The Selective Digital Integrator: A New Device for Modulated Polarization Spectroscopy.

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THE SELECTIVE DIGITAL INTEGRATOR - 
A NEW DEVICE FOR MODULATED POLARIZATION SPECTROSCOPY

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Physics and Astronomy

by

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May 1998

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To My Parents
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Figure 5.21  Comparison of model and experiment for both CD and absorbance as influenced by scattering.

Figure 5.22  The depression (i.e., dip) induced by scattering in the 198.7 nm CD peak of (+)-3-methylcyclopentanone. The lower pressure CD is shown in curves (a) and (b): (a) the CD observed at 600±30 mTorr; (b) the CD at ~600 mTorr after correction for scattering. As the pressure is increased to 1050 mTorr, a dip develops in the 198.7 nm peak, as shown in curves (c) and (d): (c) the CD observed at 1050±53 mTorr; (d) the CD for 1110 mTorr computed from that at ~600 mTorr (i.e., from curve (a)). The experimental parameters are given in Table 5-1. The theoretical curves were obtained using Eq. 5.33.
Figure 5.23 The depression induced by scattering in the 198.7 nm CD peak of (+)-3-methylcyclopentanone at intermediate pressures. The lower pressure CD observed at 600±30 mTorr is shown in curve (a). As the pressure is increased to 800 mTorr, a dip develops in the 198.7 nm peak, as shown in curves (b) and (c): (b) the CD observed at 800±45 mTorr; (c) the CD for 800 mTorr as calculated from that at ~600 mTorr (i.e., from curve (a)). The experimental parameters are given in Table 5-1. The theoretical curves were calculated using Eq. 5.33.
ABSTRACT

A new device, a selective digital integrator (SDI), for the acquisition of modulated polarization spectroscopy (MPS) signals is described. Special attention is given to the accurate measurement of very small (AC component of interest < $10^{-3}$ x DC component), rapidly modulated (~50 kHz) signals at or below noise levels. Various data acquisition methods and problems associated with the collection of modulated signals are discussed. The SDI solves most of these problems and has the following advantages: it provides the average-time resolved profile of a modulated signal; it eliminates errors if the modulation is not sinusoidal; it enables separate measurements of the various phases of the signal modulation cycle; it permits simultaneous measurement of absorption, circular dichroism (CD) and linear dichroism (LD) spectra; it facilitates 3-D absorbance measurements; it has a wide gain-switching-free dynamic range (10 orders of magnitude or more); it offers a constant S/N ratio mode of operation; it eliminates the need for photomultiplier voltage feedback, and it has faster scanning speeds. The time-resolution, selectivity, wide dynamic range, and low-overhead on-the-fly data processing are useful for other modulated spectroscopy (MS) and non-MS experiments such as pulse height distribution and time-resolved pulse counting measurements.

The advantages of the MPS-SDI method are tested on the first Rydberg electronic transitions of (+)-3-methylcyclopentanone. The experimental results validate the predicted SDI capabilities. However, they also point to two difficulties that had not been noted previously: the presence of LD in a gaseous sample and a pressure-dependence of the relative peak heights of the CD spectrum. Models for these anomalies are proposed. The presence of the oscillatory LD (but not an LD background) is explained with a sample cell model based on the observed polarization-dependent time-resolved profiles of transmitted light intensity. To obtain expressions for these intensities, a theoretical background, which provides a new approach to
the treatment of light/matter interaction, is included as an Appendix. To explain the second anomaly, present only at high optical densities, a model based on the presence of scattered light is introduced and verified. The mode of correction for the scattering problem is outlined.
1. INTRODUCTION

The phrase “Modulated Polarization Spectroscopy (MPS)” denotes the set of all experimental techniques that use periodically alternating light polarization to probe the structure of matter. As the name suggests, these experimental techniques form the intersection of the Modulated Spectroscopy (MS) and Polarization Spectroscopy (PS) sets. As such, they inherit the benefits associated with both spectroscopic approaches. In MS, modulation is imposed on a signal in order to use a lock-in data acquisition technique to improve S/N ratios [1, 2]. The benefit of PS, on the other hand, is that it can provide information about light/matter interactions that are heavily influenced by molecular structures [3] and are not otherwise available. Indeed, PS has evolved into a method of choice in areas such as structural molecular biology and biochemistry [4] (protein structures and folding dynamics), molecular electronic structure [3] (natural and field-induced chirality), and materials science [2, 5] (surfaces, molecular layers, magnetic and optical processing) and, in the last decade or so, it has expanded into the IR [2, 3, 6] and the soft X-ray synchrotron regions [7].

Unfortunately, all the problems are also inheritable. The measurement of a modulated signal becomes more complicated as modulation becomes faster, say 50 kHz, and the duration of the experiment becomes longer, say hours. Complications arise because of the extensive data load that must not be allowed to impose a crippling overhead (i.e., time spent on data processing must not be allowed to restrict the time spent on data collection). On the PS side, the controllable production of elliptically and circularly polarized light over a broad-wavelength range is limited to a few devices [7, 8], each with its own drawbacks. Once polarized, the light may be depolarized or its polarization altered while passing through, or reflecting off various elements in the optical path; the strength of light/matter interactions may vary as a function of
the light polarization; and the absorptivity difference for linear polarizations can be orders of magnitude larger than those for circular polarizations, which causes problems if the two are mixed [3]. Consequently, good execution of an MPS experiment may be difficult.

This work concerns an MPS experiment, circular dichroism\(^1\) (CD), in which the difference of absorption of left circularly polarized (LCP) and right circularly polarized (RCP) light must be measured. When performed in the UV and VUV [9, 10], it is afflicted with problems specific to both MS and PS. Circularly polarized light in this range is generated by a photo-elastic modulator (PEM), no other broad wavelength-range alternative being available. Unfortunately, in addition to LCP and RCP light, the PEM also produces elliptical and linear polarizations [3, 8, 11] which may "pollute" the measurement of CD. The polarization modulation frequency is limited to ~50 kHz, the natural frequency of the CaF\(_2\) crystal used in the PEM, which is fast enough to introduce data acquisition problems. The difference of detector output currents for the LCP and RCP components may be less than \(10^{-3}\) times their average value and CD, as a result, is very noise prone. Finally, there is a light-source/detector problem. The production of a broad range CD spectrum requires an appropriate broad range radiation source. Dye lasers satisfy this requirement, at least partially, but are expensive and hard to work with. Synchrotron radiation is also a limited (availability) option. In general, widely-available laboratory lamps are the simplest solution. Unfortunately, the light levels that such lamps produce are low compared to lasers and synchrotrons. Consequently, sensitive detectors, such as photo-multiplier tubes (PMT) [12], must be used. In addition, the low light

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\(^1\) Magnetic circular dichroism (MCD), a magnetic field-induced CD, is a variant of CD. All materials exhibit MCD but only chiral samples exhibit CD.
levels require longer experimental times and/or wider monochromator slits that lead to lower resolution.

The difficulties involved in the production of appropriate light frequencies, polarizations, and intensities carry over into data acquisition. The extraction of small, fast-modulation signals at or below noise level requires compromise: data acquisition (DAQ) methods based on the lock-in amplifier\(^2\), for example, may have to be tolerant of approximate results and/or a loss of useful information. Indeed, the lock-in amplifier, which should measure the difference of LCP and RCP absorptivities, does not do so if the signal is non-sinusoidal. Furthermore, a lock-in amplifier requires PMT voltage feedback for optimum performance and this, unfortunately, eliminates the ability to obtain absorption spectra. Some methods use two PMT's to avoid this loss [13]. However, absorption spectra obtained in this way are of low quality because of the non-linear relationship between PMT input voltage and output current, and differences of the response functions of the two detectors. Consequently, while the absorptivities generated in this way may be "informative," they may not be used to extract any additional information from the CD spectrum.

Recent attempts to interpret the MPS MCD of some molecular Rydberg transitions obtained with a lock-in amplifier DAQ system indicated [14]:

(i) A need for new polarization-selective MPS methods in which simultaneous and selective intensity measurements are performed for a variety of polarizations (e.g., linearly polarized (LP), left circularly polarized (LCP), right circularly polarized (RCP)) in a single run during which the experimental conditions remain invariant.

(ii) The need to use a single detector in order to minimize noise.

\(^2\) The lock-in amplifier is the data acquisition device most often used in CD experiments.
To satisfy these requirements, a new MS device, the "Selective Digital Integrator (SDI)," was developed. The term "Selective" describes a device capability to select and measure signal strengths of specific phases in the modulation cycle, something not previously feasible. As a result, the problems associated with non-sinusoidal signals vanish. The term "Digital" denotes utilization of a digital representation of the input signal. The advantage of digitization is that many problems, errors, or limitations imposed on further signal processing are largely eliminated\(^3\). However, digitizing also has drawbacks: digitized data is merely a representation of the input signal that is discrete in both time and amplitude. Consequently, there are tradeoffs between the analog and digital approaches. As shown later, these tradeoffs lean toward the digital approach in the MS-PMT modality, which is why it was adopted here. The PMT voltage feedback loop and the consequent inability to measure absorption spectra is also eliminated by a digital approach. The term "Integrator" is self-explanatory: since the signal intensity will usually oscillate around some average value, the value that is the actual measurement goal, signal averaging is required and is achieved by on-the-fly numerical integration of the digitized signal. This approach provides the low data-processing overhead essential for MPS experiments of long duration.

The main goals of this work are:

(i) To review current MS and MPS DAQ methods in order to demonstrate the need for an SDI capability;

(ii) To describe both the hardware and the software solutions that are essential to SDI operation;

\(^3\) In the analog mode, the resistances, capacitances, etc., may change with time and temperature, non-linear effects are present, signals are susceptible to noise, and voltage and current limits on electronic components can cause saturation problems, etc.
(iii) To verify SDI capabilities by experiment;
(iv) To provide theoretical models that validate the experimental results.

It will be shown that there is total congruence of predicted and experimental SDI capabilities. As a result, new types of experiment may be performed and new types of data can be collected. However, as with any new experimental capability, these new types of data (or even more accurate versions of older data) can pinpoint difficulties that had not been noted previously. Two such conundrums appear in this work. One is the presence of linear dichroism (LD) in a gaseous sample. Such an LD signal had not been observed previously, either because it was not expected or because the experimental sensitivity was inadequate for detecting the weak signals. The other effect is a pressure-dependence of relative peak heights of a CD spectrum observed at the high optical densities required for a test of the high-dynamic range of the SDI. This anomaly was not observed previously, presumably because other workers were unable to track optical densities large enough for the effect to become significant. In any event, since no comparable data are available, one must resort to theoretical modeling in an attempt to explain the observations and to eliminate the possibility of instrumental error (i.e., SDI misbehavior). This theoretical analysis is included in the text because it appears to be both original and significant. A literature search reveals no similar treatment of polarized-light/matter interactions: it uses Kramers-Kronig transforms [3, 15] to reduce the number of theoretical parameters from eight to four.

The remainder of this text consists of four Chapters and three Appendixes. These are:

- The manner in which modulated signals are generated, with emphasis on the PEM-PMT experimental apparatus, is discussed in Chapter 2. The operation of a PEM is described in detail because of the SDI ability to measure "simultaneously" the absorbancies of light of
different polarizations. Finally, the concepts of average time-resolved profiles and point-by-point averaging are introduced.

- Information extraction from various types of modulated signals using lock-in, (gated) photon-count, (gated) integration, and time-resolved DAQ methods are discussed in Chapter 3, and the need for an SDI capability is demonstrated. Particular attention is paid to the modulated signals that are generated by the experimental apparatus described in Chapter 2.

- A formal description of the SDI is given and the available DAQ modes are discussed in Chapter 4.

- The experimental results that illustrate performance of the SDI are elaborated in the first part of Chapter 5. We have chosen the first Rydberg electronic transitions of the (+)-3-methylcyclopentanone molecule for this evaluation because of their well known optical activity and optical strength [10, 16]. In the second part of Chapter 5, the theoretical background required to vindicate new experimental results is given. Two models, one for absorption in sample cells and one for light scattering are introduced. These latter two models are required in order to interpret the anomalies mentioned previously.

- The derivation of the theoretical expressions for the interaction of polarized light with matter in a special case when all molecules are oriented in the same direction and only one transition is active is given in Appendix A. These expressions are generalized in Chapter 5 for an isotropic samples and partially-oriented thin films.

- A detailed low-level description of the SDI is provided in Appendix B.
2. MODULATED POLARIZATION SPECTROSCOPY

When the entity of concern is the "signal," the elements of any measurement apparatus can be grouped into three, functionally-separate groups (blocks): the signal source, the data acquisition system, and the control modality. The first group contains all elements prior to, and inclusive of detector(s). The second group consists of all instrumentation after the detector(s). The third group is responsible for control and synchronization of the first two groups. The focus of this Chapter is the "source," the entity that generates the modulated signals. The DAQ component, which is responsible for signal collection and information extraction, will be discussed in subsequent chapters. Issues concerning control and synchronization are scattered throughout the text: even though the control elements constitute a distinct and separate group, they can only be described in conjunction with specific elements from the two preceding groups.

A description of the source block for every experimental technique in the MS category would require a number of volumes. Consequently, we will focus on one MS representative, the apparatus of Figure 2.1 that was used for development of the SDI. The generalized block diagram of Figure 2.2, of which the apparatus of Figure 2.1 is a subcase, will be used to show that the specific analysis of this Chapter, and the conclusions based upon it, apply to all MS experiments that generate related signals.

2.1 Experimental Apparatus

The laboratory apparatus is shown in Figure 2.1. The electromagnetic (EM) radiation is produced by a Hinteregger lamp: a discharge in a quartz capillary filled with ~1.2 Torr hydrogen is controlled by a DC power supply that uses feedback to maintain a constant current flow. The lamp is attached to a McPherson\(^4\), Model 225, 1 m normal incidence VUV

\(^4\) 530 Main Street, Acton, MA 01720, (508) 263-7733
Figure 2.1 The experimental apparatus. Double solid lines represent high vacuum boundaries. Dashed lines denote boundaries between functional groups. The two signals processed by the DAQ group are in italics. Arrows on the lines connecting elements of the DAQ and Control Groups and the two signals indicate the flow direction of electronic information.
monochromator, equipped with a 1200 lines/mm grating which provides monochromatic light of wavelength 160 nm and above. For experiments in the visible range, a 600 lines/mm grating is also available. The intensity and resolution (i.e., the wavelength spread) of the "monochromatized light" is controlled by the size of entrance and exit slits. Both slits used in this work of identical size.

The monochromatized light beam is bent and focused using an aluminum mirror of 25 cm focal length, the focal point being located inside the sample cell. Light reflected from the mirror is passed through a Wollaston prism in order to generate linearly polarized light [11, 17]. The prism splits the incident light into horizontally and vertically polarized beams, the spatial angle between them being wavelength dependent. Both beams then transit the PEM which alters their polarization at a ~50 kHz frequency. The extra-ordinary beam is blocked by a mask inserted after the PEM: a mask between the prism and the PEM is not feasible because
of the small exit angle between the two linearly polarized beams. However, by the time the beams transit the PEM, the separation is large enough for masking even when the wavelength dependence of the exit angle is taken into account.

The sample cell is embedded in an 8 T superconducting magnet in order to study magnetic field-induced phenomena. The light transmitted through the sample is collected and converted to current by the PMT. This current is then fed to the DAQ device. In the original apparatus, the DAQ setup consisted of a lock-in amplifier, an analog integrator, PMT voltage feedback electronics, a PEM voltage amplitude control, and an analog divider [9]. All these elements have been replaced by the SDI and a computer, as shown in Figure 2.1. The SDI is responsible for data collection and basic on-the-fly signal processing, whereas the computer stores the collected data on hard disk, performs user-requested post-processing, controls the monochromator wavelength (via a stepper motor) and the PMT voltage, and displays data and experimental parameters in a user-friendly fashion. The PEM power supply is used in a local mode (a knob on the chassis) or remote mode (computer via digital-to-analog converter) to control the pressure applied to the PEM crystal. The power supply also provides the synchronization signal used by the SDI.

Experiments in the VUV require all elements in the light path to be in vacuum. In order to minimize the effects of vacuum breach and to permit optical realignment without having to destroy the vacuum in the entire system, the apparatus of Figure 2.1 consists of three parts isolated by MgF windows, each separately evacuable: the monochromator, the metal box containing the optics and the PMT extension-sample cell assembly.

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5 Oxford Instruments - Oxford Magnet Technology, Wharf Road, Eynsham, Witney, Oxon OX8 1BP, UK, Tel: + 44 (0) 1865 880880
6 The extension minimizes the effects of high magnetic field strength on the PMT.
The main purpose of the apparatus is to measure the polarization dependence of the absorption spectrum. Such measurements can be performed in two different ways. In one approach, the polarization of light is kept constant during a single run. Once the wavelength dependent profile for that polarization is recorded, the polarization is altered, and the scan repeated. Any comparison of these two spectra requires the polarization dependent differences to be larger than those caused by errant changes in the experimental conditions, such as differences of light intensity and/or sample pressure, between the two runs.

If on the other hand, the errant changes are too large, another approach is required: the polarization must be altered during a single run so that measurements for different polarizations are done "simultaneously" and are similarly influenced. Therefore, at each wavelength, the absorption information is collected for different light polarizations. The wavelength is then changed and the whole process repeated. This latter type of experiment, in addition to being representative of the MS group, is also a member of that specific MS subgroup which uses light polarization modulators to perform "modulated polarization spectroscopy." As pointed out in the introduction, the LD and CD are good examples of molecular properties that can be studied with MPS. The former type of experiment in which polarization of light stays constant, however, does not belong in the MPS category and will not be discussed here.

2.2 Other Sources of Signal Modulation

References will be made often to the MPS apparatus of Figure 2.1. However, other types of modulation will be discussed also. These general modulations and the elements that characterize all MS experiments are shown in Figure 2.2. Modulations can be performed at three different locations:

(i) Light polarization may be modulated immediately after the source. For example, the polarization of synchrotron radiation can be modulated with parabolic mirrors or vertically
moving slit because its polarization and handedness changes as one moves across the plane of the ring [15].

(ii) Light intensity may be modulated either immediately after the source or between the monochromator and the sample. For example, if a CW laser is used, choppers may be inserted into the beam path [2].

(iii) Light polarization may be modulated between the monochromator and the sample. The optics of Figure 2.1 are example of such an approach.

(iv) The sample itself may be subjected to various modulations. For example, alternating magnetic and/or electric fields can be applied to the sample, solid samples can be rotated, pressure can be cycled, etc.

In any case, the reflected or transmitted light eventually reaches the detector, usually a PMT or a semiconductor diode, where the photons are converted into current [12]. The signal emanating from the detector is amplified, collected and processed by the DAQ device. The DAQ device itself is merely a component of a DAQ block which also contains computers and/or other entities for additional signal or data processing. In addition, the DAQ block of Figure 2.2 contains all the elements required for control of the experimental parameters (e.g., wavelength and PMT voltage), elements that normally are incorporated into the control group.

The DAQ block requires certain other information in order to collect and process modulated signals. That information, referred to as the “reference signal,” is provided by the elements of the control group that dictate modulation in the source block. These latter elements are known as “modulation control unit(s).” A PEM power supply is a good example of such a unit. In a general experimental arrangement, more than one reference signal might be present. The DAQ block uses these signals to determine initiation of the full or half period modulation (i.e., to provide synchronization). For example, a reference signal from the beam chopper can
be a square wave of voltage \( v_{on} \) when light passes through the chopper slit and \( v_{off} \) when the beam is blocked (i.e., the change from \( v_{off} \) to \( v_{on} \) signals the start of a new period whereas the change \( v_{on} \) to \( v_{off} \) signals the start of the second half-period).

One can conclude, based on the Figure 2.2, that it is irrelevant how the modulated signals have been generated because the only information needed for processing is the reference signal(s) provided by the modulation control unit(s). For example, a lock-in amplifier triggered by a reference signal can be used for detection of modulated signals regardless of their source. Or, the other way around, a single experimental apparatus capable of producing different kinds of modulated signals can be used as a representative of all MS experiments insofar as signal production is considered. Thus, the results of an SDI evaluation based on the apparatus used in this work, and obtained by using only reference and modulated signals, should apply to a broad group of MS experiments.

### 2.3 Photoelastic Modulator

The main element that distinguishes the MPS subgroup of the MS group is the light polarization modulator. And it is also this modulator that is the prime source of MPS difficulties. Linearly polarized light is relatively easy to generate. However, the production of a circularly polarized light with low attenuation and broad frequency range is very difficult. Indeed, only a few solutions exist: a) a PEM, based on the photo-elastic effect occurring when a sinusoidal force of resonant frequency causes controllable changes of light retardation in a crystal [8]; b) a four-mirror polarizer [7], a very recent solution, in which reflection from each of four mirrors, whose relative position can be altered, is used to produce circularly polarized light; and c) selection of light of different polarizations from synchrotron radiation. Unfortunately, none of these solutions is perfect. The PEM's are cheap, they can be used in the IR, VIS and VUV, but they do not produce a time-invariant polarization (for example, pure
LCP and RCP light). Instead, the polarization oscillates at the natural crystal frequency between LCP and RCP, with intermediates that are elliptical and linear. For the CaF₂ crystal used in Figure 2.1, the natural frequency is ~50 kHz. This fast modulation complicates collection of the PEM modulated signals. The four-mirror polarizer, on the other hand, produces light of constant polarization, but it is exceedingly expensive and, at this time, it does not cover the UV, VIS and IR. Finally, the use of an up/down vibratory mirror to select synchrotron radiation with different polarizations has not been perfected, the problem being the change of polarization during reflections in monochromator and directional mirrors.

The main goal of the MPS apparatus shown in Figure 2.1 is measurement of LD and (M)CD, i.e., the difference of absorption of two types of polarized light. Other polarizations generated by the polarizer are usually an unwanted but unavoidable burden. However, the use of an SDI permits the measurement of all different polarizations in one scan and turns the PEM drawback into an advantage. Consequently, a detailed description of the PEM is provided.

Mechanical pressure applied to a PEM crystal alters the linear polarization of the incident light. Stretching or squeezing the crystal produces a phase change of the light polarization component that lies along one of the major optical axes of the crystal. The light is almost completely circularly polarized when the applied force is close to the maximum and minimum values. In the intermediate regions, the light is left or right elliptically polarized. In the region where polarization handedness changes sign, the light is almost completely linearly polarized. In the apparatus of Figure 2.1, linearly polarized light is generated by a Rochon or Wollaston prism [17] positioned before the PEM. To ensure that the polarization components along x- and y-axes, as determined by the optical axes of the crystal, are equal, the coordinate system of the PEM crystal must be rotated 45° with respect to an axis determined by the linear polarization of the incident light. For the analysis that follows, the coordinate system is
determined by the major axes of the crystal and it is the y-component of the polarization vector that is considered to be retarded.

