profile. For example, if  $\delta = \pi$ , only LD can be measured, even though both of the circular polarizations required for a CD measurement are also present.

(2) The second approach is that of an SDI:<sup>8</sup> subsequent periods of the signal, as many as 20 000 000 of them, are averaged in order to generate an average "histogram" of the polarization-dependent light intensity. Because of a low processing overhead, one that approaches zero, the SDI can record a complete time-resolved average polarization profile in the same amount of time it takes a lock-in amplifier to

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**Figure 1.** Time-resolved intensity profile at different polarizations for gaseous (+)-3-methylcyclopentanone at 198.8 nm obtained from an average of 20 000 000 PEM periods and a smoothing algorithm. Points corresponding to the various polarizations are obtained using the equation  $I_{\text{avg}}(t) = I_0/2\{1 + \cos[\delta \sin[\Omega t]]\}$  where  $\delta = 0.95\pi$  and  $\Omega = 1.018$ . This latter equation describes an experimental arrangement in which a linear polarizer is inserted into the beam immediately following the PEM, and no absorber is present. This equation has been verified experimentally. The values for  $\delta$  and  $\Omega$  are conditioned<sup>8</sup> by frequency mismatches of PEM and SDI. The small black circles on the measured profile, left to right, correspond to the following polarizations: RCP,  $LP_{x+y}$ , RCP,  $LP_{x-y}$ , LCP,  $LP_{x+y}$ , LCP, and  $LP_{x-y}$ .

extract the amplitude of only one dichroism. The number of different polarizations for which light intensity can be measured is determined by the number of points per modulation period at which the SDI can perform averaging. For example, in the case of the 50-kHz modulation imposed by photoelastic modulators, the SDI can collect 239 points per period. That is, it can measure the absorption at 239 different polarizations. An example of such a 239-point time-resolved polarization profile is shown in Figure 1 for (+)-3-methylcyclopentanone.

**Time-Resolved Polarization Profiles.** A means of determining the polarization of light corresponding to any point on the experimental profile of Figure 1 can be generated and is illustrated in Figure 1.  $LP_{x+y}$  light corresponds to the maxima of this curve,  $LP_{x-y}$  light corresponds to the minima of this curve, and circular polarizations occur on the curve at the half-heights. Since each linear polarization is generated twice in one period, the average of corresponding points may be taken to be the appropriate value for individual linear polarizations. In any event, the CD and LD signals can be obtained as shown in Figure 1.

Two distinct representations of polarized light are available. The Jones representation<sup>10,13,14</sup> uses a two-dimensional complex electric field vector. The other, the Stokes representation,<sup>7,9,10</sup> describes light by a real four-dimensional vector. Both representations have advantages and disadvantages. The latter, however, is preferred by experimentalists because one of the representation coordinates is the power carried by the light beam, the quantity most often measured in experiments. The connection between these two representations is contained in the  $4 \times 4$  transfer matrix developed by Jensen,<sup>11</sup> who also, in collaboration with Schellman, published an extensive review of the use of such matrices in polarization modulation spectroscopy. The Jones and Stokes representations are macroscopic.

However, the results of polarization spectroscopy are also relevant at the microscopic level. Indeed, if it is the electronic

structure of a material that is of primary interest, the eight macroscopic experimental parameters of Jones<sup>5</sup> must be rephrased. Consequently, another goal of this work is to express the light intensity measured by the SDI directly in terms of microscopic quantities (i.e., in terms of transition matrix elements). In other words, we wish to relate the shape of the time-resolved profile to the electronic structure. In the process, it will be shown that the Jones matrix can be obtained directly in terms of transition matrix elements: a semiclassical treatment of light-matter interaction, photons being treated as oscillations of the classical EM field and photon-molecule interactions being handled quantum mechanically, suffices for that purpose. As a result, the number of parameters is reduced from eight to four.<sup>12</sup> To our knowledge, such a derivation of the Jones matrix has not been given previously. The Jensen results are not used: the representational change from the Stokes to the Jones formalisms and the subsequent replacement of characteristic parameters by their transition matrix counterparts is much too complicated and indirect.

The time-resolved polarization profiles constitute new experimental information for which no theoretical analysis is available. This analysis is desirable for the following reasons:

(1) The profiles contain linear dichroism, circular dichroism, and standard absorption, all obtained in one single experimental run. Thus, all three quantities are of identical quality, a rather significant improvement relative to the situation that requires three separate runs, each under conditions that are extremely difficult to control.

(2) An increase of spectral resolution is expected. It can be shown<sup>8</sup> that a least-squares fit to the time-resolved profile yields a better  $S/N$  ratio than the Fourier transform approach common in the use of lock-in amplifiers. If the average time-resolved profile is denoted  $f_{\text{avg}}(t)$  and an  $n$ -parameter fit function is denoted  $f_{\text{fit}}(p_1, \dots, p_n, t)$ , then the least-squares fit is defined as that procedure which generates the  $n$  parametric values for  $p_1, p_2, \dots$ ,

$$J = \int_0^T [f_{\text{avg}}(t) - f_{\text{fit}}(p_1, \dots, p_n, t)]^2 dt \quad (\text{I.2})$$

that minimize the cost function of eq I.2. The implementation of such an algorithm requires an appropriate fit function.

(3) Various samples, for example, crystals, can exhibit simultaneous CD and LD. Another example is provided by a combination of a gaseous sample and a thin film created by adsorption of the gas on the optical windows. This film may cause presumptively gaseous systems, ones that should exhibit CD only, to also display LD. Consequently, it is important to generate a fit function that permits simultaneous extraction of the LD and CD components.

In this work, we will derive theoretical expressions for the polarization-dependent intensity of transmitted light for uniformly oriented, isotropic, and partially oriented samples. These theoretical expressions are then employed to construct a three-parameter fit function for extraction of the absorbance, LD, and CD from the time-resolved profiles. This fit function is applied to the experimental, wavelength-dependent, time-resolved profiles of (+)-3-methylcyclopentanone, for which the CD, LD, and absorption spectra are then generated. The isotropic case will be used as a test case.

The origin of the LD attributed to a partially oriented film will be discussed.