The electric field of an electromagnetic wave traveling in the z-direction and linearly polarized at 45° can be written \[ 15 \]

\[ \vec{E}(z, t) = \frac{E}{\sqrt{2}} (\hat{x} + \hat{y}) \exp \left( i \omega t - k z \right) \]

where \( \hat{x} \) and \( \hat{y} \) are unit vectors in the x- and y-directions, respectively, and \( E \) is the amplitude of the electric field. After the wave passes through the crystal, its electric field vector changes to

\[ \vec{E}(z, t) = \frac{E}{\sqrt{2}} \vec{\Pi}(t) e^{i \omega t - k z} \]

where

\[ \vec{\Pi}(t) = \hat{x} + \hat{y} e^{i \delta \sin(\Omega t)} \]

The wave retardation amplitude \( \delta \) is determined by the amplitude of the sinusoidal pressure applied to the crystal, \( \Omega = 2\pi/T \) is the angular frequency of the modulation (in our case \( 1/T = 50 \) kHz) and \( \vec{\Pi}(t) \) describes the polarization of the light exiting the crystal \[ 3, 8 \]. \( \vec{\Pi}(t) \) is a periodic function with period \( T \)

\[ \vec{\Pi}(t) = \vec{\Pi}(t + nT) \]

\( n \) being an integer and \( T \) a positive, non-zero number. Using

\[ \vec{\Pi}_{RCP} = (\hat{x} + \hat{y}) \]

\[ \vec{\Pi}_{LCP} = (\hat{x} - \hat{y}) \]

for the RCP and LCP polarization vectors, Eq. 2.2 can be decomposed into amplitudes corresponding to RCP and LCP light,
\[ \vec{E}(z,t) = \vec{E}_{RCP}(z,t) + \vec{E}_{LCP}(z,t) \]  

where

\[ \vec{E}_{RCP}(z,t) = \frac{E}{2\sqrt{2}} \left[ 1 - ie^{i\delta \sin(\Omega t)} \right] \vec{\Pi}_{RCP} e^{i(\omega t - k z)} \]

\[ \vec{E}_{LCP}(z,t) = \frac{E}{2\sqrt{2}} \left[ 1 + ie^{i\delta \sin(\Omega t)} \right] \vec{\Pi}_{LCP} e^{i(\omega t - k z)} \]

Since the two polarization vectors are orthogonal

\[ \vec{\Pi}_{LCP} \cdot \vec{\Pi}_{RCP}^* = \vec{\Pi}_{RCP} \cdot \vec{\Pi}_{LCP} = 0 \]

the same must hold for the electric vectors of Eq. 2.7, where the asterisk denotes complex conjugation and the dot a vector inner product. Thus, the corresponding light intensities are

\[ I_{LCP}(t) = \vec{E}_{LCP}^*(z,t) \cdot \vec{E}_{LCP}(z,t) \]

\[ I_{RCP}(t) = \vec{E}_{RCP}^*(z,t) \cdot \vec{E}_{RCP}(z,t) \]

which, after combination with Eq. 2.7, become

\[ I_{LCP}(t) = \frac{E^2}{2} \left( 1 - \sin[\delta \sin(\Omega t)] \right) \]

\[ I_{RCP}(t) = \frac{E^2}{2} \left( 1 + \sin[\delta \sin(\Omega t)] \right) \]

If losses in the polarization crystal are negligible, the total light intensity exiting the PEM, \( I_0 \), is equal to the intensity incident upon the crystal and the following holds

\[ I_0 = I_{LCP}(t) + I_{RCP}(t) = E^2 \]

If polarizer losses are not negligible or if they depend on the state of light polarization, a time-dependent \( I_0 \) must be used. Indeed, since \( I_0 \) may also be wavelength dependent, the situation can become quite complex. Thus, to simplify analysis, the wavelength dependence of all quantities will be dropped henceforth.
Single-period profiles of the RCP component $^7$ for different values of $\delta$ are shown in Figure 2.3 and Figure 2.4. To ensure that both pure LCP and RCP polarized light occur at least once in each period one must choose $\delta \geq \pi/2$. The retardation amplitude is usually adjusted to either $\pi/2$, a CD measurement that yields RCP ($\hat{x} + i\hat{y}$) and LCP ($\hat{x} - i\hat{y}$) light at $t = T/4$ and $3T/4$ respectively, or to $\pi$, an LD measurement that yields linearly polarized light $\hat{x} + i\hat{y}$ at $t = 0$ and $T/2$ and $\hat{x} - i\hat{y}$ at $t = T/4$ and $3T/4$. It will be shown in Chapter 5 that the SDI can measure these two dichroisms simultaneously (i.e., in a single experimental run). Since $\delta$ is wavelength dependent, the amplitude of the applied sine voltage may have to be altered during the experiment, an alteration that can be done locally or remotely.

2.4 The Nature of the Signals

The light next passes through the sample cell where it is absorbed. The absorption of unpolarized light is described by the Beer-Lambert law $^{18}$,

$$I(z) = I_0 10^{-\alpha c L}$$  \hspace{1cm} 2.11

where $I_0$ is the intensity of light entering the sample cell, $\alpha$ is the decadic extinction coefficient of the sample, $c$ is the sample concentration, and $L$ is the sample cell length. Therefore, if the light intensity emanating from the sample cell, $I$, is measured, the absorbance is

$$A = \alpha c L = -\log \frac{I}{I_0}$$  \hspace{1cm} 2.12

The value of $I_0$ is usually measured when the sample cell is completely evacuated.

Unfortunately, the interaction of polarized light with matter is not quite so simple, the main problem being a breakdown of the Beer-Lambert law$^8$ [3]. More precisely, this law is

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* The corresponding values of $I_{LCP}(t)$ can be calculated as $I_0 - I_{RCP}(t)$.

* More about polarized light/matter interaction can be found in Chapter 5 and Appendix A.
Figure 2.3 The RCP intensity, Eq. 2.9, for four different values of the retardation amplitude $\delta$, $\delta \leq \pi/2$: $0.1$ (dotted line), $0.5$ (short-dash line), $1$ (long-dash line), and $\pi/2$ (dash-dot-dash line). Intensity is shown relative to the total light intensity exiting the PEM, $I(t)$. A sinusoid (solid line) is shown for comparison.

Figure 2.4 The RCP intensity, Eq. 2.9, for three different values of the retardation amplitude $\delta$, $\delta > \pi/2$: $2$ (dotted line), $2.5$ (dashed line), and $\pi$ (dash-dot-dash line). Intensity is shown relative to the total light intensity exiting the PEM, $I(t)$. A sinusoid (solid line) is shown for comparison.

When periodic signals are shown, the time unit will always be chosen so that the angular frequency of the signal, for example $\Omega$ in Eq. 2.3, is unity (i.e., $T = 2\pi$).
valid only for two particular polarizations, the "characteristic polarizations," which are functions of both the sample orientation and the transition probabilities. Light of characteristic polarization suffers no polarization change upon passage through the sample, whether chiral or not: the propagating radiation merely exhibits absorption and phase shifting. If the sample is isotropic (i.e., the molecules are randomly oriented in space), the two characteristic polarizations are LCP and RCP. Since these are also orthogonal, the power loss and polarization change for an arbitrary polarized light impinging on the sample cell can be determined by

(i) separation of the incident light into LCP and RCP components;

(ii) passage of the two individual components through the sample cell, each being absorbed according to Eq. 2.11, but with different extinction coefficients; and

(iii) addition of both components at the sample cell exit.

The extinction coefficients, obtained as above (Eq. 2.12), for non-characteristic polarizations will be functions of the sample cell length. As such, they will be different from the coefficients defined by the quantum-mechanical treatment of light/matter interaction as functions of transition matrix elements. This difference must be taken into account whenever a quantitative analysis of the experimental results is required.

The transmitted intensity, I(t), is now a function of time because absorptivity is a function of light polarization. One obtains I(t) by combining Eq's. 2.10 and 2.11 as

\[ I(t) = I_{LCP}(t)10^{-\epsilon_{LCP}cl} + I_{RCP}(t)10^{-\epsilon_{RCP}cl} \]

where \( \epsilon_{LCP} \) and \( \epsilon_{RCP} \) are the LCP and RCP extinction coefficients, respectively, and \( I_{LCP}(t) \) and \( I_{RCP}(t) \) are given by Eq. 2.9. Some I(t) curves are shown in Figure 2.5 for different values of \( \epsilon_{LCP} \) and \( \epsilon_{RCP} \).
Figure 2.5 $I(t)$ obtained when left and right circular polarizations are characteristic components, Eq. 2.13. $I_0$ and $c_L$ are both set equal to unity. $I_{LCP}(t)$ and $I_{RCP}(t)$ are defined in Eq. 2.9. The different pairs ($\varepsilon_{LCP}$, $\varepsilon_{RCP}$) are: (0.7, 0.03) dash-dot-dash line, (0.3, 1) dotted line, (1.5, 1.5) horizontal dashed line, and (0.2, 10) solid line.

If the sample is partially-oriented, the two characteristic polarizations are difficult to determine unless the molecular orientations and the exact wavelength dependence of the induced transitions are known in advance. Furthermore, the three-step isotropic-sample procedure for determining the effect of sample absorptivity on arbitrarily polarized light is limited to cases in which the two characteristic polarizations are orthogonal, a condition satisfied only if all operative transitions have the same shape function. If this condition is satisfied, an expression similar to Eq. 2.13 is applicable, but the shape of $I(t)$ may be different from those of Figure 2.5. Sample profiles for one particular pair of characteristic polarizations are shown in Figure 2.6. On the other hand, if the characteristic polarizations are not orthogonal, Eq. 2.13 does not apply and the polarization-dependent profile of $I(t)$ can only be obtained by a solution of a differential equation that is discussed in more detail in Chapter 5 and Appendix A. Again, the measured extinction coefficients must be distinguished from their theoretical counterparts.

The behavior of $I(t)$, based on the last two figures, can be classified into three groups determined by the relative magnitudes of $\varepsilon_{LCP}$, $\varepsilon_{RCP}$, and $\varepsilon_{LP}$. Some representatives of each
such grouping are shown in Figure 2.7, Figure 2.8, and Figure 2.9. Some shape features are exaggerated for clarity, but that does not preclude their observation. In Figure 2.7, cases for which $e_{LCP} = e_{RCP}$ are shown. In Figure 2.8, cases for which $e_{LCP} > e_{RCP}$ are shown. Finally, in Figure 2.9, cases for which $e_{LCP} < e_{RCP}$ are given.

![Figure 2.6](image)

Figure 2.6 $I(t)$ obtained when $\Pi_1 = N_1(1+3i, 2+2i)$ and $\Pi_2 = N_2(1, \alpha)$ are characteristic components. $N_1$, $N_2$, and $\alpha$ are constants that can be calculated from the ortho-normality condition $\Pi_i \cdot \Pi_j^* = \delta_{ij}$, where $\delta_{ij}$ is the Kronecker-delta symbol [19].

The pairs of corresponding extinction coefficients for the characteristic components $(e_1, e_2)$ are: $(0.7, 0.03)$ dash-dot-dash line, $(0.3, 1)$ dotted line, $(1.5, 1.5)$ horizontal dashed line, and $(0.2, 10)$ solid line.

Each signal is characterized by four parameters: (i) the Fourier component of the same frequency and phase (also referred to as the "AC component"); (ii) the average value of the signal (also referred to as the "DC component"); (iii) the value of $I(T/2)$, which corresponds to $\bar{I} = LP$; and (iv) $\Delta AC$, the difference $I(1/4T) - I(3/4T)$. As shown in Figure 2.9, $\Delta AC$ sometimes equals the signal amplitude (curves (b), (c), and (e)) while in other cases it does not. These characteristics of the $I(t)$ profiles will be used throughout the text.

The above conditions for shape classifications are appropriate for a discussion of MPS signals. However, they can also be generalized for the classification of any MS signal by...
replacing $\varepsilon_{\text{RCP}}$ by $I(T/4)$, $\varepsilon_{\text{LCP}}$ by $I(3T/4)$, $\varepsilon_{\text{LP}}$ by $I(0)$ or $I(T/2)$, and exchanging the "<" and ">", relations. For example, $\varepsilon_{\text{LCP}} > \varepsilon_{\text{RCP}}$ may be replaced with $I(3T/4) < I(T/4)$.

![Graphs](image)

Figure 2.7 $I(t)$ for three different cases for which $\varepsilon_{\text{LCP}} = \varepsilon_{\text{RCP}}$. The diagrams are: (a) $\varepsilon_{\text{LCP}} = \varepsilon_{\text{RCP}} > \varepsilon_{\text{LP}}$, (b) $\varepsilon_{\text{LP}} > \varepsilon_{\text{LCP}} = \varepsilon_{\text{RCP}}$, (c) $\varepsilon_{\text{LCP}} = \varepsilon_{\text{LP}} = \varepsilon_{\text{RCP}}$. The $I(t)$ profiles are shown as solid lines, the corresponding Fourier components with frequency $f = 1/T$ as dash-dot-dash lines, the values of DC components as horizontal dotted lines, and the values of $I(\pi)$ (i.e., $\varepsilon_{\text{LP}}$) as horizontal dashed lines. The amplitudes of the Fourier components in (b) and (c) are -0.258 and 0.342, respectively. In (c), the DC component is equal to $I(\pi)$. The value of $\Delta AC$ is 0 in all three cases.
Figure 2.8  $I(t)$ for five different cases for which $\varepsilon_{\text{LCP}} > \varepsilon_{\text{RCP}}$. The diagrams are: (a) $\varepsilon_{\text{LCP}} > \varepsilon_{\text{RCP}} > \varepsilon_{\text{LP}}$, (b) $\varepsilon_{\text{LCP}} > \varepsilon_{\text{RCP}} = \varepsilon_{\text{LP}}$, (c) $\varepsilon_{\text{LCP}} > \varepsilon_{\text{LP}} > \varepsilon_{\text{RCP}}$, (d) $\varepsilon_{\text{LP}} > \varepsilon_{\text{LCP}} > \varepsilon_{\text{RCP}}$, and (e) $\varepsilon_{\text{LP}} = \varepsilon_{\text{LCP}} > \varepsilon_{\text{RCP}}$. The $I(t)$ profiles are shown as solid lines, the corresponding Fourier components with frequency $f = 1/T$ as dash-dot-dash lines, the values of DC components as horizontal dotted lines, and the values of $I(\pi)$ (i.e., $\varepsilon_{\text{LP}}$) as dashed lines. The value of $|\Delta AC|$ equals 1 and the amplitude of the Fourier component equals 0.342 in all five cases.
Figure 2.9 I(t) for five different cases for which $\varepsilon_{RCP} > \varepsilon_{LCP}$. The diagrams are: (a) $\varepsilon_{RCP} > \varepsilon_{LCP} > \varepsilon_{LP}$, (b) $\varepsilon_{RCP} > \varepsilon_{LCP} = \varepsilon_{LP}$, (c) $\varepsilon_{RCP} > \varepsilon_{LP} > \varepsilon_{LCP}$, (d) $\varepsilon_{LP} > \varepsilon_{RCP} > \varepsilon_{LCP}$, and (e) $\varepsilon_{LP} = \varepsilon_{RCP} > \varepsilon_{LCP}$. The I(t) profiles are shown as solid lines, the corresponding Fourier components with frequency $f = 1/T$ as dash-dot-dash lines, the values of DC components as horizontal dotted lines, and the values of I($\pi$) (i.e., $\varepsilon_{LP}$) as dashed lines. The value of $|\Delta AC|$ is 1 in all five cases. The amplitudes of the Fourier components are -0.41, -0.3, -0.38, -0.19, and -0.49 for the curves shown in (a), (b), (c), (d), and (e), respectively.
2.5 Modulated Signals and Noise

When the unabsorbed light hits a detector, photons are converted into current, $i(t)$. If the detector is operating in the linear regime, the $i(t)$ shapes will be identical to the $I(t)$ shapes and, for purposes of qualitative analysis, they are interchangeable.

Since both $I(t)$ and $i(t)$ are functions of $\ddot{I}(t)$, they have been treated as ideal periodic functions that satisfy equation 2.4. As such, a graphical representation over one period is complete. For example, it is evident that the curves of Figure 2.3 and Figure 2.4 are complete representations of Eq. 2.9. If noise is present, a periodic signal is inappropriate because $i(t)$ and $i(t+nT)$ may not be identical. However, they will oscillate around some average value and, as a result, $i(t)$ can be represented by $i_{avg}(t)$, where $i_{avg}(t)$ is referred to as a "(modulation-period) average time-resolved profile." The average profile, $i_{avg}(t)$, can be obtained as a point-by-point integration of $N$ consecutive periods of $i(t)$, a procedure demonstrated in Figure 2.10 and described by

$$i_{avg}(t) = \frac{1}{N} \sum_{n=0}^{N-1} i(t + nT) \quad 2.14$$

where $T$ is the period and $0 \leq t < T$. The phrase "time-resolved" signifies that values of $i_{avg}(t)$ are known at different times within the period.

In summary, then, the signal collected and processed by the DAQ device of Figure 2.1 may be characterized by the following statements:

(i) It is a periodic current signal whose period is determined by the natural frequency of the PEM crystal;

(ii) Its average profile can have different shapes that depend on the sample and on the relative values of the extinction coefficients corresponding to different light polarizations; and
Average value around which \( i(t) \) oscillates or exact \( i_{avg}(t) \)

Noisy "periodic" signal \( i(t) \)

DC component

Points ..., \( i(0.9+(N-1)T) \), \( i(0.9+NT) \), \( i(0.9+(N+1)T) \), ... added together to obtain \( i_{avg}(0.9) \)

Figure 2.10 (a) An illustration of modulation-cycle time-resolved averaging as a point-by-point integration of subsequent periods of a signal mathematically described by Eq. 2.14 with \( T = 2\pi \) seconds. The \( i(t) \) curve has been artificially created as a superposition of a sinusoid, referred to as the exact \( i_{avg}(t) \), and a few randomly chosen sinusoidal noise components. (b) The error in \( i_{avg}(t) \) relative to the exact \( i_{avg}(t) \) when point-by-point averaging is carried out over 2 (dotted line), 4 (solid line), and 16 (dashed line) periods. The exact \( i_{avg}(t) \) that is obtained if averaging is carried out over an infinite number of periods is shown in (a).

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(iii) If light choppers or other modulators are used, very different types of \( i(t) \) profiles will occur.

The problems associated with the extraction of information from these signals are discussed in the next Chapter.
3. SIGNAL ANALYSIS - INFORMATION EXTRACTION

It was concluded in the previous Chapter that the time-resolved profile of the average PMT current depends on both the sample and the experimental apparatus. Furthermore, depending on the relationship between extinction coefficients for LCP, RCP and LP light, these current profiles were classified into three groups, a dozen representatives of which were selected and shown in Figure 2.7, Figure 2.8, and Figure 2.9. The main goal of this Chapter is to discuss the information contained in these profiles and how to extract it. The problem will be approached in steps. The extraction of a difference of two points on an average profile by the lock-in method will be illustrated first. In the process, a short description of the lock-in amplifier will be given and the drawbacks of the technique will be discussed. The decomposition problem will be emphasized and alternative DAQ methods, namely gated photon count and gated integration, will be explored. The ideas behind “windowing” and “time-resolved” techniques will be discussed. And, finally, the SDI will be introduced as a solution to the problems that have been identified.

However, prior to any discussion of signal processing, a review of analog to digital conversion and related language will be given because digitization plays an important role in the data acquisition improvements discussed in this work.

3.1 Analog to Digital Conversion

The main purpose of ADC is to convert an analog signal expressed in volts at input into an integer number at output [20]. The conversion is performed through a many-to-one mapping in which an interval of input values, referred to as the y-interval, is mapped onto a corresponding integer, as shown in Figure 3.1. A sequence of such integers, each referred to as a “sample,” can then be used as a representation of the signal. The time interval that elapses between two consecutive samples is the “conversion time,” and the inverse of the conversion...
Figure 3.1 The principle of ADC conversion.
(a) A one-to-one mapping of intervals of input values onto integer numbers. All input values below the sum "lower limit of the range" + "half the size of the y-interval" are converted into $n_{\text{min}}$. All input values above the sum "upper limit of the range" - "half the size of the y-interval" are converted into $n_{\text{max}}$.
(b) The effects of ADC resolution and sampling rate on the representation of a continuous analog input signal. Vertical lines represent the digital equivalents (samples) of the input signal for the following ADC's (bits range \ sampling-rate): 3-bit | [0.0,0.7] V | 1 MHz (thin solid line), 4-bit | [0.0,0.75] V | 1 MHz (thick solid line), 5-bit | [0.1,1.55] V | 2 MHz (dashed line). A missing thick solid line (e.g., at $t = 3 \mu s$) has height equal to that of the corresponding thin solid line. A missing dashed line (e.g., at $t = 1 \mu s$) has height equal to that of the corresponding thick solid line. Triplets of numbers on the right side of the graph denote integers to which input signal values shown on the left are converted for 3, 4, and 5-bit converters, respectively.
(c) The envelopes of the digital representation of the actual signal for each converter from (b). The envelopes are shown using the same pattern as for the corresponding ADC samples in (b). Dashed and solid-line envelopes are arbitrarily shifted for better discrimination. The quality of the envelope increases as the ADC resolution and sampling rate are increased.
time is referred to as the "sampling or conversion rate." For example, a conversion time of 1 ms implies a sampling/conversion rate of 1 kHz. The range of a converter, as shown in Figure 3.1, is a pair of voltages which are half the size of the y-interval below and above these voltage values for which the converter will register extreme values at output. Namely, if the input signal is below the lower voltage, the "lower limit of the range," the converter will output 0; if the input signal is above the higher voltage, the "upper limit of the range," the converter will output the maximum value\(^\text{10}\). The maximum number of different converter output values is a function of the number of bits (digits of a binary number) that are used to describe the input. This number of bits is usually taken as a measure of ADC resolution. For example, for an n-bit ADC with \([0,1]\) V range, all values of the input signal below \(1/(2^{n-1}-2)\) V are converted to 0, while all values above \((2^{n-1}-3)/(2^{n-1}-2)\) V are converted to \(2^n-1\). The input range is divided into \(2^n\) y-intervals, \(2^n-2\) of them being \(1/(2^n-1)\) V in size. The other two intervals cover all values below \(1/(2^{n-1}-2)\) V and above \((2^{n-1}-3)/(2^{n-1}-2)\) V.

The two main parameters involved in the selection of an ADC are its resolution and sampling rate. Consider, for example, the signal of Figure 3.2 which consists of 0.6 V DC and 15 mV AC (or ripple) components. Furthermore, suppose that an 8-bit converter with \([0,1]\) V range is used for digitization. In such a case, only eight integer values are available for a description of the ripple, and much of the substructure information it contains is inevitably lost. This difficulty can be solved by using a converter with better resolution (more bits). However, higher resolution ADC's also have drawbacks: conversion time goes up as the number of bits increases. For example, an 18-bit ADC needs at least 10 ms to perform conversion (i.e., the

---

\(^{10}\) Some converters are designed to output signed numbers. In such cases, the minimum value that can appear on the output will be less than 0.
maximum conversion rate is about 100 kHz [21]. The ultra-fast 6-bit converters, on the other hand, have conversion rates as fast as 1 GHz [22]. Therefore, if conversion must be fast, tradeoffs between speed and resolution must be considered. Finally, complete use of the ADC resolution requires that the input signal cover as much of the converter input range as possible. For example, if a [0,1] V 16-bit converter is used but the input signal never crosses 0.25 V, the effective resolution of the converter drops to 14 bits.

Figure 3.2 Demonstration of the finite resolution problem for ADC converters when the AC component is small. The ADC has 8-bit resolution, [0,1] V range, and 1 MHz sampling rate. A signal with 0.6 V DC component (dashed line) and a small ripple of ~0.015 V amplitude (solid line) is shown in (a). When expanded in (b), it is seen that only 8 different values of the initial batch of 256 values are available to describe the AC component, which leads to loss of information. The amplitude of the signal is shown on the left y-axis and the corresponding conversion scale is shown on the right y-axis.

3.2 Lock-in Amplifier

Suppose that the detector output current, \( i(t) \), consists of the two components shown in Figure 3.3: (i) a periodic part \( i_{\text{signal}}(t) \), in this case a sine wave of frequency \( \omega_s \), phase \( \phi_s \), and amplitude \( A_s \); and (ii) a noise part \( i_{\text{noise}}(t) \) whose average amplitude is larger than \( A_s \). The exact
amplitude, phase and frequency of a noise may not be specified because it is generally composed of many different frequency components (ωa) with (non)random amplitudes and phases. Because the noise is of larger amplitude, the signal is said to be "buried" in the noise. Suppose further that the measurement goal is to find the signal amplitude. Extraction of the two components can be performed per Eq. 3.1,

\[
\begin{align*}
N \int_{t_1}^{t_2} \sin(\omega_s t + \phi_s) i(t) dt &= N \int_{t_1}^{t_2} \sin(\omega_s t + \phi_s) [i_{\text{signal}}(t) + i_{\text{noise}}(t)] dt \\
&= N \int_{t_1}^{t_2} \sin(\omega_s t + \phi_s) [A_s \sin(\omega_s t + \phi_s) + i_{\text{noise}}(t)] dt \\
&= A_s + \Delta_{\text{noise}}
\end{align*}
\]

Figure 3.3 The composition of the modulation and reference signals. Phase shifts are denoted \( \phi \). The frequency of the modulated signal is \( \omega_s \).

\[\text{If the noise component originates in a device which is involved in signal modulation, it can have a fixed (i.e., non-random) amplitude and/or phase.}\]
where $N$ is a normalization constant dependent on the integration boundaries $t_1$ and $t_2$, and $\Delta_{\text{noise}}$ is the amplitude of the noise that has survived integration. The origin of $\Delta_{\text{noise}}$ can be twofold. If the noise contains a component of the same frequency as the sine wave (signal), it will always contribute to the final result except when it is exactly $\pm 90^\circ$ out of phase (see discussion of Eq. 3.3). In such a case, the only hope of extracting the signal from noise exists when

(i) $\sigma_{\text{signal}} > \sigma_{\text{noise}}$, $\sigma$ being the variance (e.g., the changes in $A_s$ with wavelength are larger than those in $\Delta_{\text{noise}}$), or

(ii) $\Delta_{\text{noise}}$ is a systematic error that can be measured in advance.

The second reason for persistence of a finite $\Delta_{\text{noise}}$ is a finite integration time. All noise components for which $\omega_n \neq \omega_s$ are filtered out only if the integral of Eq. 3.1 extends from $-\infty$ to $+\infty$. Otherwise, these frequencies for which $\omega_n - \omega_s$ will contribute according to Eq. 3.2. This contribution is schematized in Figure 3.4.

$$A_n = \frac{2}{NT} \int_0^N \sin(\omega_s t) \sin(\omega_n t) \, dt$$

In an actual experiment, the frequency and phase for extraction of $A_s$, $\omega$, and $\phi_s$ of Eq. 3.1, are supplied by the reference signal. Therefore, the reference signal must originate in a device which has direct control over signal generation\(^1\). However, untoward shifts of phase may occur between the two signals as shown in Figure 3.3. When that happens, the reference phase must be adjusted prior to integration. If phase adjustment is not made, the measured amplitude $A_s$ will depend on the phase difference $\Delta\phi$. Thus, if the difference of integration boundaries $t_1$ and $t_2$ in Eq. 3.3 is close to an integer multiple of the signal period or if the

\(^1\) In the setup of Figure 2.1, this device is the PEM power supply. It controls the pressure applied to the PEM crystal, and thus the modulation frequency and phase of the light polarization.
Integration is carried over many signal periods, $A_s(\Delta \phi)$ is proportional to $\cos(\Delta \phi)$. As a result, even though a strong sinusoidal component may be present, $A_s$ will vanish if no phase adjustments are made and $\Delta \phi$ equals or is close to $\pi/2$ or $-\pi/2$. By the same token, a noise component with frequency $\omega_n$ and out of phase by $\pm90^\circ$ with respect to the signal will not contribute to $A_{\text{noise}}$ of Eq. 3.1.

$$A_s(\Delta \phi) = N \int_{t_1}^{t_2} \sin(\omega_s t + \phi_s) \sin(\omega_s t + \phi_s + \Delta \phi) A_s \, dt$$  \hspace{1cm} 3.3

Measurement of the amplitudes of periodic signals buried in noise is the main task of a lock-in amplifier (LA) \cite{1, 21, 23}. The process of amplitude extraction in either the analog or digital versions of this instrument can be illustrated using Figure 3.5. In the analog LA, the input signal is first passed through a band-pass filter which strips the signal of all but a small band of frequencies centered about $\omega_0$ \cite{21, 23}. This filtering operation is described by Eq. 3.4.

![Figure 3.4](image_url)  

Figure 3.4 Amplitudes of the noise component as a function of integration time (in units of the period $T$). The amplitudes, given by Eq. 3.2, are shown for $N = 100, 500, 1000, 10000$. Positions on the x-axis correspond to a frequency of the noise component $\omega_n = (1+x)\omega_s$, where $\omega_s$ is the frequency of $i_{\text{signal}}(t)$.

---

\footnote{The band-pass and low-pass filters were named according to the shapes of the attenuation vs. frequency profiles shown in Figure 3.5 \cite{20}.}
Figure 3.5 Block diagrams of analog and digital lock-in amplifiers with corresponding band-pass and low-pass filter attenuation diagrams. The reference frequency is denoted \( \omega_0 \). \( H(\omega) \) is the filter transfer function, 1 (unity) corresponding to maximum and 0 (zero) to minimum attenuations.

\[
f_{out}(t) = F^{-1}\left\{F\{f_{in}(t)\}\left[1 - H_{bandpass}(\omega)\right]\right\}
\]

where \( F\{\cdot\} \) denotes a Fourier transformation, \( f_{in} \) is the signal at the filter input, \( H(\omega) \) is the band-pass filter transfer function in the frequency domain, \( F^{-1}\{\cdot\} \) denotes the inverse Fourier transformation, and \( f_{out} \) is the signal at the filter output. In the next stage, the filtered signal is amplified so that the full range of a mixer can be used. The incoming signal is multiplied in the mixer by the reference sine wave before being fed to the output integrator (low-pass filter). The combined effect of the last two stages is the integration of Eq. 3.1. By changing the integrator...
time constant (i.e., by controlling the length of integration), the elimination of noise components with frequencies close to the signal frequency (i.e., those which had not been removed by the band-pass filter) can be improved. For example, in an analog lock-in amplifier, the combination of a band-pass filter and output integrator can eliminate all noise components for which $|\omega_n - \omega_s|/2\pi > 0.01$ Hz [23] when $\omega_s = 10$ kHz.

In the digital LA, a low-pass filter is used instead of a band-pass filter [21]. It filters out higher frequencies in the signal so that aliasing$^{14}$ does not occur during the Fast Fourier Transform (FFT) operation. This filtering operation is also described by Eq. 3.4, $H_{\text{bandpass}}$ being replaced by the low-pass filter transfer function. The amplifier that follows the low-pass filter amplifies the filtered signal to cover as much of the ADC input range as possible. Integration, FFT, or any other signal processing may be performed numerically after the digitization is complete.

Even though the analog and digital LA's approach the problem quite differently, their goal is identical: determination of the amplitude of that Fourier component of the input signal that has the same frequency and phase as the reference signal. The main difference is that one does it in analog fashion, and the other numerically (i.e., by use of a digital representation of the input signal). However, both types depend on the presence of an amplifier. In the analog LA, the amplifier is used to expand the signal at the mixer input in order to reduce errors and noise, and to eliminate the finite range limit problem of the output integrator (as will be discussed in more detail in Section 3.3). In the digital LA, on the other hand, the finite resolution of the ADC must be taken into consideration. Unfortunately, both the amplifier stages of Figure 3.5

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$^{14}$ Aliasing is an effect in which high frequency components appear in the FFT spectra as 'ghost' components of lower frequency [24].
are also a source of problems. To show why, the role of an LA in a CD experiment must be discussed. This discussion is the topic of the next Section.

3.2.1 Information Extraction Using A Lock-in Amplifier

The CD of a sample is defined as a difference of LCP and RCP light absorbances

\[ CD = \frac{1}{2} \left( A_{LCP} - A_{RCP} \right) = \frac{1}{2} cL \left( \varepsilon_{LCP} - \varepsilon_{RCP} \right) \]

The main goal of this Section is to show that the CD of an isotropic sample, when small compared to absorbance, is proportional to the average difference between the two points of the PMT current that correspond to LCP and RCP polarized light, and that such differences can be under certain circumstances measured by incorporating an LA into the experimental apparatus \[9, 10\] of Figure 2.1.

It was shown in the previous Section that the LA extracts the amplitude of one particular Fourier component of the input signal. Consequently, the presence of an LA in the experimental apparatus for CD measurements implies the assumption that the modulated signal is sinusoidal. To satisfy this condition, \( \sin(\delta \sin(\omega t)) \) term of Eq. 2.13 will be replaced temporarily by \( \sin(\omega t) \) in the expressions for \( I_{LCP}(t) \) and \( I_{RCP}(t) \) that now follow. Issues raised by the fact that the signal is not sinusoidal will be addressed later.

If in addition to the sinusoidal shape, a linear relationship between light intensity, \( I(t) \), and PMT output current, \( i(t) \), is assumed, one obtains

\[ i(t) = K_l \frac{I_0}{2} \left[ 10^{-\varepsilon_{LCP}cL} + 10^{-\varepsilon_{RCP}cL} \right] + K_l \frac{I_0}{2} \sin(\omega t) \left[ 10^{-\varepsilon_{RCP}cL} - 10^{-\varepsilon_{LCP}cL} \right] \]

where \( K_l \) is a proportionality constant that relates light intensity to current. This equation may be rewritten as

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\[ i(t) = DC + AC \sin(\omega t) \quad \text{(3.7)} \]

where

\[ DC = K_{li} \frac{l_0}{2} \left[ 10^{-e_{LCP}cL} + 10^{-e_{RCP}cL} \right] \]

and

\[ AC = K_{li} \frac{l_0}{2} \left[ 10^{-e_{RCP}cL} - 10^{-e_{LCP}cL} \right] \]

which, as their names suggest, are the DC and AC components of \( i(t) \), respectively; other frequency components of the noise are ignored because the LA, given enough time, will eliminate them anyway. From this point on, different approaches are needed depending on whether one does or does not use voltage feedback\(^{15}\). When a PMT voltage feedback loop is used, Eq. 3.7 becomes

\[ i_{\text{feedback}}(t) = N i(t) \quad \text{(3.8)} \]

where \( N \) represents feedback control. If \( N \) is chosen to keep the DC component constant\(^{16}\) such that

\[ N(\lambda)DC(\lambda) = K' \quad \text{(3.9)} \]

and if Eq. 3.9 is substituted into Eq. 3.8, one finds

\[ i_{\text{feedback}}(t) = K' \left[ 1 + \frac{AC}{DC} \sin(\omega t) \right] \quad \text{(3.10)} \]

Since the LA extracts the amplitude of the sinusoidal part of the signal, its output is given by

---

\(^{15}\) The purpose of the voltage feedback is discussed in the next Section.

\(^{16}\) In Eq. 3.9, the \( \lambda \)-dependence of the feedback control \( N \) and the DC component of the signal is explicitly stated in order to emphasize that they are functions of wavelength. Thus, in all equations whose \( \lambda \)-dependence is not explicitly stated, independence of \( \lambda \) is inferred. \( N \) may also be used to compensate for changes in \( i(t) \) caused by variations of \( i_0 \). Changes of \( i(t) \) caused by a PEM-induced polarization alternation are too fast for pick-up by feedback circuitry, and need not be considered.
where $K''$ is a constant dependent on the original constant $K'$ and on others, all combined into $K_1$, introduced by the filters and amplifiers of the LA. When no feedback loop is used, the LA operates directly on $i(t)$ of Eq. 3.7 and the output is $K_1AC$. Therefore, to obtain the form of Eq. 3.11, separate devices must be used to measure the DC component and normalize the LA output.

If one now defines

$$\Delta \varepsilon \equiv \varepsilon_{LCP} - \varepsilon_{RCP}$$

Eq. 3.11 can be rewritten as

$$A_{norm} = K'' \frac{1 - 10^{-\Delta \varepsilon L}}{1 + 10^{-\Delta \varepsilon L}}$$

3.12

Since, $10^{-\varepsilon_{LCP}cL} \sim 10^{-\varepsilon_{RCP}cL} \sim 0.1$ and $\Delta \varepsilon < 0.01 \varepsilon_{LCP}$ ($\varepsilon_{RCP}$) are typical, the exponential functions in Eq. 3.12 can be expanded and approximated as

$$A_{norm} = K'' \frac{1 - (1 - 2.303\Delta \varepsilon L)}{1 + (1 - 2.3030\Delta \varepsilon L)} + O(\Delta \varepsilon^2) = K'' \frac{2.303\Delta \varepsilon L}{2 - 2.303\Delta \varepsilon L} + O(\Delta \varepsilon^2)$$

Retention of first order terms yields

$$A_{norm} = K \frac{\Delta \varepsilon L}{2}$$

3.13

where $K = 2.303K''$. Finally, by combining Eq's. 3.5 and 3.13, the CD becomes

$$CD = \frac{A_{norm}}{K}$$

3.14

Therefore, if the value of $K$ is determined by measuring the CD of a standard [10], the LA can be used to measure CD. However, it is important to emphasize that $K$ depends on the gain and
the filter characteristics of the LA as well as on the mode of PMT voltage feedback and that, therefore, it is a constant only for a particular experimental arrangement.

The step from Eq. 3.10 to 3.11 can also be made by measuring either \(i_{\text{feedback}}(t)\) or \(i(t)\) at \(T/4\) and \(3T/4\) such that

\[
2K' \frac{AC}{DC} = i_{\text{feedback}}\left(\frac{T}{4}\right) - i_{\text{feedback}}\left(\frac{3T}{4}\right) \tag{3.15}
\]

or

\[
\frac{AC}{DC} = \frac{i\left(\frac{T}{4}\right) - i\left(\frac{3T}{4}\right)}{i\left(\frac{T}{4}\right) + i\left(\frac{3T}{4}\right)} \tag{3.16}
\]

These expressions, apart from a multiplicative constant, yield the same \(A_{\text{norm}}\), thus validating the assertion that the CD can also be phrased as a difference of \(i(t)\)'s corresponding to LCP and RCP light. Indeed, as will be shown, this approach provides the only means of extracting the CD from a signal that possesses a non-sinusoidal average time-resolved profile.

In the next Section, a discussion about amplifier-related and other lock-in technique problems is continued.

3.2.2 Limitations Imposed by the Lock-in Amplifier

The absorbance of a material is a function of wavelength, as also is the intensity of the light incident on the PMT. If the sample pressure is high, large light intensity oscillations may occur, and the difference between minimum and maximum values of the PMT current can be a few orders of magnitude. For an LA to keep up with such changes without a loss of sensitivity, a gain-switching amplifier must be used. Unfortunately, gain-switching comes equipped with its own set of problems:
(i) The point at which the preamplifier gain must be changed in order to maintain optimal sensitivity may not be precisely defined;

(ii) A gain switch performed at large time constant must be followed by a scan pause for re-stabilization of the lock-in;

(iii) The signal becomes noisier as amplification increases; and

(iv) The proportionality constant K required to calculate the CD from the LA signal may depend on the gain selection.

Unfortunately, changes of signal intensity cannot be avoided and their effects must be minimized by either decreasing the sample pressure to the point where intensity oscillations can be handled without gain changes or using a voltage feedback loop to hold the DC component of the PMT current constant. Both solutions have disadvantages: voltage feedback destroys absorption spectra, whereas lowering the sample pressure reduces the CD quality. The quality of the absorption spectrum is destroyed because PMT voltage feedback flattens the PMT output (Eq. 3.10) and because the relationship between high-voltage applied to the PMT and PMT output current is not linear. The lowering of CD quality follows from Eq’s. 3.13 and 3.14: at higher sample pressure (concentration), both $A_{\text{norm}}$ and CD are stronger, and the signal to noise (S/N) ratio, one of the main factors that influences spectral resolution, is better. Even if one can forego absorption spectra and use the feedback loop to handle high sample pressures, the voltage feedback cannot keep pace with the light intensity changes. There are limits: the feedback compensation range is about one order of magnitude. Thus, feedback can only handle minimum to maximum sample absorbance difference of ~1.

Signal shape can also represent problems for a lock-in. In the above analysis, the shape of the AC part of $i(t)$ was taken to be sinusoidal. In general, that is not true. Indeed, based on Eq’s. 2.9 and 2.14, the AC component is actually proportional to $\sin(\delta \sin(\omega t))$. A chopper
inserted into a laser beam, which yields a signal of the type shown in Figure 3.6, provides another example: if two crystals that provide different polarizations are on the same chopper, the signal might look like one of those shown in Figure 3.7. Finally, an actual average time-resolved profile of \( i(t) \), as measured at one particular wavelength, is shown in Figure 3.8: the signal is both non-sinusoidal and asymmetric with respect to the middle of the period.

![Figure 3.6 Modulated signals for an ON/OFF light chopper (dashed line) or four-mirror polarizer (solid line). The small non-zero signal in the chopper case when the light is OFF is the result of a detector bias such as dark current in the PMT. Units for x- and y-axes are arbitrary.](image)

One must now question whether an LA can be used to measure the difference of two points, for example \( i_{\text{avg}}(T/4) \) and \( i_{\text{avg}}(3T/4) \), for such signals. Based on Eq. 3.17, as derived from equation 3.1 by dropping the noise component and choosing a time reference point so that the reference phase goes to zero, the answer is "no," not unless the signal shape is known in advance. The LA cannot measure such differences exactly because, as the profile departs from sinusoidal, the value of \( A \), the amplitude of the Fourier component in phase with and at the frequency of the reference signal, is merely proportional\(^{17} \) to \( 1/2\Delta AC \), where the constant of proportionality, \( K_{\text{shape}} \), is dependent on the signal shape and is usually different from unity.

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\(^{17}\) The factor of \( 1/2 \) is needed because the LA measures amplitudes, whereas \( \Delta AC \) corresponds to peak-to-peak amplitudes of Fourier components.
\[ \frac{1}{2} \Delta AC = \frac{1}{2} \left[ i_{\text{avg}} \left( \frac{T}{4} \right) - i_{\text{avg}} \left( \frac{3T}{4} \right) \right] \]

\[ = K_{\text{shape}} \Delta A = K_{\text{shape}} \int \sin(\omega t) i_{\text{avg}}(t) dt \]

Figure 3.7 Modulated signals produced by a two crystal chopper. The dashed curve corresponds to an OFF/ON/OFF/ON/OFF case (see the remark regarding the OFF state in Figure 3.6). For the solid line case, the light passes through the chopper even when none of its crystals is in the light path. Units for x- and y-axes are arbitrary.

Figure 3.8 An example of the average time-resolved profile collected at one wavelength using the apparatus of Figure 2.1. Units for x- and y-axes are arbitrary.

An illustration of this shape problem is given in Figure 2.9 where the \( \Delta AC \) values and the corresponding Fourier components measured by the LA are shown for five different profiles. Even though \( \Delta AC = -1 \) is the same for all five signals, the Fourier components are

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very different. The peak-to-peak amplitude of the sine component is largest in (e) where it equals $0.92\Delta AC$ and is weakest in (d) where it has a value of only $0.38\Delta AC$. The proportionality constant $K_{\text{shape}}$, which is inversely proportional to the peak-to-peak amplitude of the Fourier component, is $-1/[0.41*2]$ for case (a), implying that $\Delta AC$ will be obtained by multiplying the LA output by 1.22. More precisely, if the expected signal shape is denoted $i_{\text{form}}(t)$, $K_{\text{shape}}$ can be calculated from Eq. 3.18 as

$$K_{\text{shape}} = \frac{i_{\text{form}}(\frac{T}{4}) - i_{\text{form}}(\frac{3T}{4})}{2\int_0^T \sin(\omega t)i_{\text{form}}(t)dt}$$

whence, one finds $\Delta AC = 2AK_{\text{shape}}$. Combination of Eq.'s 3.11, 3.14, and 3.15, and the definition $K = 2.303K''$, yields

$$CD = \frac{1}{2.303} \frac{\Delta AC}{DC}$$

If the voltage feedback mode has been used, $\Delta AC$ already contains the $1/DC$ term. Otherwise, as previously discussed, a separate instrument will be required in order to measure the DC component.

Finally, when the time difference between two points of interest does not equal $T/2$ (e.g., the difference between the extremes of the signal of Figure 3.9), an amplitude difference cannot be extracted by LA, because a corresponding Fourier component does not exist.

To summarize, when an LA/PMT feedback loop is used, the following disadvantages result: the constant $K$ must be determined using a standard, the absorbance change in any one single scan may not exceed 1, and a good quality absorption spectrum cannot be measured. If a feedback loop is not used, an additional device, one that functions over a broad intensity range, must be employed to measure the DC component of Eq. 3.11. The processes of division and the
adjustments of $K$ attributable to different gains can be handled by a computer. However, $K$ might well require a standard for its determination. Finally, as signals depart from sinusoidal shape, the lock-in amplifier will either extract only approximate information or will fail totally.

![Graph of modulated signal](image)

Figure 3.9 An example of a modulated signal in which the two extremes are not separated by $\Delta t = T/2$. Units for $x$- and $y$-axes are arbitrary.

### 3.3 Decomposition Problem

The focus now is the extraction of the absolute value(s) of one or more points in an averaged signal, the information that might be required in order to measure the CD of a sample for which the average profile is not sinusoidal\(^{18}\) and/or the time difference between the LCP and RCP signals\(^{19}\) is not $T/2$. Another motivation for performing such a measurement is to avoid the decomposition problem that arises in the analysis of CD spectra obtained by a lock-in technique. Suppose, for example, that one wants to get the individual LCP and RCP components in order to extract LCP and RCP transition energies and/or their oscillator strengths. Since decomposition of the CD spectrum via Eq. 3.5 will be inadequate to this task, one is forced to solve the two simultaneous equations.

\(^{18}\) It will be shown later that a partially-oriented sample has a non-sinusoidal average polarization-dependent absorbance profile.

\(^{19}\) When the PEM retardation constant $\delta \geq \pi/2$. 

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\[ CD = \frac{1}{2} (A_{LCP} - A_{RCP}) \]
\[ ABS = \frac{1}{2} (A_{LCP} + A_{RCP}) \]

in order to find \( A_{LCP} \) and \( A_{RCP} \). While mathematically simple, this procedure is difficult in practice because a good solution requires absorption and CD spectra of equal quality. This is not achievable in the lock-in mode:

(i) If voltage feedback is used, the absorption spectra are lost. Collection, indeed, requires a separate scan. However, because of inability to control such experimental conditions as lamp intensity or sample pressure, the spectra collected in consecutive scans rarely match to better than 1%. Such a variance is not tolerable in the present circumstances.

(ii) The simultaneous collection of absorption signals using a separate instrument is equally fruitless because the two outputs will usually vary by more than 1%.