## II. THEORETICAL BACKGROUND

Investigations of polarization spectroscopy are relevant at two different levels. If the macroscopic properties of the material are of interest, the experimental results are usually discussed in terms of eight parameters identified by R. Clark Jones.<sup>13,14</sup> According to Jones, the state of arbitrarily polarized light moving along the  $z$  axis, after it has passed through matter, can be described by

$$\vec{E}(z) = \begin{bmatrix} E_x(z) \\ E_y(z) \end{bmatrix} = \mathbf{M}(z) \begin{bmatrix} E_x(0) \\ E_y(0) \end{bmatrix}$$

where  $E_x(0)$  and  $E_y(0)$  are the  $x$  and  $y$  electric field components of the incident light,  $E_x(z)$  and  $E_y(z)$  are the  $x$  and  $y$  electric field components of the emerging light, and  $\mathbf{M}(z)$  is a complex  $2 \times 2$  matrix given by

$$\mathbf{M}(z) = \exp(z\mathbf{N})$$

Matrix  $\mathbf{N}$  is obtained as a weighted linear superposition of eight  $2 \times 2$  matrices

$$\mathbf{N} = -\eta \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix} - \kappa \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \omega \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} + \delta \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + g_0 \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} + p_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + g_{45} \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} + p_{45} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad (\text{II.1})$$

or, more compactly,

$$\mathbf{N} = \begin{pmatrix} -\kappa + p_0 - i\eta + ig_0 & -\omega + p_{45} - i\delta + ig_{45} \\ \omega + p_{45} + i\delta + ig_{45} & -\kappa - p_0 - i\eta - ig_0 \end{pmatrix}$$

where the constants, in order of appearance in eq II.1, represent the following properties of the material through which the light has propagated:<sup>15</sup>  $\eta = 2\pi n/\lambda$ , the phase retardation (PR) per unit length;  $n$  is the index of refraction;  $\kappa = 2\pi\epsilon/\lambda$ , the absorption coefficient (ABS) per unit length;  $\epsilon$  is the extinction coefficient;  $\omega = 1/2(\eta_r - \eta_i)$ , the circular birefringence (CB) per unit length;  $\delta = 1/2(\kappa_r - \kappa_i)$ , the circular dichroism (CD) per unit length;  $g_0 = 1/2(\eta_y - \eta_x)$ , the linear birefringence (LB) per unit length;  $p_0 = 1/2(\kappa_y - \kappa_x)$ , the linear dichroism (LD) per unit length;  $g_{45} = 1/2(\eta_{-45} - \eta_{45})$ , the  $(45^\circ/135^\circ)$  linear birefringence (LB') per unit length; and  $p_{45} = 1/2(\kappa_{-45} - \kappa_{45})$ , the  $(45^\circ/135^\circ)$  linear dichroism (LD') per unit length.

On the other hand, if the electronic structure is of primary interest, a translation of these eight macroscopic parameters to a microscopic level is required. The goal of this section, then, is to express light intensity, as measured by the SDI, at a microscopic level (i.e., in terms of transition matrix elements).

**(A) Polarized Light–Matter Interaction in a Uniformly Oriented Sample.** The electric field of an EM wave propagating in a vacuum along the  $z$  axis, the default direction if not otherwise stated, can be written<sup>7</sup> as

$$\vec{E}(t, z) = E_0 \vec{\Pi} \exp[i(\omega t - kz)] \quad (\text{II.2})$$

where  $\vec{\Pi}$  is a polarization vector in the  $xy$  plane,  $E_0$  is a wave amplitude,  $\omega = 2\pi\nu$  is the angular frequency, and  $k$  is

the wave vector ( $2\pi/\lambda$ ). The corresponding magnetic field is obtained<sup>7</sup> from Maxwell's equations as

$$\nabla \times \vec{E}(z, t) = \frac{1}{\mu} \frac{\partial \vec{H}(z, t)}{\partial t} \quad (\text{II.3})$$

where  $\mu$  is the magnetic permeability. The power in the wave is given<sup>7</sup> by a time average of the Poynting vector ( $\vec{S}$ ) as

$$\langle \vec{S} \rangle = \frac{c}{8\pi} \text{Re}[\vec{E} \times \vec{H}^*] \quad (\text{II.4})$$

where  $c$  is the speed of light.

When the EM wave enters a medium, interaction between radiation and matter occurs. That interaction is manifested by absorption (power loss) and polarization changes and may be described by a complex index of refraction ( $N$ ) whose real and imaginary parts are related to the real index of refraction ( $n$ ) and the absorption coefficient ( $\alpha$ ) as

$$N(\omega) = n(\omega) - \frac{i}{2k} \alpha(\omega) \quad (\text{II.5})$$

If the first-order perturbation solution of the time-dependent Schrödinger equation is manipulated (the Einstein absorption coefficients;<sup>5,16</sup> the Fermi Golden Rule<sup>17</sup>), if terms to the level of electric dipole, magnetic dipole, and electric quadrupole are retained, and if only a single active transition and a uniformly oriented molecular sample are assumed, one finds<sup>5</sup>

$$N(\omega) = 1 - \frac{im}{\hbar c} [\vec{M}(0f) \cdot \vec{\Pi} + \vec{M}(0f) \cdot (\hat{z} \times \vec{\Pi}) + i \frac{\omega}{2c} \hat{z} \cdot \vec{Q}(0f) \vec{\Pi}]^2 [g_{\text{abs}}(\omega) - ig_{\text{disp}}(\omega)]$$

where  $m$  is the concentration (number of molecules per cubic centimeter),  $\vec{M}(0f)$  and  $\vec{M}(0f)$  are the electric and magnetic dipole transition vectors,  $\vec{Q}(0f)$  is the electric quadrupole transition tensor, 0 and  $f$  label the initial and final states, respectively, and  $g_{\text{disp}}(\omega)$  and  $g_{\text{abs}}(\omega)$  are the dispersion and absorption curves, respectively.<sup>5,7</sup> The last expression can be rewritten as

$$N(\omega) = 1 - i |M_f(\vec{\Pi})|^2 g_f(\omega) \quad (\text{II.6})$$

by defining a vector operator  $M_f$

$$M_f(\vec{v}) = \sqrt{\frac{m}{\hbar c}} [\vec{M}(0f) \cdot \vec{v} + \vec{M}(0f) \cdot (\hat{z} \times \vec{v}) + i \frac{\omega}{2c} \hat{z} \cdot \vec{Q}(0f) \cdot \vec{v}] \quad (\text{II.7})$$

or, more compactly,

$$M_f(\vec{v}) = \mathbf{M}_f(\vec{v}) + \mathbf{M}_f(\vec{v}) + Q_f(\vec{v})$$

and combining the absorption and dispersion shape functions into one imaginary shape function,  $g_f(\omega)$ . The  $\omega$  dependence of the transition elements is implied but not explicitly stated. The shape function ( $g_f(\omega)$ ) and the vector operator ( $M_f$ ) carry the index  $f$  to emphasize their dependence on the final state in those cases in which more than one transition from the same initial state can be induced by light of frequency  $\omega$ .

Simple insertion of eq II.5 into eq II.2 to obtain

$$\vec{E}(t,z) = E_0 \vec{\Pi} \exp\{i[\omega t - N(\omega)kz]\} \quad (\text{II.8})$$

may be improper even though eq II.8 does have the correct vacuum limit (i.e., for  $N = 1$ , it yields eq II.2). The problem with Eq II.8 is that it requires some development in order to cope with all polarization changes of the light. This problem can be “fixed” by decomposing the incoming wave into two orthogonally polarized components,<sup>18</sup> each of which propagates through the material according to eq II.8 with its own complex index of refraction: if the absorption coefficients of the two components are different, each will be absorbed to a different degree, and when combined after passage through the sample, they will yield a polarization different from that of the incident light. The same is also correct if the phasing (real refraction) is differentially altered. However, the result obtained for the power loss will be a function of the choice of the orthogonal polarization pair. Thus, in order for eq II.8 to apply, the polarization of the components must not be affected by the material. Consequently, in order for such a decomposition to work, two characteristic orthogonal polarizations, ones for which the electric field vector obeys eq II.8, must be found.<sup>19</sup>

One obvious candidate, denoted  $\vec{\Pi}_2$ , is polarization for which light does not interact with the matter at all (i.e., for which  $N = 1$ ). The requirement  $N = 1$  implies that

$$M_f(\vec{\Pi}_2) = 0 \quad (\text{II.9})$$

If  $\vec{\Pi}_2$  is split into its  $x$  and  $y$  components,  $\Pi_{2x}$  and  $\Pi_{2y}$ , respectively, and the linear property of  $M_f$  is used

$$M_f(a\vec{v} + b\vec{w}) = aM_f(\vec{v}) + bM_f(\vec{w}) \quad (\text{II.10})$$

eq II.9 becomes

$$\Pi_{2x}M_f(\hat{x}) + \Pi_{2y}M_f(\hat{y}) = \Pi_{2x}M_{fx} + \Pi_{2y}M_{fy} = 0 \quad (\text{II.11})$$

The obvious solution to eq II.11 is

$$\begin{aligned} \Pi_{2x} &= M_{fy} \\ \Pi_{2y} &= -M_{fx} \end{aligned} \quad (\text{II.12})$$

Therefore, the normalized polarization vector ( $\vec{\Pi}_2$ ) is given by

$$\vec{\Pi}_2 = \frac{1}{\sqrt{|M_{fx}|^2 + |M_{fy}|^2}}(M_{fy}\hat{x} - M_{fx}\hat{y}) \quad (\text{II.13})$$

The other component, denoted  $\vec{\Pi}_1$ , may now be determined from the orthogonality condition

$$\vec{\Pi}_1 \cdot \vec{\Pi}_2^* = \vec{\Pi}_2 \cdot \vec{\Pi}_1^* = 0 \quad (\text{II.14})$$

as

$$\vec{\Pi}_1 = \frac{1}{\sqrt{|M_{fx}|^2 + |M_{fy}|^2}}(M_{fx}^*\hat{x} + M_{fy}^*\hat{y}) \quad (\text{II.15})$$

Inserting eq II.15 into eq II.7 yields

$$M(\vec{\Pi}_1) = \sqrt{|M_{fx}|^2 + |M_{fy}|^2} \quad (\text{II.16})$$

In the case in which only the electric dipole term is present in eq II.7,  $M_{fx}$  and  $M_{fy}$  are real and eqs II.15 and II.16 correctly imply that light, when linearly polarized at an angle determined by the ratio  $M_{fx}/M_{fy}$ , propagates with no polarization change and an absorptivity that is related to the dipole moment vector length, whereas the orthogonal linear component,  $\vec{\Pi}_2$ , propagates with no changes at all.

Therefore, one may calculate the effect of matter on any polarized beam ( $\vec{\Pi}$ ) by decomposing it into the two characteristic components  $\vec{\Pi}_1$  and  $\vec{\Pi}_2$  of eqs II.13 and II.15, each of which then interacts with matter according to eq II.8 and with its own complex index of refraction. Finally, after transit through the sample, the two components may be rejoined. This procedure can be described mathematically as

$$\begin{aligned} \vec{E}(t,z) &= E_0 \exp(i\omega t) \times \{ \gamma_1 \vec{\Pi}_1 \times \\ &\exp[-ikz(1 - i|M_{fx}(\vec{\Pi}_1)|^2 g_f(\omega))] + \gamma_2 \vec{\Pi}_2 \exp(-ikz) \} \end{aligned} \quad (\text{II.17})$$

where

$$\gamma_i = \vec{\Pi} \cdot \vec{\Pi}_i^*$$

and eq II.9 has been used. Differentiation of eq II.17 and an equation of similar components yields the two coupled differential equations

$$\begin{aligned} \frac{\partial E_x(z,t)}{\partial z} &= -A E_x(z,t) - B_1 E_y(z,t) \\ \frac{\partial E_y(z,t)}{\partial z} &= -B_2 E_x(z,t) - C E_y(z,t) \end{aligned} \quad (\text{II.18})$$

where

$$\begin{aligned} A &= k[i + g_f(\omega)|M_{fx}|^2] \\ B_1 &= kg_f(\omega)M_{fx}^* M_{fy} \\ B_2 &= kg_f(\omega)M_{fx} M_{fy}^* \\ C &= k[i + g_f(\omega)|M_{fy}|^2] \end{aligned} \quad (\text{II.19})$$

In other words, the matrix

$$\mathbf{N}' = \begin{bmatrix} A & B_1 \\ B_2 & C \end{bmatrix} \quad (\text{II.20})$$

describes the effects of an infinitesimally thin slab of matter on the incident radiation. As such, it is equivalent to the Jones  $\mathbf{N}$  matrix, and the two characteristic polarizations  $\vec{\Pi}_1$  and  $\vec{\Pi}_2$  of eqs II.13 and II.15, respectively, are the orthogonal eigenvectors of  $\mathbf{N}'$ . The latter may be verified by combining the definitions of eq II.19 into eq II.20. One obtains  $\mathbf{N}'$  as

$$\begin{aligned} \mathbf{N}' &= \begin{bmatrix} ik + kg_f(\omega)|M_{fx}|^2 & kg_f(\omega)M_{fx}^* M_{fx} \\ kg_f(\omega)M_{fx} M_{fy}^* & ik + kg_f(\omega)|M_{fy}|^2 \end{bmatrix} = \\ &ik \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + kg_f(\omega) \begin{bmatrix} |M_{fx}|^2 & M_{fx}^* M_{fy} \\ M_{fx} M_{fy}^* & |M_{fy}|^2 \end{bmatrix} \end{aligned} \quad (\text{II.21})$$