Thus, decomposition requires separate and simultaneous measurement of both the LCP and RCP components. Since the acquisition of such results depends on average signal profiles, our discussion will proceed in two phases. We will consider the modulated signals of Figure 3.6 first. These signals might correspond to the use of a four-mirror polarizer such that one obtains pure RCP light in the first half-period and pure LCP in the second half. Figure 3.6 also describes the signal profiles obtained with a chopper: in the first half-period, light is transmitted through the chopper and sample, and a signal is present; in the second half-period, the light is blocked and there is no signal. As far as signals are considered, both cases are similar except that the differences between the two extremes correspond to different phenomena. Because of this similarity, we will restrict discussion to the LCP-RCP case. In the second phase, more general situations in which part of the signal does not carry useful information and/or signals have non-stepwise transitions between points of interest will be discussed.
3.3.1 Gated Integrator

Two gated integrators may be employed to measure the absolute extremal values [21]. Based on the PEM reference signal, one integrator can be gated (allowed to integrate) for the first half-period and the other for the second half. Thus, one integrator records the intensity of the RCP light and the other the intensity of the LCP light. Unfortunately, problems do arise: 1) no two integrators that match to less than 1% exist [21] and, since CD signal strengths are usually less than that, they are of no value; and 2) the problems imposed by the gain switching required to handle large intensity changes still exists. The matching problem can be solved by using a single dual-gated integrator for both the first and second half-period. The gain switching problem, however, must be considered separately for analog and digital integration:

- In the analog approach, the problem cannot be solved because of power and voltage limits on the electronic components of the integrator. For example, given a particular gain, suppose that 10 ms integration of a constant 0.1 V signal applied to the integrator input produces an output of 10 V, and that the output voltage limit is 15 V. If the input voltage is doubled, the output should read 20 V. However, because of the 15 V limit, the integrator "saturates" at 15 V, and an overflow problem occurs. Therefore, the ability to measure the stronger signal requires a reduction of integrator gain. Suppose, on the other hand, that the oscillations of the input signal are small, say 0.1 V to 1 V. A gain can be selected for this case so that the output varies between 1 and 10 V and no further adjustments are necessary during the course of measurement. However, if the lower limit is changed to 0.01 V and same gain retained, the changes of output for an input in the range 0.01-0.1 V volts are

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20 Technology is now fast enough to handle the resetting of the integrator between the two gates.
very small. Therefore, when the input signal is less than 0.1 V, a dynamic range problem occurs, and the gain must be increased.

- The second approach is digitization: an ADC is used to convert the analog signal and the integration becomes numeric. Overflow problems are now eliminated. However, difficulty may arise with conversion rate and resolution. If a single sample every 10 ms is adequate, a high-resolution ADC can be used and a dynamic range of $\sim 10^5$ is achievable with a fixed-gain amplifier; if that range is too small, the sampling rate may be reduced and higher precision ADC's can be employed. On the other hand, faster conversion requires a gain-switching amplifier because, as pointed out in the discussion of Figure 3.2, a faster 8-bit converter simply does not have enough resolution to detect small signal oscillations without some additional analog signal pre-processing.

In other words, the question of whether an analog or digital integrator and whether or not a gain-switching preamplifier should be used, depends on the nature of the signal.

3.3.2 Gated Photon Counter

When observed with a high frequency oscilloscope, the PMT current does not look like that of Figure 3.2. Rather, it looks more like that of Figure 3.10 where each current pulse, usually about 5 ns wide, is the result of photon registration by the PMT [21]. The fact that pulse heights are governed by statistical amplification processes inside the tube and, therefore, that only the number of pulses is significant, permits approaches other then current integration for the measurement of light intensity. One may do photon-counting: each time the pulse height exceeds a certain threshold value, the counter is incremented. Since the number of counts per unit time is proportional to photon flux, it is also proportional to light intensity. If two counters are used, each being incremented only during a corresponding gate, a dual-gated photon counter.
is born [21]. It measures light intensity in the same way as a dual-gated integrator, except it does so in a photon-counting and not in a current-integration mode.

![Figure 3.10 An example of a PMT current signal consisting of photon pulses of 5 ns width (sharp solid-line pulses). The four peaks occur at 10, 100, 170, and 300 ns and have amplitudes of 40, 4, 80, and 10% of maximal value, respectively. The effects of pulse widening are also illustrated. The widening factors are x10, wider solid line pulses; x25, dashed line; and x50, dash-dot-dash line. The horizontal line represents a threshold setting for which the 5 ns-wide pulse that appears at 100 ns will not register. However, even this method has its problems. As light intensity increases, pulse overlaps or pulse "overflows" become possible. And, if the pulse detection threshold is not properly chosen, information can be lost and/or noise can be made real (e.g., see Figure 3.13). The light intensities produced by the strongest known sources, once attenuated by monochromator optics and sample cells, are not intense enough to saturate the best photon counters available today or to cause significant photon overlap. Indeed, the attenuated intensities rarely approach the $2 \times 10^8$ photons per second that, in a standard photon-count PMT,

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21 The time separation between two consecutive photons is too small to be resolved by a PMT and the photons register as one. These overlaps are more likely to occur in PMT's with large time constants.

22 All incident photons are resolved by the PMT but more of them are registered per unit time than a photon counter can handle. This usually happens when low resolution photon counters are used.

23 The fastest photon counters have a resolution of 500 ps [25].
would produce almost total overlap of 5 ns pulses and complete undetectability\(^24\). The selection of a proper threshold, however, remains a constant difficulty in all photon-count experiments.

### 3.3.3 Fast Low-Resolution Digital Integrator

Consideration of the advantages and disadvantages of dual-gated photon-counters, suggests that pulsed PMT signals are particularly suited for fast low-resolution digital integration. The current pulses represent significant changes of signal intensity, precisely the type of signal required by fast low-resolution ADC's. In addition, since all peaks are created by the same internal PMT process they have similar shapes and a few consecutive samples can describe their areas. However, the lower the peak intensity, the cruder this description becomes. As a result, the threshold problem recurs. For an 8-bit ADC, this threshold is 1/510 of the full range of the converter\(^25\) and all peaks of lower height will not register. If one inspects a typical peak-area distribution, say the experimental distribution of Figure 3.11, it becomes evident that over-amplification can solve at least part of this problem. If the preamplifier gain is increased to the point that some pulse intensities overshoot the converter range, not too much information will be lost since the number of very high peaks is small\(^26\). At the same time, the threshold will be effectively lowered and previously undetectable peaks will now register.

It is important to emphasize that the threshold imposed by an ADC is not identical to that imposed by photon counters. In photon counting, any signal that exceeds threshold,

\(^{24}\) The number of photons generated by the H\(_2\) lamp of Figure 2.1 is less than 1/100 of the critical value.

\(^{25}\) The threshold is equal to 1/2 the size of the y-interval.

\(^{26}\) The gain, however, cannot be increased too much because false information about peak area might cause errors.
whether real or noise, is registered and counted. The digital integrator, however, behaves differently:

- If the noise is generated after the amplifier, only those threshold crossings that immediately precede the sampling interval will be recorded. Thus, only ~2 ns of the entire sampling period is susceptible to noise.

- Peak areas are based on multiple sampling. Consequently, if high-frequency\(^{27}\) noise produces sample values that are excessively large or small, the averaging process will tend to diminish their significance.

![Figure 3.11](attachment:image.png)

**Figure 3.11** A histogram of the area-distribution of PMT current pulses. Each interval covers 0.357% of the total x-axis range. Pulse height (area), relative to that of the largest pulse, is plotted along the x-axis. The number of pulses registered on the PMT output per interval, again relative to the total number of registered pulses, is plotted along the y-axis. The connected histogram was obtained with light incident on the PMT, the total number of pulses being ~120,000. The disconnected histogram was generated by ~36,000 dark-current pulses. The two histograms demonstrate that the number of pulses of large area (height) is large is small and that over-amplification should not cause problems.

\(^{27}\) On the order of, or larger than the inverse of the peak width for noise originating before the amplifier or on the order of, or larger than the sampling rate for noise originating after the amplifier.
• The noise amplified in the pre-amplifier stage is weighted according to "peak" area\textsuperscript{28}. For example, a noise peak of unit height in an ADC mode represents 33% of the total area of "just-above-threshold" pulses when three samples of the total of all samplings exceed threshold. However, it represents only 0.1% of the area of that peak whose amplitude is 70% of maximum (vide infra). The same noise peak in a photon counting mode represents a 100% error.

• Very small pulses that barely cross threshold may be missed in the ADC approach if their maximum occurs before or after sampling. This will not happen in the photon-count approach because the time at which a pulse appears on the PMT output is irrelevant.

3.3.4 Pulse Widening

The manner in which a 48 MHz converter might detect a 5 ns pulse must now be considered. These considerations devolve immediately on the preamplifier. As the I/V conversion is performed, the PMT pulses are simultaneously widened. The number of samples required for an adequate description of pulses of different amplitudes and heights as a function of the delay between pulse initiation and the first sample may be determined from Figure 3.12: approximately five samplings suffice to avoid all problems. The pair-sampling interval of ~84 ns used in this work, therefore, dictates a pulse width\textsuperscript{29} of ~420 ns. The effect of widening consecutive PMT pulses for different time resolutions is shown in Figure 3.10 and Figure 3.13. These sample signals have been calculated using Eq. 3.20 which is a two-exponential\textsuperscript{30} fit to the shape of a unit-height 571 ns wide pulse recorded by the oscilloscope. Both the actual and the fitted shapes are shown in Figure 3.13.

\textsuperscript{28} Noise may appear as peaked even when it is not.

\textsuperscript{29} It has been found that this pulse width suffices (i.e., does not cause significant pulse overlap) for light intensities obtained even with monochromator slits as large as 250 microns.

\textsuperscript{30} One exponent for pulse initiation and one for pulse decay
\[
\text{peak}_{\text{fit}}(t, t_0) = \begin{cases} 
0 & t \leq t_0 \\
\exp \left[-2.5 \left(\frac{t-t_0-122}{100}\right)^2\right] & t_0 < t \leq t_0 + 146 \text{ ns} \\
\exp \left[-0.63 \left(\frac{t-t_0-122}{100}\right)^4\right] & t_0 + 146 \text{ ns} < t \leq t_0 + 571 \text{ ns} \\
0 & t_0 + 571 \text{ ns} < t
\end{cases}
\]

Figure 3.12 The quality of pulse area as a function of number of samples, pulse amplitude, and delay between pulse initiation and the first sampling period. The results are shown for the case when the sum of two 8-bit samples is generated every 83.33 ns, the time delay between samples being 20.83 ns (i.e., a 48 MHz conversion rate). Proceeding downwards, curves correspond to 8, 6, 5, and 3 pairs per peak, respectively. Graphs (a), (b), and (c) correspond to peak amplitudes of 1, 0.1, and 0.01 relative to the highest peak that remains in the ADC input range. Peak areas have not been normalized in order not to damage discrimination. Units for the y-axes are arbitrary.

If four photon pulses occur in a 400 ns interval, as in Figure 3.10, significant overlap begins to develop as soon as the base width exceeds \(\sim 150\) ns. On the other hand, at the light intensities with which we are concerned, Figure 3.13 indicates that base widths below \(\sim 3000\) ns on the average do not produce significant overlap. Since integration avoids most overlap problems, intensities 100 times larger than those available from standard laboratory lamps can

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31 The reason for this particular timing and conversion resolution will be explained in Chapter 4.
be handled with this device. If the intensities are larger than that, the monochromator slits can always be reduced and/or filters can be inserted in the light path, and the light throughput correspondingly diminished. However, besides the overlap problem, widening also produces a shift of PMT pulse maxima by as much as 1/4 of the pulse width, and this shift must be taken into consideration when a real-time mode is used to determine photon polarization.

We now query problems that might exist at low light levels, and conclude that no difficulty exists. The distribution of pulse heights in a PMT output does not depend on light intensity (i.e., pulses do not on the average become smaller because of less light intensity) and, as a result, even a one photon per year situation presents no difficulty. The same is true of photon-counters.

![Figure 3.13 Pulse widening at low light intensities](image)

(a) An example of a PMT current signal consisting of 5 ns photon pulses widened to two different widths (widening expressed as a multiple of the original size): x100, solid line; and x500, dashed line.

(b) Comparison of measured pulse shape (solid line) and numerical fit of Eq. 3.20 (dashed line). Both theoretical and measured pulses are normalized to unit height.
3.3.5 High Time-Constant Detectors

Other light detectors, ones with larger time constants (e.g., semiconductor diodes), may also be considered. However, large time constants flatten the output currents, thereby eliminating both the pulsing characteristics and the possibility of photon-counting. Nonetheless, fast 10 or 12-bit ADC's may well be usable. If not, two solutions exist: stripping the DC and amplifying the residual AC component or employing slower, higher resolution digital and/or analog integrators. The former solution, by elimination of the DC component, destroys the ability to measure absorption spectra whereas the latter is encumbered with the gain-switching problems discussed in Sect. 3.3.

In sum, a dual-gated photon counter or a digital integrator coupled with a preamplifier/shaper eliminate all problems connected with gain switching and resolution when a pulsed detector is used. The separate LCP and RCP current contributions are given by Eq 3.21 and decomposition is not needed.

\[
i_{\text{avg}}(RCP) = \frac{1}{N} \int_0^{NT} i(t)W_{RCP}(t)dt \left[ \int_0^T W_{RCP}(t)dt \right]^{-1}
\]

\[
W_{RCP}(t) = \begin{cases} 
1 & nT \leq t < (n + \frac{1}{2})T, \ n \text{ is an integer } \geq 0 \\
0 & \text{otherwise}
\end{cases}
\]

\[
i_{\text{avg}}(LCP) = \frac{1}{N} \int_0^{NT} i(t)W_{LCP}(t)dt \left[ \int_0^T W_{LCP}(t)dt \right]^{-1}
\]

\[
W_{LCP}(t) = \begin{cases} 
1 & \frac{n}{2} \leq t < (n + 1)T, \ n \text{ is an integer } \geq 0 \\
0 & \text{otherwise}
\end{cases}
\]

Moreover, the equations

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\[ CD = \frac{1}{2.303} \frac{i_{\text{avg}}(RCP) - i_{\text{avg}}(LCP)}{i_{\text{avg}}(RCP) + i_{\text{avg}}(LCP)} \]

\[ ABS = \frac{\log[i_{\text{avg}}(RCP)] + \log[i_{\text{avg}}(LCP)]}{2} - \log(i_0) \]

where \( i_0 \) is the PMT current intensity when the sample cell is empty, permit the collection of both the CD and absorption spectra. Indeed, the quality of the absorption spectrum will equal that of the CD spectrum (i.e., usually better than one part in \( 10^3 \)). Since the \( cL \) product can be determined from sample pressure and cell geometry, \( \varepsilon_{\text{LCP}} \) and \( \varepsilon_{\text{RCP}} \) can also be obtained. Finally, standard samples are not required because all unknown constants either cancel (CD) or are included in \( i_0 \) (absorption).

### 3.3.6 Windowing

The above analysis pertains to modulated signals of the type shown in Figure 3.6. One must now consider the measurement of the absolute values of one or more points on curves for which part of the signal does not carry useful information (see Figure 3.7) and for which signals have non-stepwise transitions between points of interest (see Figure 3.8). In the first case, samples collected when no useful information is present will produce erroneous values whereas in the second case, samples collected during the “transition period” will “pollute” the information of interest (e.g., the effects of elliptically polarized light will mix with that of pure LCP and/or RCP components).

Gated integrators and photon-counters, as discussed in Sect’s. 3.3.1 and 3.3.2, may be used. The gates, however, do not equal the entire first or second half-periods but may be of any length and may be positioned anywhere within the period to ensure that only signals of interest are collected. For example, the influence of elliptical polarization may be reduced by replacing the windowing functions \( W(t) \) of Eq. 3.21 by..
\[
W_{RCP}(t) = \begin{cases} 
1 & \text{if } (n + \frac{1}{6})T \leq t < (n + \frac{2}{6})T \\
0 & \text{otherwise}
\end{cases}
\]

\[
W_{LCP}(t) = \begin{cases} 
1 & \text{if } (n + \frac{4}{6})T \leq t < (n + \frac{5}{6})T \\
0 & \text{otherwise}
\end{cases}
\]

In photon counters and integrators, the "gates" are implemented at the hardware level as voltage signals that trigger data acquisition. In the SDI, however, these gates are implemented at the software level. Because of that, they can also be imposed after collection of the average time-resolved profile. Therefore, to distinguish the hardware and software approaches, the terms "window" and "windowing" are employed instead of "gate" and "gating" (triggering). Gates and windows also differ in that gates do not overlap and may last more than one period, whereas windows may overlap but cannot exceed one period. Indeed, the concept of a "window" defined here makes sense only if a signal is periodic.

3.4 Transient Signal Detection Device (TSDD)

To this point, the intensity difference of two points separated by T/2, the intensity difference of two points not separated by T/2, and the absolute intensities of one or two points within a modulated signal have been discussed. It has been shown that a lock-in amplifier can handle the first kind of measurements, but only if certain conditions are met: the signal must be sinusoidal or its shape must be known in advance. The other two types of measurement require gated photon counter(s) or gated integrator(s). It has also been shown that a single dual-gated photon counter or integrator must be used when the intensity difference of interest is small in order to avoid matching problems in the analog circuitry. And, it has been emphasized that a gated integrator is the instrument of choice when detectors with large time-constants (e.g., semiconductor diodes) are used.
The remainder of this Chapter deals with cases in which more than two absolute values must be measured, the limiting case being that in which the number of windows/gates equals the maximum number of samples that can be collected in one modulation period. One particular method, the least squares method, for extracting information from time-resolved curves will be emphasized. Finally, the S/N ratios of the time-resolved and lock-in methods will be compared.

It may be concluded from Figure 2.8 that the absolute values of more than two points may be needed. All signals in this figure have the same ΔAC and corresponding Fourier components. Therefore, an LA cannot distinguish them. The same is true of dual-gated photon counters and integrators. Even though these can provide the absolute values of two points, the differences are again identical and, on the basis of them, the curves remain indistinguishable. Therefore, the absolute value of one more point, say that for $i_{avg}(T/2)$, is needed. However, even three points may be inadequate for some signals (e.g., case (c), Figure 2.7) because they may have the same value. Consequently, case (c) requires determination of a fourth point. The logical conclusion of these arguments leads to the limiting case in which values of $i_{avg}(t)$ are required for all $t$.

Such a complete time-resolved profile cannot be obtained with a digital gated integrator because it sums the contributions from all points within the gate. For example, if the gate positioned between 2 and 4 μs is imposed on the signal of Figure 3.1 and a 5-bit / [$0, 1.55$] V / 2 MHz ADC is used, the integrator supplies the sum of all samples within the gate, namely $14+15+12+12+7 = 60$. Similar problems are encountered with the dual-gated photon-counter, which delivers only two numbers: the total number of photons registered in each of two gates. Therefore, the required device must record and separately store the value of each consecutive sample.
A device that can perform time-resolved data acquisition, termed a "Transient Signal Detection Device (TSDD)," is based on a fast ADC and on a buffer in which the collected data are stored [26]. A TSDD-based experiment is performed in the following stages: (i) data collection to the TSDD data buffer; (ii) data transfer from the buffer; and (iii) data processing. Once the data are processed, the results may be used to alter the experimental conditions and the run may be repeated. If the average of a number of experimental runs is needed, new scans can be initiated immediately after completion of step (ii) (i.e., immediately after removal of data from the TSDD buffer). Thus, new data may be collected while the old is being processed.

Data processing of the signal may consist, for example, of any or all of the following:

- Point-by-point averaging of subsequent periods of the signal is feasible because the TSDD buffer can store data for a number of periods. For example, a 50 MHz 1 Mword buffer TSDD can store 1000 periods of a 50 kHz modulated signal.

- Re-synchronization, if the length of the period does not equal an integer multiple of the ADC conversion time or if the number of samples varies from period to period.

- Plotting the data so that the user remains informed about the progress and appropriateness of the experiment.

- Controlling the experimental environment (e.g., drivers, modulators, gauges, etc.).

Point-by-point integration of consecutive periods of \( i(t) \) is required in noisy experiments in order to improve the S/N ratio and to reduce the total amount of data that must be stored. An experiment in which only a few photons are detected in any one period and in which a signal consisting of 5 ns pulses, similar to that shown in Figure 3.10, is generated at the PMT output, is a good example of a high-noise experiment. Since the shape of the signal in any one period is very different from the average profile, long integration times are required to obtain a good S/N ratio. As a result, the experiment may last hours. For one such 5 hour run in which one sample...
is collected every 25 ns, the total number of data points accumulates to $5 	imes 3600 \times 40,000,000$ 8-bit numbers (i.e., 5.76 terra bytes). No available hard disk can handle such loads and, as a result, data processing must be simultaneous with the experiment. Such simultaneity, using a simple 1 s point-by-point time averaging over the modulation period\textsuperscript{32}, can reduce the scan data to 17 MB.

A device known as the Photon Count Multichannel Analyzer/Averager operates much like a TSDD but in a photon detection mode \cite{21, 25}. However, because it operates by photon-counting, it possesses the same problems with threshold and photon overlap as all photon counters. The TSDD advantages are:

- A TSDD has other uses, such as the determination of peak-height distributions in all pulse detector outputs; and
- Photon-counters run into problems when higher time-constant detectors are used (e.g., semiconductor diodes).

However, because the photon count multichannel analyzer can be viewed as a TSDD that operates as a one-bit converter (signal above or below threshold) of such poor resolution that "conversion times"\textsuperscript{33} as low as 500 ps are possible, it is implicitly considered to be a TSDD.

Once an average time-resolved profile is obtained, the desired information can be extracted from it by various numerical methods. Indeed, a least squares approach works quite well if the shape of the signal $i_{\text{form}}(t)$ is known in advance. The method is based on finding the two coefficients in

\textsuperscript{32} In the present situation, the data load is proportional to the number of wavelength steps because all points collected at any wavelength are averaged into a single time-resolved profile regardless of the length of time this averaging lasts.

\textsuperscript{33} "Discrimination" might be a more appropriate word than "conversion"
\[ i_{\text{avg}}(t) = A i_{\text{form}}(t) + B \]  \hspace{1cm} 3.23

that minimize the objective function \( J \)

\[
J(A,B) = \int_{0}^{T} \left( i_{\text{avg}}(t) - A i_{\text{form}}(t) - B \right)^2 dt \]  \hspace{1cm} 3.24

If the minimum condition is expressed as

\[
\frac{\partial^2}{\partial A} J(A,B) = \frac{\partial^2}{\partial B} J(A,B) = 0 \]  \hspace{1cm} 3.25

one finds the amplitude \( A \) to be

\[
A = \frac{\int_{0}^{T} i_{\text{avg}}(t)i_{\text{form}}(t)dt - \int_{0}^{T} i_{\text{avg}}(t)dt \int_{0}^{T} i_{\text{form}}(t)dt}{\int_{0}^{T} i_{\text{form}}(t)i_{\text{form}}(t)dt - \int_{0}^{T} i_{\text{form}}(t)dt \int_{0}^{T} i_{\text{form}}(t)dt} \]  \hspace{1cm} 3.26

which, once available, generates the CD as

\[
CD = \frac{A}{2.303} \frac{i_{\text{form}} \left( \frac{T}{4} \right) - i_{\text{form}} \left( \frac{3T}{4} \right)}{i_{\text{form}} \left( \frac{T}{4} \right) + i_{\text{form}} \left( \frac{3T}{4} \right)} \]  \hspace{1cm} 3.27

Apart from providing time-resolved profiles, a TSDD has another advantage relative to gated photon counters and integrators: for a CD signal, the TSDD may have better S/N ratios and, therefore, better spectral resolution. The comparison of S/N ratios for various data acquisition devices is the subject of the next Section.

3.4.1 Signal-to-Noise Ratio

The S/N ratio is a measure of the way in which noise superimposed on the signal alters the outcome of a measurement. Therefore, when \( i_{\text{avg}}(t) \) is supposed to consist of two components, \( i_{\text{avg-signal}}(t) \) and \( i_{\text{avg-noise}}(t) \), the S/N ratio of a TSDD may be obtained as the ratio of
two amplitudes $A_s$ and $A_n$, as calculated from Eq. 3.26 with $i_{avg}(t)$ replaced by $i_{avg-signal}(t)$ and $i_{avg-noise}(t)$, respectively. This ratio yields

$$\frac{T}{T} \int_{0}^{T} i_{avg-signal}(t) i_{form}(t) dt - \frac{T}{T} \int_{0}^{T} i_{avg-signal}(t) i_{form}(t) dt$$

$$\frac{T}{0} \int_{0}^{T} i_{avg-noise}(t) i_{form}(t) dt - \frac{T}{0} \int_{0}^{T} i_{avg-noise}(t) i_{form}(t) dt$$

Comparison of S/N ratios for various devices requires pertinent S/N expressions. In the specific case of CD or LD, in which a difference of two points separated by T/2 is required, it can be shown, using Eq’s. 3.17 or 3.21, that the S/N ratios for LA’s and gated integrators (photon counters) follow from Eq. 3.28 by replacing $i_{form}(t)$ by $\sin(\omega t)$ and $W_{RCP}(t)-W_{LCP}(t)$, respectively. A comparison of these ratios for various forms of $i_{avg-signal}(t)$ is given in Figure 3.14. Since the form of $i_{avg-noise}(t)$ is generally not known, the S/N ratio is expressed as a ratio of the signal amplitude to that of a single sinusoidal noise component (i.e., $i_{avg-noise}(t) = \sin(\omega_s t)$). The three shapes of $i_{avg-signal}(t)$ are shown in Figure 3.15.

![Figure 3.14](image)

Figure 3.14 S/N ratios for LA relative to TSDD devices for the three different signal shapes of Figure 3.15 vs. $\omega_n/\omega_s$, where $\omega_n$ and $\omega_s$ are noise and reference frequencies, respectively. As expected, the LA S/N ratio deteriorates relative to that of a TSDD as the signal shape departs from sinusoidal, being on average ~4.5 smaller for the least-sinusoidal signal.

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Figure 3.15  Three average time-resolved profiles used for comparison of S/N ratios for LA, gated integrator/photon counter, and TSDD. These curves are characterized by the extent to which they differ from a sinusoid of the same frequency and phase, the curve with shorter-dashes being most and the curve with a solid line being least similar to the sinusoid.

Figure 3.14 demonstrates that the LA S/N ratio deteriorates with respect to that of the TSDD as $i_{\text{avg-signal}}(t)$ departs from sinusoidal and the least squares fit with the known average signal profile is performed. Similar conclusions, as shown in Figure 3.16, apply to the S/N ratio of a dual gated integrator (photon counter) relative to that of TSDD.

Figure 3.16  S/N ratios for a dual gated photon counter/integrator relative to TSDD devices for the three different signal shapes of Figure 3.15 vs. $\omega_n/\omega_s$, where $\omega_n$ and $\omega_s$ are noise and reference frequencies, respectively. As expected, the photon counter/integrator S/N ratio deteriorates relative to that of a TSDD as the signal shape departs from sinusoidal, being ~4.5 smaller for the case of the least-sinusoidal signal.
However, if the signal shape is not known in advance, the situation alters. For example, if the signals are non-sinusoidal (e.g., those of Eq. 3.13) and if the only advance knowledge about shape is that the half period profiles resemble gaussians, a half-period by half-period fit is necessary. Such a fit uses Eq. 3.26, the integration boundaries being \((0, T/2)\) and \((T/2, T)\) for the first and the second half-periods, respectively. Under these conditions, the S/N advantage of a TSDD depends on the departure of each half-period of the signal from sinusoid \((W(t))\) rather than on the shape function for the whole period and, in the case of the non-sinusoidal signal of Figure 3.15, the S/N ratios for the lock-in (dual-gated photon counter and/or integrator) and TSDD become very similar.

### 3.5 Selective Digital Integrator (SDI)

In Section 3.4, a case was made for a time-resolved data acquisition mode as the method of choice for the analysis of modulated signals. It was also demonstrated that the spectral resolution provided by a TSDD is better than that of lock-ins or dual-gated photon counters (integrators). Unfortunately, there are significant problems associated with the use of off-the-shelf TSDD's for MPS measurements: they do not perform any on-the-fly data processing because they are designed for experiments that do not last longer than the time needed to fill their data buffers. An MPS experiment using a 50 kHz PEM and a 20 MSPS data acquisition rate, say 400 points per 20 µs modulation period, will fill a 1 mega word data buffer in 50 ms. The experiment, however, may last 10 hours or more! And, if every 1 s of data acquisition requires another 3 s for data transfer and processing, the 10 hours extend to 40! Therefore, an immediate processing of the incoming signals is of the essence. Indeed, that is the main advantage of lock-in amplifiers and it is the reason, despite their lack of precision, that they are still used. The same is true of dual gated photon-counters and integrators.
The digital signal processor (DSP)-based device, the SDI, was designed and built for situations in which:

- Lock-in devices cannot extract correct information from non-sinusoidal periodic signals;
- Gated photon counters and integrators cannot be used because time-resolved rather than cumulative data acquisition is required; and
- TSDD's require excessive times for data collection.

The SDI combines the best of two approaches: it has the on-the-fly integration capability of a lock-in amplifier and the time-resolved capability of a TSDD. The SDI samples the signal at 48 MSPS and integrates data in a predetermined number of windows, with a maximum time resolution of ~84 ns. When 240 windows per "integration period" (240x84 ns ~ 20 μs) are used, the SDI can integrate for times Δt > 100 s at maximum signal strength, using only 4K words of DSP internal memory, before it is forced to transfer the data. The polarization resolution of the SDI is equivalent to the smallest feasible data acquisition interval δt for which values of the signal corresponding to the different polarizations Π(t) and Π(t+δt) can be measured. A detailed description of the SDI is the subject of Chapter 4.

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34 The term "integration period" is used to denote the time in which the SDI updates all window sums once. This time may not equal the actual signal modulation period as discussed further in Chapter 4.
4. THE SELECTIVE DIGITAL INTEGRATOR: A FUNCTIONAL DESCRIPTION

The SDI was introduced in Chapter 3 as a solution to various problems that bedevil MS, its main advantages being on-the-fly data processing and time-resolving capabilities. This Chapter focuses on SDI architecture (i.e., how the above advantages arise). The software component, namely the algorithms for the various data acquisition modes, is also discussed. These algorithms are given in flow diagram form, except for the time-resolved mode algorithm which, because of its complexity, is written in a pseudo-code. Finally, communication between a host computer and the SDI is addressed. In Section 4.5.1, a communication protocol using a PC parallel port and a DSP Host Interface Port (HIP) is discussed in low-level detail. More information on the Host Interface Port can be found in the DSP manual [27]. The complete technical description of the device, including electronic schematics, are given in Appendix B.

The SDI, as shown in Figure 4.1, consists of six functional blocks: reference interface, I/V converter/preamplifier, 48 MHz 8-bit ADC block, 24 MHz DSP, parallel interface, and serial interface. The reference signal is transformed in the reference interface into a transistor-transistor logic (TTL) pulsed signal that is used for synchronization by the DSP [20]. The incoming PMT signal, after conversion, amplification and conditioning by the preamplifier, is digitized in the ADC block. After processing by DSP, data may be exchanged between the SDI and computer via parallel or serial SDI interfaces using hardware present in the respective SDI blocks. The parallel interface is also used for downloading programs into DSP internal memory.

Each functional block will be described in detail in this Chapter. However, because a description of the DSP is available elsewhere [27], the DSP Section will merely review the
Figure 4.1  Block Diagram of the SDI
basic processor features and discuss different DAQ modes. These modes require attention because they must be implemented with minimum overhead (i.e., the fraction of time during which data is not collected) which, as shown in Chapter 3, is the main reason why TSDD's are not suitable for MPS. Since all DSP-executed instructions (clock cycles) that do not access ADC-block data are overhead, the DSP software must be optimized to contain as few such instructions as possible.

The SDI prototype was designed and built at LSU without professional tools, and compromises were necessary in order to reduce hardware to a minimum. Consequently, some desirable elements are missing (e.g., external RAM and ROM), while other desirable elements are specific to this apparatus (e.g., the type of signal expected on the reference interface). However, these are "polishing" details which do not influence the ability of the SDI to perform the required tasks. Indeed, they only make it more user-friendly and more "stand-alone" (i.e., less dependent on the host computer).

4.1 The Reference Interface

The main task of the reference interface is to enable the DSP to synchronize data processing and signal modulation. The reference signal originating in the modulation control provides essential information. Depending on the apparatus, this signal may have different shapes and/or amplitudes. However, because the DSP can only accept a TTL signal\(^{35}\) (i.e., either "logical 1" (+5 V) or "logical 0" (0 V)), conversion\(^{36}\) is necessary. This conversion takes

\[\text{Some DSP's have analog ports. However, built-in converters are too slow for the applications of interest (i.e., in which PEM's are used).}\]

\[\text{The voltages that represent logical values are not limited to 0 and 5 V. The logical 0 is actually represented by all voltages smaller than \(-1\) V, and logical 1 by all voltages greater than \(-2.5\) V. Other values represent a "gray area" (i.e., they can be understood as both 0 and 1)\[20\]. Sometimes, 0 and 1 are also referred to as "high" and "low," respectively. In the text that follows, the word "logical" will no longer be used in this context.}\]
place in the reference interface where a voltage comparator (discriminator) [20] is used to compare the reference signal with some predefined threshold value. If the reference is above threshold, 1 appears at the output; if the reference is below the threshold, the output is 0. For example, the PEM power supply of Figure 2.1 generates a sinusoidal reference signal whose average value is 0 V. Therefore, if the threshold voltage is set to 0 V, the output is 1 when the reference signal is positive (right-handed polarization) and 0 when this signal is negative (left-handed polarization). On the other hand, if the PEM power supply had a positive square wave reference signal, the threshold voltage would have to be set half way between the minimum and maximum of the reference signal. If shapes are more complicated, other quite different approaches may become necessary.

Unfortunately, the existing implementation of the interface has noise problems: as the reference signal approaches threshold, any small ripple superimposed on top of it may cause rapid oscillations at the output. This problem can be solved by filtering the signal before feeding it to the SDI\(^3\).

### 4.2 The Preamplifier

Pulse widening, the most important feature of the preamplifier, was discussed in detail in Chapter 3. In addition, the preamplifier is also responsible for current-to-voltage conversion, amplification, and the amplifier output voltage offset and amplitude control. These tasks are performed at the five amplifier stages shown in Figure 4.2:

1) The current-to-voltage conversion/amplification stage converts the current signal from the PMT output into a voltage signal. This stage is based on an ultra-fast high-input-resistance

\(^3\) A new interface design is described in Appendix B: it employs a feedback loop on the comparator in an attempt to solve this noise problem. This design will be incorporated in a new SDI version. Even though this interface is very simple, it should be able to handle all PEM applications.
operational amplifier capable of amplifying 5 ns pulses with minimal distortions [28]. The amplification can range from $-120$ V/A to $-5120$ V/A.

2) The amplification stage amplifies the converted signal even further. The amplification is performed in several small gain increments in order to minimize distortions. This stage also employs a fast operational amplifier whose gain can range from $-x-0.5$ to $-x-4.5$.

3) The pulse shaping (widening) stage.

4) The offset/amplification stage compensates the offsets generated in the other preamplifier stages [20] and provides amplification from $-x-0.2$ to $-x-5.2$.

5) The output stage is responsible for protecting the SDI converters by limiting the preamplifier output voltage. Converters used in the existing SDI version have a range $[0, 1.5]$ V and can handle overload voltages as high as 2 V [29]. Consequently, the preamplifier output is limited to 1.8 V for safety.

![Figure 4.2 Preamplifier Block Diagram](image)

4.3 The ADC Block

The main difference between DSP-based TSDD's and the SDI is that analog to digital conversion and DSP data processing are now synchronous (i.e., all data are immediately "consumed" by the DSP, and intermediate memory buffers are not required). This

---

38 In operational amplifiers, the frequency bandwidth-gain product is constant. Consequently, higher gains yield smaller frequency bandwidths, which, in turn, may cause signal distortions [20].
synchronization, if achieved by direct access of the DSP to the ADC output, imposes the processing and clock limitations of the DSP on the conversion speeds. In other words, given the use of a 33 MHz, 16-bit, fixed-point DSP (Analog Devices, ADSP2171) that executes instructions in a single 33 ns clock cycle, the maximum conversion rate would be limited to 33 MSPS in such a configuration. One can thwart this problem, while still using only one DSP and TTL logic circuitry, by employing a 24 MHz DSP clock\(^3^9\), two 8-bit 24 MHz ADC’s that are 180° out of phase and an intermediate adder as shown in Figure 4.3. The outputs of the two converters are added in one clock cycle as follows: at a time \(2\Delta t\) after the rising edge\(^4^0\) of the DSP clock, data from the intermediate buffer and data from the ADC2 are latched into adder input buffers; at a time \(3\Delta t+20.84\) ns after the rising edge, new data from ADC1 is latched into its intermediate buffer (to be added in the next clock cycle); and, on the next rising edge of the DSP clock, the sum is latched into the adder output buffer. Consequently, the ADC block provides one 9-bit number every 41.67 ns, a number that represents the sum of two consecutive samples collected 2.5 and 2 DSP clock cycles earlier\(^4^1\). The benefit of such a scheme is twofold: (i) it doubles the number of samples collected using the same DSP clock, and (ii) if each datum provided by the ADC block in the time-resolved mode is divided by two, one obtains the average of two 48 MHz samples (which is better than just one 24 MHz sample).

\(^3^9\) When the prototype was developed there was a lack of computer grade 12.5 MHz crystals on the market. Thus, we were forced to use a 12 MHz crystal whose frequency, when doubled by the DSP phase-lock loop, yields a 24 MHz clock.

\(^4^0\) \(\Delta t\) represents the average delay per inverter gate; it usually lies in the range 1 to 2 ns [30]

\(^4^1\) One clock cycle is spent on conversion. The complete timing diagram is given in Appendix B.
Figure 4.3 A Block Diagram of the ADC Block. Dashed lines represent clock signals. Solid lines marked with a slash represent digital signals. The number above the slash denotes the data size (in bits) transferred between various digital components. Because the DSP operates on 16-bit numbers, a 9-bit adder output is converted in the adder output buffer into a 16-bit number whose unused bits are filled with zeros. One pulse is used to illustrate the effect of invertors on the clock signal. All actions (e.g., start of conversion in the ADC's, loading the buffers with information at their inputs, etc.) is done on the rising edge of the corresponding clock signal. The ADC block, in addition to the digital part, also contains the analog circuitry that provides the reference voltage required by the two converters and also buffers the incoming signal [29].
4.4 The Digital Signal Processor

The main advantage of the DSP, apart from low cost, is its ability to perform more than one task simultaneously [27]. For example, the processor can simultaneously load data into two different registers and perform numerical operations. The computation can be as simple as addition or shift, or as complex as "multiply-and-accumulate (MAC)" instructions in which two numbers are multiplied and then added to another number stored in the output register. In addition to read/write and numerical operations, the DSP can also find the address of two operands stored in memory and/or determine whether a programming loop must be re-executed, all in the same clock cycle. Consequently, zero-overhead looping and circular addressing are possible. This parallel processing capability is heavily used to implement data acquisition algorithms because it minimizes overhead.

However, the particular DSP in the current SDI version has its own limitations. For example, the input data must be a 16-bit number; addition of two 16-bit numbers yields only a 16-bit result plus a 1-bit overflow; MAC instructions are performed on two 16-bit numbers, the accumulated sum being restricted to a maximum width of 40-bits; zero-overhead loops are limited to 16384 iterations or less; and the internal 16-bit wide data memory is only 2K in length. As will be shown in subsequent Sections, these limitations influence the time the SDI can collect data before running out of memory. They can also require more complicated implementations of the DAQ algorithms.

A register is a specialized storage that holds only one number. The contents of a register can be transferred to other registers, used in numerical operations such as addition, or stored outside the processor. A register can be loaded with the contents of other registers, with a number from outside the processor or with the result of some numerical operation.

These instructions are heavily used in filtering algorithms in which a product of the input data and corresponding coefficients are added to a sum, one product per clock cycle [27].

Addressing in which, when the end of a buffer is reached, access automatically reverts back to the start of the buffer.
4.4.1 The Absorption Data Acquisition Mode

The simplest data acquisition mode consists of a summation of the data samples emanating from the ADC block. Such a sum is directly proportional to the light intensity hitting the PMT and, when the wavelength does not change, can be used for the calculation of absorbance. If, in addition, the signal is modulated, this sum is proportional to the transmitted light intensity averaged over all polarizations present in the light beam.

The input to the algorithm, shown in Figure 4.4, is the number of inner and outer loop cycles\textsuperscript{45}. The inner loop contains only one instruction: read data from the ADC block and add it to the sum. As such, it has zero overhead. The outer loop skips three samples: two for initialization of the inner loop and one at the end of the inner loop. The total number of samples that can be collected with this approach is limited to 16384x16384 or, for a 24 MHz DSP, to an approximate time load of 11 s (16384x16384x41.67 ns) of data. If longer periods are needed, a third loop can be added, or the outermost loop can be implemented in such a way as to impose no limit, even though this tactic does introduce some additional overhead. However, regardless of the manner in which the loops are implemented, the overhead can be maintained below 1%.

When the input signal is maximum, the 40-bit MAC sum register has room for ~90 s of data\textsuperscript{46}. After that, information must be stored in the memory. The DSP, with 2K of data words of memory, can collect about 680 sums\textsuperscript{47} before it runs out of space. In a real experimental situation, however, the signal intensity is rarely maximal and the usual integration times for absorption spectra lie between 0.5 and 10 s, depending on the absorptivity of the sample, the

\textsuperscript{45} The time required to complete one full iteration of the outer loop is termed an "integration cycle."

\textsuperscript{46} (2\textsuperscript{32}-1)/24 MHz/510 ~ 90 s, where 510 is the output of the ADC block if the input signal is above the converter ranges

\textsuperscript{47} 2K/3. when 3 16-bit memory locations are used to store a 40-bit sum and 1K=1024
scan speed, and the spectrum quality that is desired. For example, if each sum requires a 6 s collection period, the SDI can run in the absorption DAQ mode for about an hour before it is forced to transmit data to a computer.

Figure 4.4 Absorption Mode data acquisition algorithm

Some general remarks that apply to all flow diagram figures are collected here. A square element of a flow diagram indicates action. A diamond shaped entry denotes an “if” condition: if the condition is true, the “YES” branch is executed. A square element attached directly to the “if” entry denotes an operation that is executed in the same clock cycle in which the condition is tested. A branch that ends with a circled letter continues at whichever point the same symbol reappears. The elliptically shaped elements denote starting and ending points of an algorithm. For each algorithm, the functions called and the input, output and “working” variables are listed and described. Exception occurs only if the variable name is self-explanatory, for example SUM in Figure 4.4. The “flow” is down, left, or right for shorter edges. Longer vertical edges have an “upward” flow.
A very useful variation of this method is the "constant signal-to-noise ratio" mode in which the integration time is not determined in advance but, instead, depends on the PMT signal strength: the lower the signal level, the longer the integration time. The appropriate algorithm, shown in Figure 4.5, accepts two parameters: the integration threshold (data will be integrated until the sum exceeds threshold) and the number of inner loop repetitions. The output consists of the sum and the number of integration cycles required for that sum to exceed the threshold. Light intensity can then be obtained by dividing the sum by the number of cycles.

![Figure 4.5 Constant S/N variant of an absorption mode data acquisition algorithm](image)

In actual implementation, the sum register is treated as a signed number and is loaded at the beginning of data acquisition with a negatively signed threshold. The integration then lasts until

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the sum becomes positive. Since the outer loop is a simple test and jump loop, it has an overhead of five clock cycles: two for inner-loop initialization, one for the sign test, one for the outer-loop cycles count, and one for the actual jump. Therefore, if the integration cycle consists of at least 501 inner loop iterations, the overhead can be maintained at 1% or less.

This mode is particularly efficient for maintaining a constancy of the statistical noise, the noise attributable to light source instability. However, it requires a stepper motor monochromator drive because the wavelength scan rate must be adjustable.

4.4.2 The Windowing Data Acquisition Mode

The DSP, when operating in this DAQ mode, uses the reference interface output to impose windows on the signal in the manner described in Chapter 3. A two window example for measurement of a CD signal using the apparatus of Figure 2.1 will be emphasized here.

The goal of the algorithm shown in Figure 4.6 is to collect (integrate) separately the contributions of LCP and RCP light. The input parameters are window delays and widths and the number of outer loop iterations (integration cycles). The output consists of the integrated signals for the LCP and RCP windows and, in the constant S/N ratio mode, the number of integration cycles required for the sum over windows to reach predefined threshold. Because of the overhead produced in setting up the registers needed for the summation of samples collected during one window, the maximum window widths are limited to 9 μs, leaving about 1 μs (24 clock cycles) for initialization.

The limitation of the maximum window size to 9 instead of 10 μs is irrelevant if a PEM is used. In such a case, as discussed in Chapter 3, window sizes must be reduced anyway in order to minimize the influence of non-circular polarizations. Ideally, these windows should be

\footnote{Sign testing is much faster (1 clock cycle) than the comparison of two 40-bit numbers (8+ clock cycles).}
Figure 4.6 The windowing mode data acquisition algorithm (two windows). In the non-constant S/N mode, the italicized steps are skipped and the instructions given in parentheses, if any, are executed instead. In the same mode, the OLR parameter is used instead of THR. Finally, in the constant S/N ratio mode, the OLC (outer loop counter = number of integration cycles) variable is also part of the algorithm output. The corresponding input/output parameters and variables are described in Figure 4.7.
### INPUT:

- OLR - number of outer loop repetitions (one per integration period)
- THR - threshold
- LWD - left window delay
- LWW - left window width
- RWD - right window delay
- RWW - right window width

(all window-related constants are in units of sampling time)

### OUTPUT:

- Sum for each window (LSUM, RSUM) and number of integration cycles (OLC)

### VARIABLES:

- WD - window delay
- WW - window width

### FUNCTIONS:

- get_sample() - reads data supplied by the ADC Block
- get_RLFlag() - returns 1 if in the first half-period, else it returns 0

---

Figure 4.7 Description of the input/output parameters and variables for the windowing mode data acquisition algorithm. The corresponding algorithm flow diagram is shown in Figure 4.6.

Only one sample wide, that sample being collected when only pure LCP or pure RCP light is present. However, because of the pulsed nature of the PMT signal, a window of one sample width would yield large errors. Therefore, a compromise between error and window size is necessary. For example, based on Figure 2.3, a window of size 6.32 µs with a delay of 1.83 µs relative to the start of the half-period will view light that is more than 75% LCP or RCP polarized. At the same time, only about 37% of the total light intensity will be lost.

All parts of the signal traverse the same electronic path in this mode and are influenced in the same way by any bias that might be present in the amplifiers or the two ADC’s. As a result, the two sums are of the same accuracy and additional adjustments are not required. Furthermore, because each datum on the ADC block output is a sum of two samples, one from each ADC, any problems related to a mismatch of ADC support circuitry are eliminated.