Furthermore, eq II.21 demonstrates that the two characteristic polarizations remain orthogonal even when the molecular orientation is nonuniform: the only requirement is that all active transitions possess the same complex function  $g_f(\omega)$  (i.e., the matrix  $\mathbf{N}'$  must be a superposition of the Hermitian and identity matrices). Finally, when the relationships

$$\eta(\vec{\Pi}) = k[1 - |M(\vec{\Pi})|^2 g_{\text{disp}}]$$

and

$$\kappa(\vec{\Pi}) = k|M(\vec{\Pi})|^2 g_{\text{abs}}$$

are used to obtain the eight Jones parameters,  $\mathbf{N}$  and  $\mathbf{N}'$  are found to be identical.

The solution to eq II.17, then, is

$$\begin{aligned} E_x(z,t) &= \frac{\exp(-\beta_1 z)}{\beta_1 - \beta_2} \{E_{x0}[\beta_1 - C] + E_{y0}B_1\} - \\ &\quad \frac{\exp(-\beta_2 z)}{\beta_1 - \beta_2} \{E_{x0}[\beta_2 - C] + E_{y0}B_1\} \\ E_y(z,t) &= \frac{\exp(-\beta_1 z)}{\beta_1 - \beta_2} \{E_{x0}B_2 + E_{y0}[\beta_1 - A]\} - \\ &\quad \frac{\exp(-\beta_2 z)}{\beta_1 - \beta_2} \{E_{x0}B_2 + E_{y0}[\beta_2 - A]\} \quad (\text{II.22}) \end{aligned}$$

where

$$\beta_{1,2} = \frac{A + C \pm \sqrt{(A - C)^2 + 4B_1B_2}}{2} \quad (\text{II.23})$$

and

$$\begin{aligned} E_{x0} &= E_x(0,t) = E_0 \Pi_x \exp(i\omega t) \\ E_{y0} &= E_y(0,t) = E_0 \Pi_y \exp(i\omega t) \quad (\text{II.24}) \end{aligned}$$

The  $x$  and  $y$  components of  $\vec{H}(z,t)$ , as obtained from eq II.3, are given by

$$\begin{aligned} H_x(z,t) &= -\frac{i}{k\mu} \frac{\partial E_y(z,t)}{\partial z} \\ H_y(z,t) &= -\frac{i}{k\mu} \frac{\partial E_x(z,t)}{\partial z} \quad (\text{II.25}) \end{aligned}$$

Finally, by combining eqs II.4 and II.24, the intensity of the light is found to be

$$I = \langle \vec{S} \rangle \cdot \hat{z} = \frac{c}{8\pi k} \text{Re} \left[ \frac{-i}{\mu} \left( E_x \frac{\partial E_x}{\partial z} + E_y \frac{\partial E_y}{\partial z} \right) \right] \quad (\text{II.26})$$

In the general case,  $\mu$  is a complex number. However, since the analysis that follows is for nonmagnetic materials,  $\mu$  may be set equal to 1.

**(B) Isotropic Sample.** The derivation of the electric field vector for the special case of radiation propagating through a completely oriented sample in which only one transition

is active, as given in section II.A above, will now be extended to an isotropic material. It will be shown that the generalized expressions of the previous section are still applicable. Finally, the theoretical expressions for the transmitted light intensity as a function of polarization will be used to obtain the fit function of eq I.2.

Equation II.18 is restricted to a situation in which all molecules of the sample are similarly oriented and the incident radiation excites one single transition. A general expression for  $A$  of eq II.19 is

$$A = k \left[ i + \frac{1}{F} \sum_{f=1}^F g_f(\omega) \frac{1}{G} \sum_{l=1}^G \left| \vec{M}_{lf}(\Pi_{lx}\hat{x}) \right|^2 \right] \quad (\text{II.27})$$

where  $F$  is the number of transitions induced by the radiation,  $G$  is the number of different molecular orientations in the sample,  $\Pi_{lx}$  is the  $x$  component of  $\vec{\Pi}_l$ , eq II.15, for the  $l$ th molecular orientation, and  $\vec{M}_{lf}$  is the corresponding vector operator defined in eq II.7. Similarly, the  $B_1$ ,  $B_2$ , and  $C$  coefficients can be generalized to

$$\begin{aligned} B_1 &= k \frac{1}{F} \sum_{f=1}^F g_f(\omega) \frac{1}{G} \sum_{l=1}^G \vec{M}_{lf}(\Pi_{lx}\hat{x}) \vec{M}_{lf}^*(\Pi_{ly}\hat{y}) \\ B_2 &= k \frac{1}{F} \sum_{f=1}^F g_f(\omega) \frac{1}{G} \sum_{l=1}^G \vec{M}_{lf}^*(\Pi_{lx}\hat{x}) \vec{M}_{lf}(\Pi_{ly}\hat{y}) \\ C &= k \left[ i + \frac{1}{F} \sum_{f=1}^F g_f(\omega) \frac{1}{G} \sum_{l=1}^G \left| \vec{M}_{lf}(\Pi_{ly}\hat{y}) \right|^2 \right] \quad (\text{II.28}) \end{aligned}$$

If the sum of the  $xy$  cross-terms for different molecular orientations, as multiplied by  $k$ , and for transitions to the same final state  $f$  is replaced by  $B_f$ , the expressions for  $B_1$  and  $B_2$  can be rewritten as

$$\begin{aligned} B_1 &= \frac{1}{F} \sum_{f=1}^F g_f B_f \\ B_2 &= \frac{1}{F} \sum_{f=1}^F g_f B_f^* \quad (\text{II.29}) \end{aligned}$$

The constants defined in eqs II.27 and II.28 are valid only if the sample is an “equal” mixture of different molecules and molecular orientations. That is, in any given vertical slice of the sample of thickness  $\Delta z$ , an incident photon must have equal chances of encountering all molecules and molecular orientations. Consequently, two sequential absorption cells, each containing a different sample, cannot be treated as a single cell of the same composite length containing a mixture of molecules described by one set of constants: the mixture alters the light polarization in a way that is quite different from that of the two separate samples.