### 4.4.3 The Time-Resolved Data Acquisition Mode

The advantages of time-resolved DAQ were discussed extensively in Chapter 3. Indeed, one may conclude that this DAQ mode is particularly suited to MPS measurements.
No multiplication or deconvolution takes place in both DAQ modes described earlier. The incoming data is simply summed. If additional processing is necessary, it may be prosecuted after data acquisition so that the speed of the process is not affected. The light intensity, however, is influenced by the various apparatus elements. Deformations of, or pressure effects on the PEM polarization crystal, as well as problems with other optical elements such as windows, mirrors, or polarizers have an effect on the measurements. Although many such influences are too small to be observed in absorption, they may be significant for MPS measurements. In such a case, a deconvolution of the PMT signal is necessary. However, the DSP cannot perform such a deconvolution on-the-fly and still collect data at a rate of 24 MSPS, especially when the deconvolution function is complex and/or variable in time. This problem can also be solved by using the time-resolved DAQ mode.

The time-resolved DAQ mode can be described as follows: each integration period is divided into a predetermined number of windows, and the data for each window is separately integrated for a predetermined amount of time\(^5\). The choice of an 83.33 ns interval, causing every second sample to be lost, is a consequence of the two 24 MHz clock cycles required by the DSP to fetch the previous sum for any one window, add the new data to the sum, and store the result back in the buffer. The number of windows equals the number of 83.33 ns intervals that can fit in one modulation cycle. Since that number is not necessarily an integer, the DSP periodically performs re-synchronization to the reference signal. These window sums, when divided by the number of integration periods, represent the time-resolved light intensity profile, and are stored in the computer. That data is then available for any post-processing (e.g., deconvolution): unwanted interferences can be removed if their modulation cycle time-resolved

---

50 The length of integration is usually determined by the sample absorptivity, the scan speed and the spectral resolution. One averaged profile per wavelength step is normally collected.
average profile is either known or measurable. For example, a wavelength-dependent time-resolved profile of an empty sample cell can be measured in advance and its polarization-dependent oscillations eliminated from the results of a sample measurement.

The algorithm for the time resolved data acquisition mode is given in Figure 4.8.

![Algorithm](image)

Figure 4.8 The data acquisition algorithm for the Non-Constant S/N Ratio Time-Resolved Mode

Because a 16-bit window sum is the largest that the DSP can handle in two clock cycles, a double buffering scheme is required. First, the input data is circularly added to the 16-bit
buffer. Since this buffer must not be allowed to overflow, it can hold sums for 128 integration periods \((65535/510 = 128.5)\). When filled, its contents must be transferred to the 32 bit buffer. Because each window sum is now stored as a 32-bit number, this buffer can hold approximately 168 s worth of data at maximum signal strength \((232/510/50 \text{ kHz} = 168 \text{ s})\). When it fills up, its contents must be transferred to the computer.

Unfortunately, data from all 128 integration periods cannot be circularly averaged to the 16-bit buffer at once, because the signal period may not equal the integration period. For example, suppose that the integration period consists of 239 windows and that the modulation period is not 239x83.3 ns but 239.5x83.3 ns. In such a case, after each two integration periods, data belonging to the \(n\)\(^{th}\) window falls into the \((n+1)^{th}\) window. To avoid such errors, a re-synchronization is required after each integration period. However, that produces excessive overhead: after each integration period during which data is collected, one half of the following period must be "wasted" for re-synchronization, and the experiment lasts 1.5 times longer. Resolution of this difficulty, if desired, lies in compromise. If one circularly adds the data for four integration periods, the maximum expected shift should be 2 windows; if the modulation period is longer than 239.5x83.3 ns, 240 windows per integration period might be chosen so that a shift smaller than 2 windows but oppositely directed is produced. Since 2 windows correspond to \(-1\%\) of 240, the error will not be excessive\(^5\).

Furthermore, when data transfer from the 16 to the 32-bit buffer and the determination of whether the integration should be continued or not (if operating in the constant S/N ratio mode) are carried during the idle half-period, the total data processing overhead can be kept very low. Tests under laboratory conditions show that the complete overhead, including data

\(^5\) The process of re-synchronization itself can produce errors of one window. More information about multi-period averaging can be found in Chapter 5.
transfer and graphing, on a 8 MHz Intel 80286 processor PC is ~12%, when the integration
time is greater than 2 s and averaging performed over 5 consecutive integration periods.

4.5 The Parallel Interface

Any data acquisition device with an embedded processor must be able to communicate
with "the rest of the world." Communication with tandem instrumentation may be needed for
exchange of synchronization and/or control data. Computer resources such as hard disks or
graphic displays, which also require communication, are often used to reduce the requirements
imposed on the DAQ device. Finally, the SDI must be able to communicate with boot host(s)
that download program(s) to the DSP upon power-up or reset. Unfortunately, because of the
last requirement, boot-up procedure plays the most important role in determining the
communication method and must be considered first.

The Analog Devices DSP can boot in two different ways; from a ROM attached to the
processor or through the host interface port (HIP), the HIP being a set of registers resident on
the DSP that can be read and written asynchronously\(^{52}\), externally by a host computer and
internally by the DSP processing core [27]. In order to simplify board layout and to expedite
software development, the latter method was adopted for this version of the SDI. Consequently,
it was required that the communication method be able to provide data to the HIP port.
Furthermore, since the SDI was designed to be modular, to be easily transportable and usable
with PC compatible computers, a standard interface, such as the serial (RS232), and parallel
(printer) ports\(^{53}\) were likely candidates. The parallel port was selected because booting through

\(^{52}\) An asynchronous mode of operation implies that these registers can be accessed by both the host and
DSP core at any time. For example, data that eventually must be read by a computer can be stored in
the HIP registers by the DSP core, which can then proceed to perform other functions unconcerned by
the rate of computer consumption of the stored material.

\(^{53}\) Another possibility is an expansion card with a parallel I/O port. However, such cards are not
standard on most computers.
a serial port requires considerable extra hardware. However, once the booting procedure is completed, communication can resume through either port.

Unfortunately, compatibility with the parallel port also has its own problems: 17 different signals required for data transfer and DSP control must be communicated, but only 8 digital lines are available in the interface. Consequently, a special protocol for data exchange is required. This protocol is the subject of the next Section.

4.5.1 Communication Protocol

The DSP already contains all necessary handshaking hardware to facilitate communication through the HIP. Therefore, a predefined sequence of operations must be followed in order to access the port. For example, to read/write data from a particular register, the following steps must be performed: (i) the register address must be specified; (ii) read or write control lines must be set in order to signal the operation that is desired; (iii) the data must be read from, or written into the register; and (vi) control and address lines must be de-asserted. These steps usually are executed automatically (i.e., they are hidden from the user). All one does is issue a read or write command. However, since access through a parallel printer port does not provide automatic handshaking, the handshaking must be mimicked (i.e., the read/write status signals must be explicitly controllable through the interface).

Communication through the HIP requires control of the following DSP pins:

1. HSEL* - signals DSP that HIP operation is in progress;

---

54 If ROM were available, boot-up could be accomplished from memory.
55 The word “line” is used to denote an actual wire or physical connection. In this case, it denotes the wires in the cable that connects computer and SDI. Later, it will be used to denote “wires” that are connected to corresponding DSP pins. For example, when the HSEL line is set high (logical 1), so is the corresponding DSP pin.
56 Actually, more than 8 data lines are available in the printer port but only 8 are used in order to preserve compatibility with the 8-bit digital I/O ports available on many DAQ cards.
57 The rules that must be followed and the signals that must be generated by a host processor when reading/writing data from/to a HIP register.
(2) HRW* - signals DSP whether read or write operation is required.

(3) HDS* - data strobe causing data to be loaded into or read out of a HIP register

(4) HD7-0 - data pins

(5) HA2-0 - address pins for selecting HIP register to which writing or reading will occur.

The states of these lines are controlled through the registers in the parallel interface block as shown in Figure 4.9. To set a particular signal to “high,” the corresponding bit in one of the parallel interface registers must be set to “1.”

In addition to the pins listed above, other HIP-related pins that control the DSP boot mode, acknowledgment procedure, data and addressing modes and the HIP bitwise width, to name a few, exist on the DSP. However, since these pins are already hardwired to the appropriate voltages\(^58\) on the board and cannot be changed, they will not be discussed here.

Based on the above signal list, a total of 14 bits is required to read from, or write into the HIP. If, in addition, RESET, power OFF/ON, and interrupt request (IRQ2) lines are added, the total climbs to 17. With so many bits and only an 8-bit bus connecting the computer and SDI, multiplexing becomes the only solution \[20\]: the 17 control bits are logically divided into three 6-bit registers, loaded from the lower 6 bits of the digital bus\(^59\), and the upper two bits of the bus are used for register selection, as shown Figure 4.9. The word “logically,” as used here, implies that the computer “sees” the parallel interface as three 6-bit registers even though the underlying physical hardware might be organized quite differently. Bit assignments for each register are given in Table 4-1.

---

\(^{58}\) These voltages can be found in the SDI description given in Appendix B.

\(^{59}\) In the text that follows, the lower six bits of the digital bus connecting PC and SDI will be referred to as the “external data bus” and the bits 6 and 7 will be referred to as the “external address bus.”
Figure 4.9 Parallel interface registers. The numbers above the slashes denote the number of digital lines connecting various entities.

Table 4-1 Bit Assignments for the Parallel Interface Register

<table>
<thead>
<tr>
<th>Bit#</th>
<th>Register Address $^60$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>00$_2$</td>
</tr>
<tr>
<td>0</td>
<td>D4 - fourth data bit</td>
</tr>
<tr>
<td>1</td>
<td>D5 - fifth data bit</td>
</tr>
<tr>
<td>2</td>
<td>D6 - sixth data bit</td>
</tr>
<tr>
<td>3</td>
<td>D7 - seventh data bit</td>
</tr>
<tr>
<td>4</td>
<td>IRQ2* - setting this bit low will interrupt DSP</td>
</tr>
<tr>
<td>5</td>
<td>RESET* - setting this bit low will reset DSP</td>
</tr>
</tbody>
</table>

$^60$ The last combination, 11$_2$ of the external address bus, is used to deselect any of the three registers and latch (load) data into them.
To write data into one of these three registers, the following procedure must be followed:

(i) Set the value to be read into a register on the external data bus and set the register address on the external address bus;

(ii) Set the address bus to 112 without changing the data bus.

The protocol\textsuperscript{61} for writing and/or reading of a HIP register is as follows:

Writing:

1. Set address bits (HA0-HA2) to appropriate value (address in binary, for example 110\textsubscript{2} for register #6);
2. Set HRW bit to 0;
3. Set HSEL* and HRD* bits low;
4. Write the upper four bits (a nibble)of data to register\textsuperscript{62} #0;
5. Write the lower nibble of data to register #2;
6. De-assert (set to high) HSEL* and HRD* lines.

Reading:

1. Set address bits (HA0-HA2) to appropriate value (address in binary, for example 110\textsubscript{2} for register #6);
2. Set HRW bit to 1,
3. Set HSEL* and HRD* bits low;
4. Read data (all 8 bits simultaneously);
5. De-assert (set to high) HSEL* and HRD* lines.

\textsuperscript{61}Based on the time diagrams provided by the manufacturer [27]

\textsuperscript{62}Because of the difference between logical and physical implementation of the parallel interface, steps (4) and (5) may not be interchanged!
Based on the above description, each write to the parallel interface register requires two computer I/O port access (steps (i) and (ii) above). Each HIP register access requires 4 (for read\textsuperscript{63}) or 6 parallel interface register accesses (for write). A read of one long word of data (four bytes) from the DSP in a pooling mode\textsuperscript{64}, requires 5 HIP register reads or writes (i.e., \(5 \times (4 \times 2 + 1) = 45\) computer I/O port accesses). A read of the whole buffer, requires \(239 \times 5\) HIP register reads or a total of \(239 \times 5 \times (4 \times 2 + 1) = 10755\) computer I/O accesses. Therefore, even if one computer I/O cycle requires 10 \(\mu\)s, which is a gross overestimate, transfer of a complete 239-point time-resolved signal profile will take \(-110\) ms. If this procedure is too slow or complicated, an interrupt-based transfer through the serial port, towards a PC or other device, at speeds as large as 12 Mbauds can be instituted through the serial interface block after boot-up.

4.6 The Serial Interface

Once the DSP is booted-up through the parallel interface, the serial interface can be used for data exchange with other devices or computers. This interface consists of only four NOT gates that protect the data-transmit and data-receive pins on the DSP. All other serial port logic and control registers are already included in the processor [27]. Since this particular DSP has two serial ports, the other port is used for two interrupt-request lines and one flag line. The interrupt-request lines may be used when the DSP is run in an interrupt-based mode of data acquisition, where the low-to-high and high-to-low changes in the reference interface output

\textsuperscript{63} A HIP register read operation requires an additional I/O port access to perform step (4).

\textsuperscript{64} Pooling is the non-interrupt approach to data transfer between two devices. Device #1 sets data on the bus, informs device #2 that the data is ready, and waits for device #2 to signal that it has finished reading. The second device waits for the data ready signal, reads the data, and informs device #1 that new data can be sent. Although this approach is inferior to the interrupt approach because it slows down the faster device, it provides faster data transfer and is easier to implement.
trigger two different interrupt routines (e.g., integration of the LCP and RCP data). The flag pin, in the non-interrupt data acquisition mode, is used to read the reference interface output.
5. EXPERIMENTAL RESULTS

The SDI analysis of the previous Chapters was entirely theoretical. The objective of this Chapter is to verify the predicted SDI capabilities in a real experimental situation. This will be achieved in the first part of the Chapter.

The second half of this Chapter is concerned with various aspects of the results. These are:

- The average time-resolved profiles obtained in the time-resolved DAQ mode will be shown to verify the theoretical expressions for polarization of light emerging from the PEM.
- Certain peculiarities of the time-resolved profile of gaseous (+)-3-methylcyclopentanone require discussion of the interaction of polarized light with matter. The effect of absorber on the electromagnetic radiation field will be investigated for the special case of only one active transition and identical absorber orientations. These results will then be generalized to the situation of many quasi-degenerate transitions and many molecular orientations. The power loss in two particular cases of experimental interest will be emphasized: the isotropic sample and a thin partially-oriented film. A form for a fit function that can be used to parametrize the average time-resolved profile and a model for absorptivity in the sample cell will emerge from these discussions.
- An anomalous pressure-dependent behavior of absorption and CD spectra occurs at high optical densities. This anomaly will be discussed and a model, based on light scattering, will be introduced in order to interpret it.

A detector current processed by a DAQ device was the focus of the analysis of the measuring techniques discussed in Chapter 3. However, current is merely a representation of the desired experimental quantity, namely the light intensity. Therefore, because of its focus on experiment, this Chapter will emphasize light intensity and not PMT current. This may well be
a needless distinction because the PMT current and the light intensity became interchangeable quantities when the PMT operates in the linear regime.

5.1 Experimental Verification of SDI Capabilities

Various predictions about SDI capabilities were made throughout the previous Chapters. These will now be subjected to experimental test.

5.1.1 The Average Time-Resolved Profile of a Modulated Signal

The time-resolved profile\(^{65}\) of (+)-3-methylcyclopentanone is shown in Figure 5.1.

![Figure 5.1 Average 240-window time-resolved profile\(^{65}\) of (+)-3-methylcyclopentanone at 198.8 nm (solid line). More than 20 million signal periods had to be averaged because of the high sample absorbance (i.e., low transmitted light intensity) in order to obtain shown noise levels in the absence of filtering. The polarization of light at time \(t\) is given by \(I(1.018t + 0.1)\), per Eq. 2.3 and a retardation amplitude \(\delta = \pi\). The theoretical curve is the dashed line. Each point on the profile is the intensity of transmitted light of a particular polarization. To our knowledge, these are the first PEM/PMT measurements of the complete time-resolved profile of a sample exhibiting CD. Indeed, only a difference of intensities corresponding to two different linear polarizations (LD) or two different circular polarizations (CD) had been measured.

\(^{65}\) The transmitted light intensity on the y-axis is relative (i.e., \(I_{\max} = 1\)) and only the oscillatory part of interest is shown. The time scale was chosen so that the integration period is \(T = 2\pi\).
previously. The match of experiment and theory of Figure 5.1 is excellent, and it will be discussed further in Sections 5.4.2 and 5.4.4.

Another example of a time-resolved profile is shown in Figure 5.2. In this case, signal modulation was obtained in the absence of a sample. Instead, in a PEM test measurement, a linear polarizer was inserted into the light path after the PEM. When done by oscilloscope, these measurements require powerful light sources such as lasers because the polarization dependent intensity profile must be recorded in one modulation period: oscilloscopes usually do not perform signal averaging and, if they do, the number of profiles averaged is limited to a few thousand passes because of excessive processing overhead. Consequently, unless expensive dye lasers and/or optics are used, such experiments are limited to one wavelength only, usually the 632.8 nm line of a low-cost and easy to use CW helium-neon laser. The low-overhead time-resolved averaging capabilities of the SDI, on the other hand, permit measurements at the low light intensities and at any wavelength produced by widely-available laboratory lamps.

Figure 5.2 Average 240-window time-resolved profile obtained when a linear polarizer is inserted after the PEM (solid line). Because of strong signal and high light intensity, only 1 million periods had to be averaged to achieve these noise levels. The light polarization can be estimated as $I(t) = (1.014t + 0.05)$, per Eq. 2.3, with $\delta = 2.35\pi$. The theoretical curve is the dashed line.
The average profile shown in Figure 5.2 required more than 1 million integration periods. Weaker signals, such as that of Figure 5.1, may require ten times as many periods to reduce error to acceptable levels. The measured and theoretical curves of Figure 5.2 are in excellent agreement, a facet that will be discussed in detail in Section 5.2.

5.1.2 Separate Measurement of the LCP and RCP Components

The SDI enables one to avoid deconvolution problems by separate and "simultaneous" measurement of LCP and RCP light contributions. These contributions for (+)-3-methylcyclopentanone are shown in Figure 5.3. Even though theory predicts that the two contributions should be symmetrical relative to a linear component, that is not the case. This

![Graph showing LCP and RCP components of (+)-3-methylcyclopentanone](image)

Figure 5.3 LCP and RCP components of (+)-3-methylcyclopentanone in the range 192.8 to 200 nm. The two components are shown relative to the absorbance of linearly polarized light (\( \hat{x} + \hat{y} \)) in order to provide better discrimination. Experimental parameters are given in Table 5-1.
Table 5-1 Experimental Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Smoothing</th>
<th>Step size (Å)</th>
<th>Slit width (μ)</th>
<th>Pressure (Torr) ±5%</th>
<th>Integration interval (s)</th>
<th>Constant S/N</th>
<th>Time (hours)</th>
<th>δ</th>
<th>Mode</th>
<th>File size</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 5.4 (high press.), Figure 5.22 (a), Figure 5.23 (a)</td>
<td>combined (140,5,1)</td>
<td>0.015</td>
<td>130</td>
<td>0.6</td>
<td>5 (at 200 nm)</td>
<td>yes</td>
<td>18</td>
<td>π/2</td>
<td>time resolved</td>
<td>7MB</td>
</tr>
<tr>
<td>Figure 5.16 (high press.)</td>
<td>2D gaussian (100,35,5,1)</td>
<td>0.02</td>
<td>130</td>
<td>760</td>
<td>1</td>
<td>no</td>
<td>3.5</td>
<td>π/2</td>
<td>time resolved</td>
<td>5MB</td>
</tr>
<tr>
<td>Figure 5.19 (high press.)</td>
<td>No</td>
<td>0.02</td>
<td>100</td>
<td>0.35</td>
<td>1 (at 200 nm)</td>
<td>yes</td>
<td>n/a</td>
<td>π/2</td>
<td>windowing</td>
<td>34KB</td>
</tr>
<tr>
<td>Figure 5.7, Figure 5.19 (both low pressure)</td>
<td>No</td>
<td>0.02</td>
<td>130</td>
<td>0.35</td>
<td>12 (at 200 nm)</td>
<td>yes</td>
<td>8</td>
<td>π/2</td>
<td>time resolved</td>
<td>0.5MB</td>
</tr>
<tr>
<td>Figure 5.22 (curve d)</td>
<td>Combined (71,5,1)</td>
<td>0.02</td>
<td>130</td>
<td>1.05</td>
<td>12 (at 199.5 nm)</td>
<td>yes</td>
<td>6</td>
<td>π/2</td>
<td>time resolved</td>
<td>0.4MB</td>
</tr>
<tr>
<td>Figure 5.23 (curve c)</td>
<td>Combined (111,5,1)</td>
<td>0.01</td>
<td>130</td>
<td>0.8</td>
<td>12 (at 199 nm)</td>
<td>yes</td>
<td>6</td>
<td>π/2</td>
<td>time resolved</td>
<td>0.4MB</td>
</tr>
<tr>
<td>Figure 5.3, Figure 5.4 (low press.), Figure 5.5, Figure 5.6</td>
<td>Combined (42,5,1)</td>
<td>0.1</td>
<td>130</td>
<td>0.35</td>
<td>80</td>
<td>no</td>
<td>18</td>
<td>π</td>
<td>time resolved</td>
<td>0.7MB</td>
</tr>
<tr>
<td>Figure 5.8</td>
<td>4-consecutive point average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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66 These sets of numbers describe the smoothing parameters. Smoothing is discussed in detail in Section 5.4.4.

Combined: (# of neighboring wavelength points, gaussian height at center, gaussian weight at edge)

2-D gaussian: (# of neighboring wavelength points, # of neighboring polarization points, gaussian weight at center, gaussian weight at edge)

67 PEM retardation amplitude

68 Due to high sample absorbance, the constant S/N ratio mode was disabled between 198.7 and 198.8 nm.

69 Two windows, 6.33 μs in size, centered at T/4 (RCP) and 3T/4 (LCP); T = 20 μs
deviation will be discussed latter. To our knowledge, separate LCP and RCP profiles for any molecule in the VUV region are unavailable.

Another situation in which a separate measurement of the LCP and RCP components is required is illustrated in Figure 5.4. The low and high pressure CD spectra are shown in part (a).

![Figure 5.4](image_url)

Figure 5.4 Illustration of the scattering effects on the CD of (+)-3-methylcyclopentanone in the range 193.7 to 200 nm. Experimental parameters are given in Table 5-1. The low pressure CD, after adjustment to the same scale as the high pressure CD, is shifted downwards by 0.0005 units to provide better curve discrimination.

(a) High (upper curve) and low (lower curve) pressure CD.

(b) High pressure CD (upper curve) adjusted for scattering. For comparison, the low pressure CD of part (a) is also shown. The relative heights of the two most prominent peaks in the two curves are now essentially identical.

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As may be seen, the relative heights of the 198.7 and 194.2 nm peaks are pressure dependent. It will be argued later that this dependence is due to scattered light. However, when the LCP and RCP components are measured separately, the CD spectrum can be adjusted for these effects as shown in part (b). The nature of this adjustment will be discussed in Section 5.5.

5.1.3 The Simultaneous Measurement of Absorption, CD and LD Spectra

Absorption, CD and LD spectra of (+)-3-methylcyclopentanone, all recorded in a single scan, are shown in Figure 5.5. The origin of the LD will be discussed in Section 5.4.4.