Further simplifications are possible for the isotropic sample. First, the sum over  $l$  becomes an integral over all possible orientations and  $A$  and  $C$  become equal:<sup>5</sup>

$$A = C = k \left[ i + \frac{1}{F} \sum_{f=1}^F g_{fab}(\omega) \frac{1}{3} \left| \vec{M}_f \right|^2 \right] \quad (\text{II.30})$$

where

$$\frac{1}{3}|\vec{M}_f|^2 = \frac{1}{3} \sum_{q=x,y,z} [|\vec{M}_f(\hat{q})|^2 + |\vec{M}_f(\hat{q})|^2 + |\vec{Q}_f(\hat{q})|^2] \quad (\text{II.31})$$

Furthermore, because of the orientational averaging, the  $B_f$  coefficients become purely imaginary<sup>5</sup> (i.e.,  $B_1 = -B_2 = B$ ). Using these properties, the polarization-dependent intensity of transmitted light, eq II.24, becomes

$$I = \frac{c}{8\pi k} \exp[-2 \operatorname{Re}(A)z] \operatorname{Im}[I_0 K_1 + 2 \operatorname{Im}(E_{x0} E_{y0}^*) K_2] \quad (\text{II.32})$$

where

$$K_1 = iB^* \sinh[2 \operatorname{Im}(B)L] - A^* \cosh[2 \operatorname{Im}(B)L]$$

$$K_2 = iB^* \cosh[2 \operatorname{Im}(B)L] - A^* \sinh[2 \operatorname{Im}(B)L] \quad (\text{II.33})$$

and  $I_0$  and  $L$  are the intensity of the light incident on the sample and the sample cell length, respectively.

When orientation averaging is performed for  $B_1$  and  $B_2$ , only the electric-dipole/magnetic-dipole terms survive.<sup>5</sup> As a result, the value of  $\operatorname{Im}(B)$  is of the order of  $10^{-3} \operatorname{Re}(A)$  because  $A$  contains the dominant dipole term. Consequently, the  $\operatorname{Re}(A)$  or  $\operatorname{Re}(C)$  term, which can be estimated from the exponential factor in eq II.32, becomes solely responsible for power loss. Thus, at intermediate pressures ( $\sim 600$  mTorr) of (+)-3-methylcyclopentanone at the 198.7-nm absorption peak,  $2 \operatorname{Re}(A)L$  is of the order<sup>8</sup> of 1 (i.e.,  $\operatorname{Re}(A) = \operatorname{Re}(C) \sim 10^{-1}$  when  $L = 25$  cm). Since sample absorbances do not usually exceed 3, this estimate of  $\operatorname{Re}(A)L$  (or  $\operatorname{Re}(C)L$ ) is an upper limit. Consequently,  $\operatorname{Im}(B)L$  is of the order of  $10^{-3}$  or less, and the hyperbolic terms of eq II.33 can be expanded and truncated to first order to yield

$$\cosh[2 \operatorname{Im}(B)L] \sim 1$$

$$\sinh[2 \operatorname{Im}(B)L] \sim 2 \operatorname{Im}(B)L \quad (\text{II.34})$$

Thus, one finds

$$K_1 \sim -A^*$$

$$K_2 \sim -A^*[2 \operatorname{Im}(B)L] \quad (\text{II.35})$$

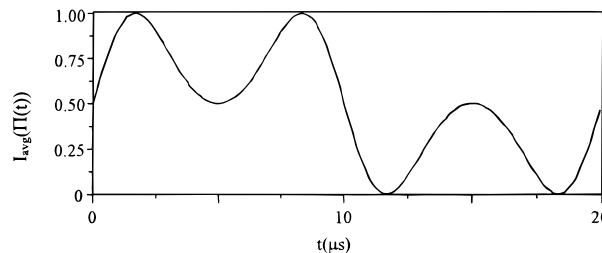
When  $A$  in the nonexponential terms is replaced by  $ik$ , a valid approximation because the second term of eq II.30 is of the order of  $\operatorname{Re}(A)/k \sim 10^{-6}$ , and when  $K_1$  and  $K_2$  of eq II.35 are inserted into eq II.32, an expression for transmitted light intensity is obtained as

$$I = \frac{c}{8\pi} \exp[-2 \operatorname{Re}(A)L] \{I_0 + 4 \operatorname{Im}(B)L \operatorname{Im}(E_{x0} E_{y0}^*)\} \quad (\text{II.36})$$

Finally, when the polarization of light passing through the sample cell is altered with a PEM, the average time-resolved profile of eq II.36 becomes

$$I_{\text{avg}}(t) = \frac{c}{8\pi} I_0 \exp[-2 \operatorname{Re}(A)L] \times$$

$$\{1 + 2 \operatorname{Im}(B)L \sin[\delta \sin(\Omega t)]\} \quad (\text{II.37})$$



**Figure 2.** Shape, for one period, of the polarization-dependent average time-resolved profile,  $I_{\text{avg}}(t)$ , eq II.37, for a retardation amplitude  $\delta = \pi$ .

and the CD and LD at  $\delta = \pi$  are obtained<sup>7</sup> as

$$\text{CD} = \frac{1}{2.303} \frac{I_{\text{avg}}\left(\frac{\pi}{6}\right) - I_{\text{avg}}\left(\frac{7\pi}{6}\right)}{I_{\text{avg}}\left(\frac{\pi}{6}\right) + I_{\text{avg}}\left(\frac{7\pi}{6}\right)} =$$

$$\frac{2}{2.303} \operatorname{Im}(B)L = \frac{L}{2.303F} \sum_{f=1}^F g_{\text{abs}}(\omega) \operatorname{Im}(B_f)$$

$$\text{LD} = \frac{1}{2.303} \frac{I_{\text{avg}}\left(\frac{\pi}{2}\right) - I_{\text{avg}}(\pi)}{I_{\text{avg}}\left(\frac{\pi}{2}\right) + I_{\text{avg}}(\pi)} = 0 \quad (\text{II.38})$$

A complete cycle of  $I_{\text{avg}}(t)$  from eq II.37 for  $0 \leq t < T$  and  $\delta = \pi$  is shown in Figure 2. It is quite different from the profile of Figure 1, confirming the assertion that the profile of Figure 1 does not solely consist of CD.

Equation II.38 also indicates that the wavelength-dependent CD and the absorption profile for a single transition should be identical.

**(C) Partially Oriented Sample.** The most general treatment of a partially oriented sample is complicated and does not provide much insight. Instead, we will consider three special pertinent cases. The first two cases refer to an “optically thin film”. They occur when the absorption is small either because the sample is very thin or, if not thin, when the extinction coefficient is small. The third case refers to an optically dense situation that exhibits weak optical activity. These three cases are similar because the square root of eq II.23 multiplied by the thickness of the sample is much smaller than unity.<sup>20</sup> Consequently, the solution to the system of differential equations of eq II.18 can be approximated by

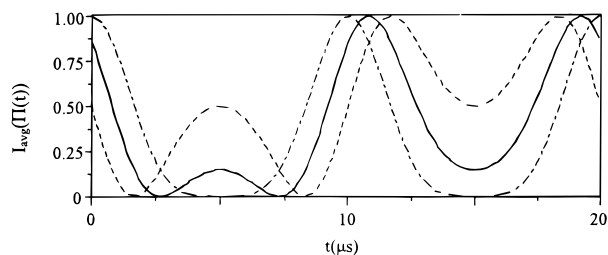
$$E_x(\Delta z) = \exp\left[-\frac{A+C}{2}\Delta z\right] \times$$

$$\left[E_{x0} - \frac{A-C}{2}E_{x0}\Delta z - B_1 E_{y0}\Delta z\right]$$

$$E_y(\Delta z) = \exp\left[-\frac{A+C}{2}\Delta z\right] \times$$

$$\left[E_{y0} - B_2 E_{x0}\Delta z - \frac{C-A}{2}E_{y0}\Delta z\right] \quad (\text{II.39})$$

When eqs II.18 and II.39 are inserted into eq II. 26, an expression for transmitted light intensity is obtained. If only terms of  $O(\Delta z)$  are retained in the nonexponential parts and the properties  $|B_1| \ll 1$ ,  $|B_2| \ll 1$ ,  $\operatorname{Re}(A) \ll \operatorname{Im}(A)$ , and  $\operatorname{Re}(C) \ll \operatorname{Im}(C)$  are used, the final expression for the transmitted



**Figure 3.** Shape of  $I_{\text{avg}}(t)$  for a thin, partially oriented film (eq II.40). The average time-resolved shape is shown for a retardation amplitude  $\delta = 0.95\pi$  and three different values of  $\varphi_{Bf}$ : 0 (dash-dot-dash line),  $\pi/4$  (solid line), and  $\pi/2$  (dashed line).

intensity simplifies to

$$I \sim \frac{c}{8\pi} \exp[-\text{Re}(A + C)\Delta z] \left\{ I_0 - \Delta z [2 \text{Re}[E_{x0}E_{y0}^*(B_1^* + B_2)] + \text{Re}\left[\frac{i}{k}(E_{x0}E_{y0}^*B_1^* + E_{x0}^*E_{y0}B_2^*)\right]] \right\}$$

which, upon insertion of eq II.29, yields

$$I \sim \frac{c}{8\pi} \exp[-\text{Re}(A + C)\Delta z] \left\{ I_0 - \frac{2}{F} \sum_{f=1}^F \left\{ 2\Delta z \text{Re}[g_f(\omega)] - \frac{1}{k} \text{Im}[g_f(\omega)] \right\} \text{Re}[E_{x0}E_{y0}^*B_f^*] \right\}$$

Finally, for light polarized by a PEM, the average time-resolved profile becomes

$$I_{\text{avg}}(t) \sim \frac{c}{8\pi} I_0 \exp[-\text{Re}(A + C)\Delta z] \times \left\{ 1 - \frac{2}{F} \sum_{f=1}^F K_f(\omega) |B_f| \cos[\delta \sin(\Omega t) - \varphi_{Bf}] \right\} \quad (\text{II.40})$$

where

$$B_f = |B_f| \exp(i\varphi_{Bf})$$

$$\varphi_{Bf} = \tan^{-1} \left[ \frac{\text{Im}[B_f]}{\text{Re}[B_f]} \right]$$

$$K_f(\omega) = \left\{ 2\Delta z \text{Re}[g_f(\omega)] - \frac{1}{k} \text{Im}[g_f(\omega)] \right\} \quad (\text{II.41})$$

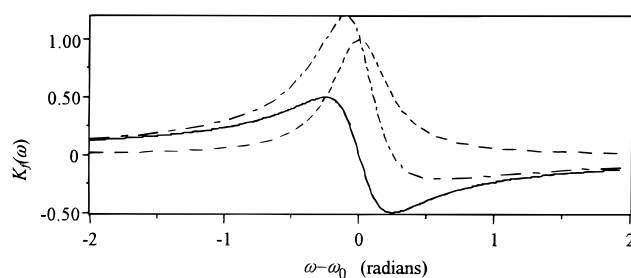
The corresponding CD and LD are given by

$$\text{CD} = -\frac{2}{2.303F} \sum_{f=1}^F K_f(\omega) |B_f| \sin[\varphi_{Bf}]$$

$$\text{LD} = -\frac{2}{2.303F} \sum_{f=1}^F K_f(\omega) |B_f| \cos[\varphi_{Bf}] \quad (\text{II.42})$$

Equations II.40, II.41, and II.42 lead to the following conclusions:

(1) The average time-resolved profile is largely determined by the ratio of the real and imaginary parts of  $B_f$  (eq II.41). Profiles for some  $\varphi_{Bf}$  values are shown in Figure 3. When  $B_f$  is purely imaginary, the profile is identical to that for the isotropic sample (except for an inversion that appears at  $\varphi_{Bf} = -\pi/2$ ). If one molecular orientation dominates,  $B_f$  being



**Figure 4.** Wavelength-dependent profile of  $K_f(\omega)$ , eq II.41, for three different ratios of  $\Delta z$  and  $k$ :  $2\Delta z \leq 1/k = 1$  (solid line),  $(2.303)2\Delta z = 1/k = 1$  (dash-dot-dash line), and  $(2.303)2\Delta z = 1 \gg 1/k$  (dashed line). The transition frequency is  $\omega_0$ . The absorption and dispersion profiles are assumed to have Lorentzian shapes<sup>4,6</sup> with  $\gamma = 0.25$  rad.

a product of complex  $M_{fx}$  and  $M_{fy}$  transition matrix components, the average time-resolved profile may exhibit a phase difference of the two components (per eq II.40).

(2) The  $2\Delta z$  term has an absorptive profile (eq II.41). The  $1/k$  term has a dispersive profile (eq II.41). As long as  $1/k$  is of the order of  $2\Delta z$  ( $\Delta z \sim 10^{-5}$  cm at 200 nm), the two shapes, dispersive and absorptive, will compete. The absorptive shape will dominate at large values of  $\Delta z$  and the dispersive shape at large values of  $1/k$ . The wavelength-dependent profiles of a single transition,  $K_f(\omega)$  of eq II.41, shown in Figure 4 for three different  $(\Delta z, k)$  pairs, illustrate these profiling conclusions.