Figure 5.5  Absorbance, CD and LD spectra of (+)-3-methylcyclopentanone in the range 192.8 to 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 LD are shown in (b) and (c), respectively. Experimental parameters are given in Table 5-1. Horizontal arrows denote the scales to which the various spectra refer.
The SDI, because of its high sensitivity, can measure CD even in the presence of a strong LD component, a phenomenon characteristic of partially-oriented samples. This is a new capability, one not feasible previously.

5.1.4 A 3-D Absorbance Measurement

The SDI can measure absorbance as a function of both polarization and wavelength. One such 3-D surface for gaseous (+)-3-methylcyclopentanone is shown in Figure 5.6. To our knowledge, no such measurements have ever been reported.

![3-D spectra of (+)-3-methylcyclopentanone](image)

Figure 5.6 The 3-D spectra of (+)-3-methylcyclopentanone in the range 193 to 200 nm. The graph depicts polarization (time) and absorbance relative to that of LP light (Eq. 3.22 with $l_{av}$ replaced by $l_{av}([\tilde{\Pi}(t)]$) and $l_{av}(RCP)$ replaced by $l_{av}(x + y)$. The time-dependent light-polarization vector $\tilde{\Pi}(t)$ is given in Eq. 2.3. Experimental parameters are given in Table 5-1.
5.1.5 A Demonstration of Wide Dynamic Range

This feature is demonstrated in the spectra of Figure 5.7. The entirety of Figure 5.7 was collected in a single pass in which no gain-switching occurred.

Figure 5.7 A demonstration of the wide dynamic range of the SDI. The high-pressure absorbance profiles are shown in (b), (c), and (d). These spectra were recorded in a single scan, with no gain switching. Two of the curves have multipliers, as shown, in order to enhance their structure. The low-pressure absorbance profile is shown in (a). The sharp peak on curve (b), just below 200 nm, was artificially generated by closing the monochromator slits, and is used to estimate the PMT dark current. Comparison of its value, ~4.5, with the value of the signal on the flat part of (b), ~2.4 (i.e., $I_{dark\text{-}current} < 10^{-2}I_{flat}$), indicates that the flattening is caused by loss of structure in the light exiting the sample cell (i.e., it is not caused by noise or biases in the system). The experimental parameters are given in Table 5-1.

The dynamic range of the SDI depends on integration time and can be calculated as follows: in a 1s integration, 239x50000 9-bit samples with values between 0 (no signal) and 510 (maximum signal) are collected from the ADC block. If all these samples are added together, the sum lies between 0 and 510x239x50000 = 6.0945x10^9. Since a difference of unity

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between any such two sums can be measured, a relative resolution of $1/6.0945 \times 10^9$ is possible. In other words, for an integration of 1.63 s, the SDI range is exactly 10 orders of magnitude.

The absorption spectrum is seen to flatten in the region below 200 nm. The cause of this flattening will be discussed in Section 5.5.

5.1.6 The Constant S/N Ratio Mode

The effects of this mode are illustrated in two ways in Figure 5.8. In the first approach, a non-filtered CD spectrum was generated. As shown in part (a), in that region of the spectrum in which the constant S/N mode was enabled, noise-related oscillations in the signal are constant. However, in the small wavelength region where the absorbance was maximum and the constant S/N ratio mode was disabled, the oscillations are much larger. The second approach uses a theoretical fit (derived in Section 5.4.4) to the measured time-resolved profile. Once the fitting constants are obtained, the error between fitted and measured profiles can be calculated as

$$\sigma = \frac{1}{N} \sqrt{\sum_{j=0}^{N-1} \left( i_{\text{avg-measured}}(j \Delta t) - i_{\text{avg-fit}}(j \Delta t) \right)^2}$$  \hspace{1cm} 5.1$$

where $i_{\text{avg-measured}}$ and $i_{\text{avg-fit}}$ are the measured and fitted average time-resolved profiles known at $N$ values of $t$ (windows), each separated by the sampling time $\Delta t = 83.33$ ns. This error is plotted in part (b) as a function of wavelength. As may be seen, the error is "constant" when the mode is enabled and increases immediately once it is disabled. These results demonstrate that the measurement of a time-resolved profile combined with a theoretical fitting procedure produces an excellent estimate of the error (noise level) for any point in the spectrum.

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Absorbance becomes essentially horizontal (i.e., "flat")
Figure 5.8  An illustration of the influence of a constant S/N ratio mode on the errors in a high pressure measurement. The mode was disabled between 198.88 and 198.70 nm. The experimental parameters are given in Table 5-1.

(a) Unsmoothed CD curve (the corresponding CD is shown in Figure 5.4). In the wavelength interval in which the constant S/N ratio mode was disabled, the CD exhibits a large increase of the noise level.

(b) The error, Eq. 5.1, between measured and fitted average time-resolved profiles as a function of wavelength. The error is expressed as a percentage of the average light intensity at each wavelength.

5.1.7  Pulse Height Distribution

The SDI can measure pulse-height distributions because it operates in a non-photon count regime. The result of one such measurement of pulses originating in a PMT was shown in Figure 3.11. This result was used to argue that over-amplification can be used to lower the threshold of an ADC.
Verification of these predicted SDI capabilities was based on experimental results. The SDI advantages that cannot be supported by other direct experimental results, but which are direct consequences of the capabilities just demonstrated will now be elaborated.

5.1.8 Elimination of Voltage Feedback

As a consequence of wide dynamic range, the SDI makes PMT voltage feedback unnecessary. Indeed, all the results shown in this work, whether at low or high sample pressures, were obtained without any voltage feedback whatsoever.

Voltage feedback is common to all methods based on the lock-in amplifier, and is beset by two major problems: a) non-linearity of PMT output current and applied voltage; and b) the increase of PMT voltage required at low light intensities for maintenance of the lock-in in the optimal working regime, while it does not alter the statistical noise inherent in the signal itself, certainly leads to a counter-productive increase of the PMT dark-current. The SDI avoids both problems.

5.1.9 Faster Scanning Speeds

Faster scanning speeds are a direct consequence of the constant S/N ratio mode. When this mode is enabled, the scanning speed need not be selected to handle the noisiest part of the spectrum. Indeed, the scan speed automatically adjusts to compensate for alterations of light intensity. For example, the constant S/N ratio illustrated in Figure 5.8 was obtained by keeping the sum over all windows in the time-resolved profile constant at all wavelengths. In other words, the scan speed is inversely proportional to the light intensity arriving at the PMT. In the region in which the mode was disabled, the integration interval was equal to that at 200 nm given in Table 5-1.
5.1.10 Post-Experimental Data Processing

The SDI performs all essential on-the-fly processing such as selective integration and re-synchronization. If required, other numerical post-processing (e.g., elimination of bias or smoothing) may be performed after data collection is completed. For example, gaussian or laplacian deconvolutions or least squares fits to a time-resolved profile are much better smoothing methods than those performed by analog integrators in the output stage of a lock-in amplifier: the latter fails if the light intensity and the CD undergo rapid alterations at higher time constants and, in such cases, slower scanning speeds must be imposed.

5.1.11 Time-Resolved Pulse-Counting

The combination of the time-resolution and on-the-fly capabilities of the SDI facilitates efficient (i.e., low overhead), low-light-intensity, time-resolved photon count measurements (less than $\sim 2 \times 10^6$ photons/sec) in which, in addition to the photon counting, an exact time of photon arrival at the detector must be recorded. This time information, for example, can be used to determine photon polarization when a PEM is used. And, if the pulse height carries useful information, this can be recorded also.

5.1.12 Commercial Aspects

The SDI is a transferable device. It can be used in any experiment that involves one or multiple modulations of the intensity of light incident on a detector. If the detector requires a preamplifier with gain switching capabilities, there exists a simple on-the-fly compensation for such changes. At this point, the applicable modulation frequencies have an upper-bound of 10 MHz and no lower bound.

\footnote{For example, the light intensity obtained from the previous wavelength step can be used to determine whether or not a gain-switch is required. If yes, the gain can be changed and the corresponding multiplication factor recorded. This factor may be used later to adjust window sums for a particular wavelength step (i.e., pre-amplifier gain).}
The SDI is in varying stages of the patenting process. Its continuing development will be funded by an LEQSF grant if a private company interested in manufacturing the device is found.

5.2 A Discussion of Results Obtained in The SDI Time-Resolved DAQ Mode

The modulation of light polarization by PEM was described in Chapter 2. The power carried by the LCP (RCP) component, as given by Eq. 2.9, was based on the assumption that the modulated light polarization was described by Eq. 2.3. This assumption can be tested using an additional linear polarizer positioned after the modulator as shown in Figure 5.1.

![Figure 5.9](image)

Figure 5.9 Optical arrangement for measurement of PEM light polarization. If the source is a laser and the detector is a semiconductor diode, an oscilloscope is the instrument of choice. For low intensities, a PMT and SDI must be used. The arrows denote the orientations of the polarization axes of the two linear polarizers. The PEM crystal must be rotated so that its major optical axes lie at angles of 45° to the arrow direction.

Different detection systems are required for high and low-level intensities: if an intense light source and a semiconductor diode detector are used, the oscilloscope is the instrument of choice; if a weak light source (e.g., an H₂ lamp) is used, a more sensitive detector and time-resolved averaging is a prerequisite. Therefore, the apparatus of Figure 2.1, rearranged...
according to Figure 5.9, represents an ideal test case for the PMT/SDI combination. The result of one such measurement is given in Figure 5.2. The purpose of this Section is to validate that measurement in terms of the theoretical profile also shown in Figure 5.2.

The effects of a 45° linear polarizer on an arbitrarily polarized light beam, $\vec{\Pi}_{in}$, is described [11] by the 2x2 matrix, $M_{x-y}$:

$$\vec{\Pi}_{out} = M_{x+y} \vec{\Pi}_{in} = \frac{1}{2} \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix} \vec{\Pi}_{in} \quad \text{(5.2)}$$

where the first and the second row of the polarization vector denote the x and y polarization components respectively, expressed in a coordinate system defined by the major optical axes of the PEM crystal. Therefore, a linear polarizer inserted after the PEM yields the polarization vector $\vec{\Pi}_{PMT}$

$$\vec{\Pi}_{PMT}(t) = M_{x+y} \vec{\Pi}(t) = \frac{1}{2\sqrt{2}} \left( 1 + \exp\left[i\delta\sin(\Omega t)\right] \right) \quad \text{(5.3)}$$

where $\vec{\Pi}$ is defined in Eq. 2.3. The intensity of the light incident on the PMT, $I(t)$, is then calculated by the procedures of Chapter 2 as

$$I_{avg}(t) = \frac{I_0}{2} \left\{ 1 + \cos\left[ \delta\sin(\Omega t) \right] \right\} \quad \text{(5.4)}$$

Unfortunately, a linear polarizer that produces a single beam of polarized light in the 200nm range was not available\(^{72}\). A Rochon beam splitter which, as described in Chapter 2, produces two spatially separated and orthogonal linearly polarized beams was used in place of the second polarizer. However, because of the particular experimental arrangement, the light beam incident on the splitter is divergent and the two linearly-polarized components overlap

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\(^{72}\) Such linear polarizers are very expensive and very scarce.
spatially. Consequently, neither component can be blocked completely and Eq. 5.4 must be modified to incorporate both polarizations

$$I_{\text{avg}}(t) = \frac{I_0}{2} \left\{ 1 + \cos[\delta \sin(\Omega t)] \right\} + \beta \frac{I_0}{2} \left\{ 1 - \cos[\delta \sin(\Omega t)] \right\}$$

5.5

where the second term corresponds to $\tilde{x} - \tilde{y}$ linearly-polarized light as obtained from Eq. 5.3 by replacing $M_{x-y}$ with $[11]$

$$M_{x-y} = \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix}$$

5.6

and $\alpha$ and $\beta$ are coefficients with values between 0 and 1. By rearranging terms, Eq. 5.5 can be cast into a form similar to Eq. 5.4

$$I_{\text{avg}}(t) = I_0 \frac{\alpha + \beta}{2} + I_0 \frac{\alpha - \beta}{2} \cos[\delta \sin(\Omega t)]$$

5.7

but in which the constant and oscillatory terms now have different magnitudes. The power is split equally between the two beams (i.e., $\alpha = \beta = 1$) in normal operation, and the intensity has no oscillatory part. If this is not the case (i.e., if one of the beams is partially blocked), the corresponding coefficient becomes smaller and an oscillatory term appears. However, since only a qualitative analysis based on the shape of the oscillatory part of $I(t)$ is of interest and since this shape is the same as that of the single-beam case of Eq 5.4, a beam splitter may be used in place of a single-beam polarizer.

The experimental and theoretical curves for $I_{\text{avg}}(t)$ for a retardation amplitude $\delta = 2\pi$ are shown in Figure 5.10(a). The two profiles of a given pair of curves may differ in several aspects:

(i) The frequencies of the two signals may differ.

(ii) The phasing may be different.
Figure 5.10 Comparison of experiment and theory for $I_{\text{avg}}(t)$ at $\delta \approx 2\pi$. The experimental profile is the solid line. It was obtained in the time-resolved mode of data acquisition, 240 windows per integration period. The time unit was re-normalized so that $T = 2\pi$. The calculated profile (dashed line) is shown for four different cases: (a) $\Omega = 1$ and $\delta = 2\pi$, corresponding to the situation in which the calculated signal period is equal to the integration period; (b) a frequency-adjusted profile for $\Omega = 1.018$; (c) a frequency-adjusted profile averaged over four integration periods; and (d) an averaged, frequency-adjusted profile for which $\delta = 0.95 \times 2\pi$. 

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(iii) The values of $I_{\text{avg}}(t)$ may be different. Different frequencies are not a surprise. As discussed in Chapter 4, the signal period will almost never be an integer multiple of the sampling time. Yet, this assumption was used to calculate the dashed profile of Figure 5.10(a). The frequency-adjusted curve is shown in Figure 5.10(b). While adjustment cures the frequency problem, it does not solve the phase shift problem. Moreover, even when the theoretical curve is phase shifted, the $I(t)$ differences of the minima remain unexplained. It turns out that these problems are associated with data averaging. In order to minimize the data processing overhead, it was necessary to average more than one period of the input signal prior to re-synchronization. As a result, errors were created. If the frequency-adjusted theoretical curve is averaged over four integration periods, Figure 5.10(c) results, and there is good congruence of experiment and theory. Finally, if the retardation amplitude $^7$ is taken to be $\delta = 0.95x2\pi$, the theoretical and measured profiles become identical, as shown in Figure 5.10(d). One might argue that the adjustability of three parameters (i.e., the number of integration periods, the value of $\delta$, and the frequency of the signal) confers too much freedom on the simulation process; that, however, is not the case because each parameter influences a quite different aspect of the profiling.

Similar comparisons have been made for four other values of $\delta$. The results for $\delta = 2.35\pi$ and $\Omega = 1.014$ were shown in Figure 5.2, and were excellent. Three other cases are presented in Figure 5.11 and, once again, theory and experiment are congruent. Based on these results, one may conclude:

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$^7$ The amplitude of the sinusoidal voltage applied to the PEM crystal was selected so that the experimental profile resembled the calculated curve. The fine tuning of the retardation amplitude $\delta$ by comparison of the two curves is then used to estimate the proper voltage. For example, a voltage of 6.2 V was estimated to be close to the correct value at 200 nm. Fine tuning, illustrated in Figure 5.10, showed that the corresponding retardation was only $0.95x2\pi$. Therefore, the voltage that should have been chosen was 6.5.
Figure 5.11 Comparison of experimental and theoretical $I_{\text{avg}}(t)$ profiles for three different PEM retardation amplitudes. Experiment (solid line) was performed in the time-resolved mode: 240 windows per integration period, four integration periods between each re-synchronization, and averaging over more than a million integration periods. The calculated curves (dashed lines) were adjusted for averaging, frequency, and retardation amplitude. The adjusted frequencies and adjusted retardation amplitudes are: (a) $\Omega = 1.016$ and $\delta = 1.5\pi$, (b) $\Omega = 1.018$ and $\delta = 0.95\pi$, and (c) $\Omega = 1.022$ and $\delta = 0.55\pi$. The time unit was renormalized so that $T = 2\pi$. 

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(i) Equation 2.3 adequately describes the polarization of the light leaving the PEM.

(ii) The SDI time-resolved mode operates exactly as expected.

5.3 The Time-Resolved Profile of (+)-3-methylcyclopentanone

An averaged time-resolved profile of (+)-3-methylcyclopentanone is shown in Figure 5.1. This profile constitutes a test of the ability of the SDI time-resolved mode to operate properly when smaller modulated signals than those discussed in the previous Section are measured. To test for the presence of CD and LD, both $\hat{x} + \hat{y}$ and $\hat{x} - \hat{y}$ linear polarizations, denoted LP$_{x+y}$ and LP$_{x-y}$, respectively, were generated at a PEM retardation constant setting of $\delta = \pi$. An increase of $\delta$ beyond this point does not, according to Eq. 2.3, generate any new polarizations. The informational content of the profile may be analyzed as shown in Figure 5.12. The polarization of light corresponding to any point on the measured curve may be determined using the adjusted theoretical profile$^{74}$ of Figure 5.11(b). LP$_{x+y}$ light corresponds to the maxima of the theoretical curve. LP$_{x-y}$ light corresponds to the minima of the theoretical curve. Circular polarizations correspond to the profile at the half-heights. Since each polarization is generated twice in one period, the average of the corresponding points is taken to be the correct value. The differences of average values are then proportional to LD and CD. Thus, using Eq. 3.22, the value of the CD is $(2.771 - 2.775)/(2.771 + 2.775) = -0.0043$, and that for the LD is $(2.767 - 2.756)/(2.767 + 2.756) = 0.002$.

Both circular and linear dichroisms are present in the time-resolved profile of gaseous (+)-3-methylcyclopentanone. However, all directions should be equivalent in an isotropic samples and, consequently, no difference between the absorption of horizontally and vertically

$^{74}$ The theoretical profile must be used since the time scales on figures are always shown with respect to the integration period and the signal averaging causes apparent phase shifting.
polarized light should occur. That is, it is expected that $\Delta D = 0$. A discussion of the interaction of polarized light with matter and of the nature of the absorbing material is required in order to interpret this happenstance.

Figure 5.12 Average time-resolved profile of (+)-3-methylcyclopentanone at 199.88 nm. The smooth profile was obtained from that of Figure 5.1 by an equal-weight averaging over 10 neighboring points (five to the left and five to the right of the point of interest). Points corresponding to the various polarizations are determined with the help of the calculated curve of Figure 5.11(b). 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$_{x,y}$.

5.4 Theoretical Background

Both the time-resolved profile and the wavelength-dependent MPS of gaseous (+)-3-methylcyclopentanone discussed in Section 5.1 are anomalous in the sense that an $\Delta D$, which should not exist, is present. In order to explain this effect, theoretical expressions for polarization-dependent transmitted light intensities are needed. These expressions may be obtained from the analysis of the interaction of polarized light with matter pioneered by R.
Clark Jones [32, 33]. Jones identified eight parameters that describe how matter interacts with polarized light. A general matrix form for computation of the intensity of a transmitted light of arbitrary polarization was later obtained by Jensen [34] in the Stokes’ representation, but in terms of these Jones’ parameters.

Jones obtained his matrix phenomenologically by identifying the ways in which matter may influence the amplitude and polarization of light passing through it. It will be shown here that this same matrix can also be obtained in terms of the transition matrix elements that emerge from a semi-classical treatment of light-matter interactions. As a result, the number of parameters reduces from eight to four. To our knowledge, such derivations of the Jones’ matrix or of the transmitted light intensities in terms of transition matrix elements are not available elsewhere. The advantage of this new approach is that the shape of the time-resolved profile can be related directly to the electronic structure. Jansen’s results are not used here: the representational change from the Stokes’ to Jones’ formalism and the subsequent replacement of the characteristic parameters by their transition matrix counterparts is too complex and too indirect compared to the approach adopted here.

A 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 is done in Appendix A. The derivation of transmitted light intensities for two more general cases, namely an

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5 The Stokes’ representation offers the advantage of specifying the light intensity as one of the four parameters used to describe light [11, 32, 33, 34].

6 Even though Jones identified eight parameters, they are not independent. The corresponding real and imaginary parts are related by Kramers-Kronig relations [15]. Therefore, there are only four independent parameters. The reason all eight parameters are retained is that it is apparently easier to measure all eight of them than to measure only four and then use the KK relations to find the other four.
isotropic sample and a thin partially-oriented film, is required in order to build a model of a sample cell that can explain the presence of an anomalous LD. These derivations, originating in the material of Appendix A, will be given now.

5.4.1 Isotropic Sample

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

$$A = k \left[ i + \frac{1}{F} \sum_{f=1}^{F} g_f(\omega) \frac{1}{N} \sum_{n=1}^{N} |\tilde{M}_{nf}(\Pi_{n1x}\hat{x})|^2 \right]$$

where $F$ is the number of transitions induced by the radiation, $N$ is the number of different molecular orientations in the sample, $\Pi_{n1x}$ is the $x$ component of $\Pi_1$, Eq. 3.20, for the $n^{th}$ molecular orientation, and $\tilde{M}_{nf}$ is the corresponding vector operator defined in Eq. A.7.

Similarly, the $B_1$, $B_2$, and $C$ coefficients can be generalized to

$$B_1 = k \frac{1}{F} \sum_{f=1}^{F} g_f(\omega) \frac{1}{N} \sum_{n=1}^{N} \tilde{M}_{nf}(\Pi_{n1x}\hat{x})\tilde{M}_{nf}^*(\Pi_{n1y}\hat{y})$$

$$B_2 = k \frac{1}{F} \sum_{f=1}^{F} g_f(\omega) \frac{1}{N} \sum_{n=1}^{N} \tilde{M}_{nf}^*(\Pi_{n1x}\hat{x})\tilde{M}_{nf}(\Pi_{n1y}\hat{y})$$

$$C = k \left[ i + \frac{1}{F} \sum_{f=1}^{F} g_f(\omega) \frac{1}{N} \sum_{n=1}^{N} |\tilde{M}_{nf}(\Pi_{n1y}\hat{y})|^2 \right]$$

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 $B_5$, the expressions for $B_1$ and $B_2$ can be rewritten as
The constants defined in Eq's. 5.8 and 5.9 are valid only if the sample is an "equal" mixture of different molecules and molecular orientations: 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 absorption cells, one after another but containing two different samples, cannot be treated as a single cell of the same 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 separated samples.