(3) For frequencies far removed from resonance, where  $g_{\text{abs}}(\omega) = 0$ , the dispersive term may dominate and produce asymmetry: the light intensity on the low-energy side of the peak will be a little higher/lower than on the high-energy side, depending on the sign of  $B_f$ . However, if the absorption is intense, this asymmetry may not be noticeable.

(4) If  $B_f$  has an imaginary part, the sample, in addition to LD, will also exhibit a CD (eq II.42) with characteristics similar to LD: an absorptive profile for frequencies near resonance and/or large values of  $\Delta z$  and a dispersive shape otherwise.

**(D) Fit Function.** The development of an appropriate fit function requires a concern for three entities: the form of the fit function or, equivalently, the nature of the terms (sinusoidal, exponential, Gaussian, etc.) of which it is constituted; the number of parameters, which should be as small as possible; the meaning of each parameter, whether separately or in combination. The main goal of this section is to address these three issues.

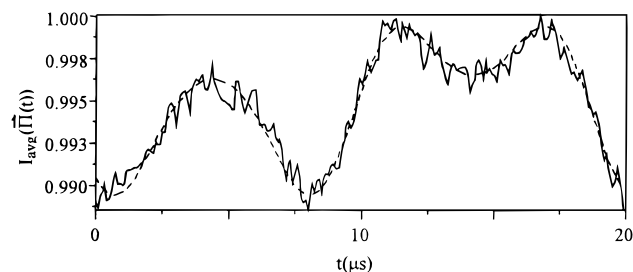
The average light intensity incident on the PMT is given, according to eq II.40, by

$$I_{\text{avg}}(t) = K_1 \{1 + K_2 \cos[\delta \sin(\Omega t) + K_3]\} \quad (\text{II.43})$$

which, when constants corresponding to linear and circular dichroism are introduced, becomes

$$I_{\text{avg}}(t) = K_1 + K_1 K_{\text{LD}} \cos[\delta \sin(\Omega t)] + K_1 K_{\text{CD}} \sin[\delta \sin(\Omega t)] \quad (\text{II.44})$$

Therefore, if the sample belongs to one of the cases discussed in section II.C, the three-parameter function of eq II.44 constitutes an appropriate fit function. Comparison of eqs II.44 and II.37 indicates that this same fit function is also applicable to an isotropic sample. Indeed, this fit function



**Figure 5.** Average 240-window time-resolved profile of (+)-3-methylcyclopentanone at 198.8 nm (solid line). More than  $20 \times 10^{-6}$  signal periods had to be averaged because of the high sample absorbance (i.e., low transmitted light intensity) and the absence of filtering in order to obtain these noise levels. The polarization of light at time  $t$  is given<sup>21</sup> by  $\bar{\Pi}(1.018t + 2 \times 10^{-6})$  and a retardation amplitude  $\delta = 0.95\pi$ . The theoretical curve is the dashed line, also at  $\delta = 0.95\pi$ .

also applies if more than one “layer” of sample intrudes on the light path. That is, as long as the polarization caused by transit of the whole system is small, the transmitted light intensity is given by the product

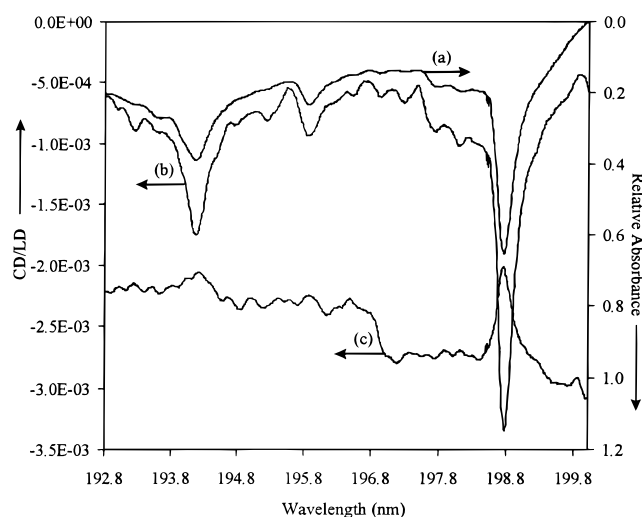
$$I_{\text{avg-total}}(t) = I_{\text{avg-1}}(t) \times I_{\text{avg-2}}(t) \times \dots \times I_{\text{avg-n}}(t)$$

where each term  $I$  on the right-hand side is given by eq II.44. When this product is evaluated, retaining only first-order terms, a three parameter expression identical to eq II.44 results:  $K_{1\text{-total}}$  becomes a product of the individual  $K_1$ 's, whereas  $K_{\text{LD-total}}$  and  $K_{\text{CD-total}}$  become sums of the individual LD and CD contributions, respectively. An example of such a multiple-layer case is a two-window absorption cell containing an isotropic sample that deposits an adsorbed layer on each window. The entire system, in this instance, consists of the three layers, film–gas–film, through which light must pass on its way to the detector.

### III. COMPARISON WITH EXPERIMENT

The experimental average time-resolved profile of gaseous (+)-3-methylcyclopentanone shown in Figure 1 does not match the theoretical cycle of  $I_{\text{avg}}(t)$  shown in Figure 2, as computed from eq II.37 for an isotropic sample. However, it does exhibit a close similarity to two of the profiles shown in Figure 3, suggesting that an LD-like component is present in the profile. The excellent agreement between the experimental average time-resolved profile of Figure 1, now unsmoothed, and the theoretical profile obtained from eqs I.2 and II.44, both shown in Figure 5, provides further support for that assumption.

If fitting is extended to all average time-resolved profiles, one for each wavelength, one generates three spectra, one corresponding to absorption, one corresponding to the CD-like component, and one corresponding to the LD-like component of eq II.44. These spectra are shown in Figure 6. Comparison of the absorption and CD spectra with those already available<sup>22</sup> validates the use of two of the parameters of eq II.44. A more complicated procedure<sup>23</sup> can be used to show that the third parameter represents an LD component. When combined, these measurements indicate the validity of the 3-parameter fit function, and the ability to extract not only linear and circular dichroisms from the experimental profile but also the absorptivity and the elliptical dichroisms. Consequently, since the polarizations contained in the



**Figure 6.** Absorbance, CD-like, and LD-like spectra of (+)-3-methylcyclopentanone in the range 192.8–200 nm. All three spectra were recorded in a single scan. The absorbance spectrum is shown in a. Note that the left and right axes have inverted scales. The CD and potential LD are shown in b and c, respectively. The experimental parameters are available in Vrancic et al.<sup>1</sup> Horizontal arrows denote the scales, left or right, to which the individual curves should be referred.

average time-resolved profiles are effectively continuous, it follows that a complete three-dimensional spectrum, one in which the absorbance is diagrammed as a function of both wavelength and polarization, can be generated. Such a spectrum, the first of its kind, is available in Vrancic et al.<sup>1</sup>

Figure 6, curve c, contains one other very interesting feature. A left-to-right steadily decreasing component of magnitude  $\sim 3 \times 10^{-3}$  is present in the measurement; it can be attributed to the effects of the optical train. However, the two peaks at  $\sim 194$  and  $\sim 198$  nm are present only when (+)-3-methylcyclopentanone is introduced into the cell. Since various tests indicate that this latter signal is not due to instrumental artifact, it may well be a true linear dichroism associated with partially oriented window adsorbants. Experimental validation of this supposition is warranted because, if the observed curve is indeed an LD, it may well provide appropriate ingress to studies of molecular orientation in thin films and membranes.

### IV. CONCLUSIONS

An expression, eq II.40, has been derived for the average time-resolved polarization profile exhibited by (a) a thin film, (b) a weakly absorbing sample, and (c) a strongly absorbing sample that is characterized by weak circular and linear dichroism. Equation II.40 is valid regardless of whether the sample is fully oriented, partially oriented, or fully isotropic. The fit function of eq II.44 can be used in all nine cases to extract absorbance, CD, and LD from the experimental profile. The only difference between the nine cases is that certain constants in the fit function will be found to zero or near-zero (e.g., for the fully isotropic case, the LD will be zero). The general, macroscopic case of a fully isotropic material is described exactly by eq II.32. This equation reduces to eq II.40,  $B_f$  being purely imaginary, when the approximations of eq II.34, ones generally applicable in all the experimental situations discussed here, are used. Thus, eqs II.40 and II.44 apply generally to the experimental profiles generated in this work.



The three-parameter fit function has been used to model the experimental profile of gaseous (+)-3-methylcyclopentanone, and the mode of extraction of absorbance, CD, and a potential LD has been demonstrated. A direct consequence of the least-squares fitting procedure is an increase of the S/N ratio, a matter of some significance when dealing with weak signals heavily embedded in noise. Extraction of parametric fits for different wavelengths leads to spectra for absorbance, CD, and LD which are all of identical quality. Comparisons of these spectra do not suffer from the lack of fidelity that characterizes the corresponding spectra obtained from three separate experiments.

The dichroic spectra of a presumptively isotropic gaseous sample, which should not exhibit LD, have been shown to contain a linear dichroic component. This component has been shown to consist of at least two parts: a smooth background of instrumental origins and a structured component which may be attributable to fully or partially oriented thin films of gaseous molecules that were adsorbed onto the window materials. These findings point to the power of the new technology and the associated analysis regimen: they represent new observations that are consequences of a new and different approach to such measurements, and they had not been observed previously.

A semiclassical treatment of the introduction of polarized light with matter leads to a derivation of the Jones representation of these interactions. The eight macroscopic Jones parameters are phrased in terms of four microscopic (i.e., molecular) terms that are functions of transition moments (see eq II.21). We have not found such a treatment anywhere else.

## REFERENCES AND NOTES

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- (2) Detailed discussions of modulated polarization spectroscopy are available in refs 5 and 9 of this text.
- (3) Dichroism is defined as a difference between the absorbance of two orthogonal polarizations. For example, circular dichroism (CD) is the difference of absorbance of left and right circularly polarized lights. Linear dichroism (LD), on the other hand, is the difference of absorbance of two perpendicular linearly polarized lights.
- (4) The terms "light" and "radiation" will be used interchangeably in this work.
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- (12) Jones identified eight parameters, all of which are not independent. Indeed, the corresponding real and imaginary parts are related by a Kramers–Kronig (KK) relation (ref 7). However, while only four parameters are independent, all eight parameters are retained because it is easier to measure all eight than to measure only four and then use the KK relations to find the remainder!
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- (14) Hurwitz, H.; Jones, R. C. *J. Opt. Soc. Am.* **1941**, *31*, 493.
- (15) The mnemonic notation of Jensen (ref 11) is given in parentheses (e.g., PR for phase retardation, etc.). The symbol  $\delta$ , as originally used by Jones, bears no relation to the symbol  $\delta$  of eq I.1. Indeed, this symbol and  $\omega$  are used in the remainder of this text to represent quite different entities.
- (16) Bernath, P. F. *Spectra of Atoms and Molecules*; Oxford University: New York, 1995.
- (17) Sakurai, J. J. *Modern Quantum Mechanics*; Addison-Wesley: New York, 1985.
- (18) All two-dimensional complex vectors can be described as a superposition of two complex two-dimensional, noncollinear vectors that constitute a basis set.
- (19) Since the electric vector is two-dimensional, a  $2 \times 2$  complex matrix can describe its interaction with matter. If this matrix can be written as a linear combination of Hermitian and identity matrixes, it will have two orthogonal eigenvectors and light with polarization identical to one of the eigenvectors will exhibit only absorption (i.e., no polarization change). It will be shown that this supposition holds only when all active transitions have identical wavelength-dependent profiles,  $g_f(\omega)$ .
- (20) To emphasize this "smallness", sample thickness will be denoted  $\Delta z$  even though the sample need not be thin.
- (21) The equation for polarization as a function of  $t$ , namely,  $\bar{\Pi}(1.018t + 2 \times 10^{-6})$ , is determined by the apparatus. The factor 1.018 arises because PEM modulation was 1.8% faster than the averaging frequency of the SDI. This frequency mismatch combined with the instrumental averaging procedure also produces a small phase shift of  $2 \times 10^{-6}$ . For example,  $I_{\text{avg}}(\bar{\Pi}(t))$  at  $t = 5 \mu\text{s}$  actually represents the absorbance of the polarization that exists at  $t = 1.018 \times 5 + 2 \mu\text{s}$ . The origins of the frequency mismatch and phase shift (and their use for gauging the small changes of the PEM frequency,  $\sim 2\%$ , produced by the alterations of retardation voltage required at different wavelengths of light) are discussed elsewhere.<sup>8</sup>
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