For an isotropic sample, further simplifications are possible. First, the sum over $n$ becomes an integral over all possible orientations, and $A$ and $C$ become equal [3]

$$A = C = k \left[ i + \frac{1}{F} \sum_{f=1}^{F} g_{f \alpha} \frac{1}{3} |\bar{M}_f|^2 \right]$$  \hspace{1cm} 5.11

where

$$\frac{1}{3} |\bar{M}_f|^2 = \frac{1}{3} \sum_{x,y,z} \left[ |\bar{M}_f(x,\hat{i})|^2 + |\bar{M}_f(y,\hat{i})|^2 + |\bar{Q}_f(y,\hat{i})|^2 \right]$$  \hspace{1cm} 5.12

Furthermore, because of the orientational averaging, the $B_f$ coefficients become purely imaginary (i.e., $B_1 = -B_2 = B$) [3]. Using these properties, the polarization-dependent intensity of transmitted light, Eq. A.24, in an isotropic sample becomes

$$I = \frac{c}{8\pi k} \exp \left[ -2 \text{Re}(A)z \right] \ln \left[ I_0 K_1 + 2 \text{Im}(E_{x0} E_{y0}^*) K_2 \right]$$  \hspace{1cm} 5.13

where
\[ K_1 = iB^* \sinh[2 \text{Im}(B)L] - A^* \cosh[2 \text{Im}(B)L] \]
\[ K_2 = iB^* \cosh[2 \text{Im}(B)L] - A^* \sinh[2 \text{Im}(B)L] \]  

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 and the electric-dipole/electric-quadrupole terms survive \([3]\). As a result, the value of \( \text{Im}(B) \) is of the order of \( 10^{-7} \text{Re}(A) \), which contains the dominant dipole term. Consequently, \( \text{Re}(A) \) (or \( \text{Re}(C) \)), which can be estimated from the exponential factor in Eq. 5.13, becomes solely responsible for power loss. For example, at intermediate pressures (~600 mTorr) of (+)-3-methylcyclopentanone at the 198.7 nm absorption peak, \( 2 \text{Re}(A)L \) is of the order of 1 (i.e., \( \text{Re}(A) = \text{Re}(C) \approx 10^{-11} \) when \( L = 25 \text{ cm} \)). Since sample absorbances do not usually exceed 3, this estimate of \( \text{Re}(A)L \) (or \( \text{Re}(C)L \)) is an upper limit. Consequently, \( \text{Im}(B)L \) is of the order of \( 10^{-3} \) or less, and the hyperbolic terms of Eq. 5.14 can be expanded and truncated to first order to yield

\[ \cosh[2 \text{Im}(B)L] - 1 \]
\[ \sinh[2 \text{Im}(B)L] - 2 \text{Im}(B)L \]  

Thus, one finds

\[ K_1 \approx -A^* \]
\[ K_2 \approx -A^* 2 \text{Im}(B)L \]  

When \( A \) in the non-exponential terms is replaced by \( \text{ik} \), a valid approximation because the second term of Eq. 5.11 is of the order of \( \text{Re}(A)/k \approx 10^{-6} \), and when \( K_1 \) and \( K_2 \) of Eq. 5.16 are inserted into Eq. 5.13, an approximate expression for transmitted light intensity is obtained as
Finally, when the polarization of light passing through the sample cell is altered with a PEM, the average time-resolved profile of Eq. 5.17 becomes

\[ I_{\text{avg}}(t) = \frac{c}{8\pi} I_0 \exp\left[-2\text{Re}(A)L\left\{ I_0 + 4\text{Im}(B)L\text{Im}(E_xE_y^*) \right\} \right] \]

5.18

and the CD and LD are obtained from Eq. 3.22, for \( \delta = \pi \), as

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

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

5.19

\[ LD = \frac{1}{2.303} I_{\text{avg}}\left(\frac{\pi}{2}\right) - I_{\text{avg}}(\pi) \]

\[ = 0 \]

A complete cycle of \( I_{\text{avg}}(t) \) for \( 0 \leq t < T = 2\pi \) and \( \delta = \pi \), shown in Figure 5.13, supports the assertion that an isotropic sample cannot produce the experimental shape of Figure 5.1.

![Figure 5.13](image-url)  

**Figure 5.13** Shape of the oscillatory part of the polarization-dependent average time-resolved profile, \( I_{\text{avg}}(t) \) of Eq. 5.12, for a retardation amplitude \( \delta = \pi \).
(or Figure 5.12). Therefore, some other factor is responsible for the observed linear dichroism.

Also, as expected, Eq. 5.19 indicates that the wavelength dependent CD and absorption profile for a single transition should be identical.

5.4.2 Partially-Oriented Sample

The most general treatment of partially-oriented sample is complicated and does not provide much insight. Instead, three special pertinent cases will be considered. 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. A.23 multiplied by the thickness of the sample is much smaller than unity. Consequently, the solution to the system of differential equations of Eq. A.17 can be approximated by

\[
E_x(\Delta z) = \exp \left[ -\frac{A + C}{2} \Delta z \right] E_{x0} - \frac{A - C}{2} E_{x0} \Delta z - B_1 E_{y0} \Delta z
\]

\[
E_y(\Delta z) = \exp \left[ -\frac{A + C}{2} \Delta z \right] E_{y0} - B_2 E_{x0} \Delta z - \frac{C - A}{2} E_{y0} \Delta z
\]

When Eq's. A.17 and 5.20 are inserted into Eq. A.26, an expression for transmitted light intensity is obtained. If only terms of \(O(\Delta z)\) are retained in the non-exponential parts, and the properties \(|B_1| < 1, |B_2| < 1, \text{Re}(A) < \text{Im}(A), \text{Re}(C) < \text{Im}(C)\) are used, the final expression for transmitted intensity simplifies to

\[
I \sim \frac{c}{8\pi} \exp \left[ -\text{Re}(A + C) \Delta z \right] \times
\]

\[
\left\{ I_0 - \Delta z \left[ \text{Re} \left( E_{x0} E_{y0}^* (B_1^* + B_2) \right) \right] + \text{Re} \left[ \frac{i}{k} \left( E_{x0} E_{y0}^* B_1^* + E_{x0}^* E_{y0} B_2^* \right) \right] \right\}
\]

**To emphasise this "smallness." sample thickness will be denoted \(\Delta z\) even though the sample need not be thin.**
which, upon insertion of Eq. 5.10, yields

\[ I \sim \frac{c}{8\pi} \exp\left(- \text{Re}(A + C)\Delta z\right) x \]

\[ \left\{ I_0 - \frac{2}{F} \sum_{f=1}^{F} \left\{ 2\Delta z \text{Re}\left[g_f(\omega)\right] - \frac{1}{k} \text{Im}\left[g_f(\omega)\right] \right\} \text{Re}\left[E_{x0}E_{y0}^*B_f^*\right] \right\} \]

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

\[ I_{\text{avg}}(t) \sim \frac{c}{8\pi} I_0 \exp\left(- \text{Re}(A + C)\Delta z\right) x \]

\[ \left\{ 1 - \frac{2}{F} \sum_{f=1}^{F} K_f(\omega) |B_f| \cos\left(\delta \sin(\Omega t) - \varphi_{Bf}\right) \right\} \]

where

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

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

The corresponding CD and LD are given by

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

\[ LD = -\frac{2}{2.303F} \sum_{f=1}^{F} K_f(\omega) |B_f| \cos\left[\varphi_{Bf}\right] \]

Equations 5.21, 5.22, and 5.23 lead to the following conclusions:

- The average time-resolved profile depends on the ratio of the real and imaginary parts of $B_f$ (Eq. 5.21). Profiles for a few different $\varphi_{Bf}$ ratios are shown in Figure 5.14. When $B_f$ is purely imaginary, the profile is identical to that for the isotropic sample, except for a negative sign that appears when $\varphi_{Bf} = -\pi/2$. If one molecular orientation dominates, $B_f$
being a product of complex $M_{\alpha}$ and $M_{\beta}$ transition matrix components, the average-time resolved profile may exhibit a phase difference of the two components (per Eq. 5.10).

- The $2\Delta z$ term has an absorptive profile (Eq. 5.22).
- The $1/k$ term has a dispersive profile (Eq. 5.22).
- 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. For larger values of $\Delta z$, the absorptive shape will dominate.

![Figure 5.14](image.png)

Figure 5.14 Shape of the oscillatory part of $I_{\text{avg}}(t)$ for a thin partially-oriented film (Eq. 5.21). The average time-resolved shape is shown for a retardation amplitude $\delta = 2\pi$, and three different values of $\varphi_{B\psi}$: $0$ (dash-dot-dash line), $\pi/4$ (solid line), and $\pi/2$ (dashed line).

The wavelength dependent profiles of a single transition, $K_{\alpha}(\omega)$ of Eq. 5.22, shown in Figure 5.15 for three different $(\Delta z, k)$ pairs, illustrate these profiling conclusions.

- 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 higher energy side, depending on the sign of $B_{\psi}$. However, if the absorption is intense, this asymmetry may not be noticeable.

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If $B_1$ has an imaginary part, the sample, in addition to LD, will also exhibit CD (Eq. 5.23) of the same wavelength-dependent profile as the LD: an absorptive profile for frequencies near resonance and/or larger values of $\Delta z$, and a dispersive shape otherwise.

![Wavelength-dependent profile of $K(\omega)$, Eq. 5.22, for three different ratios of $\Delta z$ and $k$](image)

Figure 5.15  Wavelength-dependent profile of $K_0(\omega)$, Eq. 5.22, for three different ratios of $\Delta z$ and $k$: $2\Delta z << 1/k = 1$ (solid line), $4.606\Delta z = 1/k = 1$ (dash-dot-dash line), and $4.606\Delta z = 1 >> 1/k$ (dashed line). The transition frequency is $\omega_0$. The absorption and dispersion profiles are assumed to be Lorentzians [3, 15, 18] with $\gamma = 0.25$ rad.

5.4.3 Fit Function

It has been shown in Chapter 3 that the least-squares fit to the time-resolved profile may yield a better S/N ratio than the Fourier transform approach common to the use of lock-in amplifiers. However, not every function is a good fit function. The selection 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 and to obtain a correct fit function. This function will then be used in the next Section to build a model of absorptivity in the sample cell that can explain the presence of the anomalous LD.

The average light intensity incident on the PMT is given, according to Eq. 5.21, by

$$I_{avg}(t) = K_1 \left\{ 1 + K_2 \cos\left[ \delta \sin(\Omega t) + K_3 \right] \right\}$$

5.24

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

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

5.25

Consequently, if the sample belongs to one of the three cases discussed in the previous Section, the three-parameter function of Eq. 5.25 should constitute an appropriate fit function. This is confirmed by the results of Figure 5.1: the dashed curve was obtained for $K_{LD} = 0.047$ and $K_{CD} = 0.01$, and was adjusted for errors due to averaging (re-synchronization). Moreover, comparison of Eq.'s 5.21 and 5.18 indicates that the same fit function should also be applicable to an isotropic sample.

The form of the fit function can be tested further by using the 3-D results shown in Figure 5.6. Namely, one can compare the wavelength-dependent experimental values for the three constants of Eq. 5.25 obtained from the wavelength-dependent average time-resolved profiles in two different ways:

- In the first approach, $K_1$ is estimated as $I/I_0$. The other two constants, $K_{LD}$ and $K_{CD}$, may be obtained from the differences $I_{LP \times \gamma} - I_{LP \times \gamma}$ and $I_{RCP} - I_{LCP}$, respectively.

- The second approach uses the least squares fit of Eq. 5.25 to the complete time-resolved profile.

A similarity of these two sets of results should confirm the correctness of the fit function because the results obtained using the first method are obtained in the absence of any
assumptions about the shape of the time-resolved profile. It may be concluded from the results shown in Figure 5.16 and Figure 5.5, the latter of which corresponds to the second approach, that the form of the fit function is vindicated.

Figure 5.16 Absorbance, CD and LD spectra of gaseous (+)-3-methylcyclopentanone in the range 192.8 to 200 nm obtained by 2-D gaussian smoothing. All three curves were recorded in a single experimental run. The absorbance spectrum is shown in (a). The values on the corresponding y-axis (right) are given in reverse order. The CD and LD are shown in (b) and (c). Experimental parameters are given in Table 5-1. A similar graph obtained using a least squares fit to Eq. 5.25 is shown in Figure 5.5.

The slight differences between the CD and LD values shown in the two figures may be attributable to different smoothing methods. The results of Figure 5.16 were obtained using the 2-D weighted averaging described by
\[ i_{smooth}(x, y) = \sum_{l=-L}^{L} \sum_{p=-P}^{P} w(l, p) i_{avg}(x+l, y+p) \]

where \( i_{avg}(x, y) \) is a matrix containing the time-resolved profiles for each wavelength, \( w(x, y) \) is a normalized weight function (usually gaussian), \( 2L+1 \) and \( 2P+1 \) are the numbers of neighboring points used when smoothing over wavelength and polarization respectively, and \( i_{smooth}(x, y) \) is the smoothed value. The number of rows in both matrices is equal to the number of different wavelengths at which the time-resolved profile is measured and the number of columns is equal to the number of windows used in the time-resolved averaging. The set of curves shown in Figure 5.5, on the other hand, was obtained using a 1-D gaussian-weighted averaging over wavelength (i.e., a 1-D version of Eq. 5.26 in which \( p \) is kept constant) and a least squares fit over polarization. Consequently, since the least squares fit should provide a better S/N ratio than a gaussian-weighted averaging, because it is based on all points of the time-resolved profile, and since it should introduce a smaller “damping” of the peaks, especially those of smaller width than the gaussian weight function, the smaller CD and LD values, especially those in the region where the constant S/N mode was disabled and the noise is larger, are readily explicable.

5.4.4 Sample Cell Model

The discussion of the previous Section demonstrated that wavelength-dependent average time-resolved profiles of isotropic samples, as well as the average time-resolved profiles of samples that satisfy the weak absorption and/or weak optical activity conditions stated in Section 5.4.2, can be parametrized by a fit function whose three variable parameters are proportional to absorption, LD, and CD. However, the same discussion did not offer any
explanation concerning the origin of the anomalous LD. The main goal of this Section is to introduce a model of absorptivity in the sample cell that can explain the spurious dichroism.

The results of Figure 5.1 demonstrate that the average time-resolved profile of gaseous (+)-3-methylcyclopentanone can be fitted by the function of Eq. 5.25 and that, consequently, the sample behaves as if it were partially oriented. However, another model, one that does not require the entirety of the gaseous sample to be partially oriented, can also account for the presence of both dichroisms. This model is shown in Figure 5.17.

The (+)-3-methylcyclopentanone molecule is polar, and consequently, likely to interact with the window materials. Such an interaction can lead to formation of partially or fully-oriented films at the interface between the gaseous sample and the window surface. In such a case, light will pass through three layers of sample: thin film deposited on the interior of the entrance window, gaseous sample, and thin film deposited on the interior of the exit window. If the two films are partially oriented, the $B_r$'s of Eq. 5.23 are almost purely real because the
dipole term dominates (Eq. A.7). If any change of polarization caused by passage through the sample cell is neglected\(^7^8\), the exit light intensity can be approximated as

\[
I_{\text{avg}}(t) = K_1 \left\{ 1 + K_{\text{film-entrance}} \cos(\delta \sin(\Omega t)) \right\} \\
1 + K_{\text{film-exit}} \cos(\delta \sin(\Omega t)) \\
1 + K_{\text{gas}} \sin(\delta \sin(\Omega t)) \tag{5.27}
\]

Unfortunately, in addition to the two thin films, other elements in the light path may be sources of LD and/or CD. For example, the LD spectrum of Figure 5.5 exhibits a background of \(-3 \times 10^{-3}\) which cannot be explained by this model: if the two films were solely responsible for the observed LD, the spectrum would oscillate around zero\(^7^9\), which it does not. Nonetheless, if these stray LD and CD contributions are small, they also can be modeled by adding appropriate terms to Eq. 5.27.

If all such terms are multiplied out, Eq. 5.25 is obtained, where \(K_{\text{LD}}\) is now the sum of all LD contributions and \(K_{\text{CD}}\) is the sum of all CD contributions. As far as profiles are concerned, it is only the ratio of these two constants that is significant\(^8^0\). The assertion that the model of Figure 5.17 can explain the presence of an LD in the MPS spectrum of (+)-3-methylcyclopentanone that is not attributable to the background is supported by the fact that this LD component vanishes when the sample is evacuated from the cell, whereas the background LD component does not.

\(^7^8\) In the case of an isotropic sample, \(B_1\) and \(B_2\), which according to Eq. A.22 are responsible for mixing the \(x\) and \(y\) components of the radiation, are three orders of magnitude smaller than \(A\) and \(C\). In the thin film case, given by Eq. 5.20, this mixing will be small because \(\Delta z\) is small.

\(^7^9\) At this point, the origin of the background is unknown.

\(^8^0\) The shape of the curve will be the same for \(K_{\text{LD}} = 0.047\) and \(K_{\text{gas}} = 0.01\), or \(K_{\text{LD}} = 0.00047\) and \(K_{\text{CD}} = 0.0001\). The values of \(K_{\text{LD}} = 0.47\) and \(K_{\text{CD}} = 0.1\) yield a slightly different shape, but these values are too large and the expansions and approximations used in deriving Eq’s. 5.24 and 5.25 become invalid.
5.5 Scattering

The SDI was designed to handle large changes of transmitted light intensity or, equivalently, large changes of the $I/I_0$ ratio. This ability was tested at different sample absorptivities by varying the absorber pressure. When this was done, some anomalous behavior was noted at small $I/I_0$ ratios: 1) the relative intensity of the two most prominent CD peaks of (+)-3-methylcyclopentanone was a function of pressure, as shown in Figure 5.4; and 2) the absorption spectrum became flat, as shown in Figure 5.7, at lower pressures than might be expected. Flattening normally occurs at transmitted light intensities that produce a PMT current of the order of the dark current. However, inspection of Figure 5.4 indicates that the flattening observed here occurs at intensities a hundred or so times larger. A model is now proposed to explain both of these observations.

Two possible causes for this anomalous behavior were considered: low light intensities and scattering. Low light intensities produce error because noise acquires higher significance. However, because of the absence of voltage feedback and the wide dynamic range of the SDI, and because repeated measurements under identical operational conditions have produced identical results, noise attributable to low light levels cannot be responsible. Indeed, all arguments suggest that scattering is the culprit.

The scattering model is based on the assumption that the intensity of arbitrarily polarized light incident on the PMT is given by

$$I(\lambda) = [I_0(\lambda) - I_{\text{SCATT}}(\lambda)]10^{-A(\lambda)} + I_{\text{SCATT}}(\lambda) \approx I_0(\lambda)10^{-A(\lambda)} + I_{\text{SCATT}}(\lambda)$$

where $I_0$ denotes the light intensity entering the sample cell, $A$ is the absorbance, and $I_{\text{SCATT}}$, which is taken to be proportional to $I_0$, is the light scattered by monochromator, optical

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81 The dark current is current generated in the PMT when no light is present [12, 21].
elements and/or sample. Scattering in the monochromator, as well as the presence of higher orders of diffraction, may cause light of different wavelengths to contribute to the overall light intensity at other wavelengths. Scattering at surfaces destroys collimation. In other words, scattering, whatever its origin, presupposes improper light transmission at large optical densities in somewhat the same way. Unfortunately, the existing experimental apparatus makes it virtually impossible to determine which component might be a major contributor to $I_{\text{SCATT}}$. Indeed, the only certain way to determine what is going on would be to add another monochromator after the sample cell.

The intensity of scattered light emanating from the sample cell, as shown here, may be determined by various methods: from the high-pressure absorbance measurements in which flattening occurs; from comparison of the absorbance peaks at different pressures; and from a fitting of the theoretical and experimental curves. It was found in all instances that $0.005I_0 \leq I_{\text{SCATT}} \leq 0.02I_0$ and, as result, the approximation $I_{\text{SCATT}} \ll I_0$ is valid. In addition, the $\lambda$-dependence of both $I_{\text{SCATT}}$ and $I_0$ may be ignored because they remain essentially constant in small $\lambda$-range considered here. Nonetheless, the picture based on this assumption is valid even when that dependency must be taken into consideration.

According to Eq. 5.28, when sample absorbance is large, the first term on the extreme right will not dominate and the intensity of transmitted light should flatten (i.e., the spectrum should lose definition). Since the absorbance, $A_{\text{EXP}}(\lambda)$, is defined as

$$A_{\text{EXP}}(\lambda) \equiv \log \frac{I_0}{I(\lambda)} \quad 5.29$$

when the true absorbance, $A(\lambda)$, increases and as $I(\lambda)$ converges on $I_{\text{SCATT}}$, $A_{\text{EXP}}(\lambda)$ will approach its maximal value of $\log(I_0)-\log(I_{\text{SCATT}})$, as shown in the high-pressure absorption spectra of Figure 5.7. Indeed, in the region below 200 nm, sample absorbance becomes so
large that only scattered light exits the cell and the expected spectroscopic $A(\lambda)$ variations vanish entirely.

The hypothesis of Eq. 5.28 can be tested by comparing the "true vs. experimental absorbance" curves obtained from the model and from low and high pressure measurements where the absorbances are designated $A_{\text{LOW}}(\lambda)$ and $A_{\text{HIGH}}(\lambda)$, respectively. However, non-trivial procedures are required to extract the appropriate information from the experimental data. First, a specific reference wavelength $\lambda_{\text{REF}}$ must be chosen in the low absorbance region where the influence of $I_{\text{SCATTER}}$ in both the low and high pressure measurements can be neglected. These absorbances are referred to as $A_{\text{REFLOW}} = A_{\text{LOW}}(\lambda_{\text{REF}})$ and $A_{\text{REFHIGH}} = A_{\text{HIGH}}(\lambda_{\text{REF}})$. The high-pressure absorbance difference $\Delta A_{\text{HIGH}}(\lambda) = A_{\text{HIGH}}(\lambda) - A_{\text{HIGH}}(\lambda_{\text{REF}})$ is then plotted vs. the low-pressure absorbance difference $\Delta A_{\text{LOW}} = A_{\text{LOW}}(\lambda) - A_{\text{REFLOW}}(\lambda)$ to yield Figure 5.18(a). The slope of the linear part of the curve, the part corresponding to data collected at absorbances at which scattering exerts negligible effects, can be used to estimate the ratio of sample concentrations of the low and high pressure gases, $K_c$, as shown in Figure 5.18(a). Finally, if either one of the two reference absorbances is available, the actual "measured vs. true absorbance" curve can be obtained, as shown in Figure 5.18(b). In that situation in which a point where $A_{\text{HIGH}}(\lambda) = A_{\text{LOW}}(\lambda) = 0$ does not exist in the $\lambda$-range of interest, part of the curve will be missing. However, if that part is in the low absorbance region, it can be replaced with a $45^\circ$ line, as was done in Figure 5.18(b).

According to Eq. 5.29, the asymptotic value at high true absorbance provides an estimate of $I_{\text{SCATTER}}/I_0$. If this ratio is inserted into Eq. 5.28, the theoretical "measured vs. true absorbance" curve is obtained, and is shown in Figure 5.18(b). The excellent match of theory and experiment validates the model.
Figure 5.18 Comparison of model and experiment

(a) $\Delta A_{\text{HIGH}}$ vs. $\Delta A_{\text{LOW}}$, as obtained from data of Figure 5.7 by the procedure described in the text at $\lambda_{\text{REF}} = 200.5$ nm. The slope of the dashed line yields $K_c = 18$.

(b) $A_{\text{EXP}}$ vs. $A$, obtained from part (a) as $A = K_c \Delta A_{\text{LOW}} + A_{\text{REFHIGH}}$ and $A_{\text{EXP}} = \Delta A_{\text{HIGH}} + A_{\text{REFHIGH}}$. The value of $A_{\text{REFHIGH}}$ was obtained from the data of Figure 5.7. The relative high-pressure absorbance at 205 nm is 0.66. To obtain $I_0(200.5 \text{ nm})$, a separate measurement of $I_0$, according to which $I_0(210 \text{ nm})/I_0(200.5 \text{ nm}) = 1.22$, was performed. If this ratio and the assumption that sample absorbance at 210 nm is 0 are combined, $A_{\text{REFHIGH}} = 0.66 - \log(1.22) = 0.57$ is obtained. The theoretical curve (dashed line) was calculated for $I_v/I_{\text{SCATT}} = 180$, as obtained from the asymptotic part of the experimental curve at high true absorbances. That part of the experimental curve missing below $A_{\text{REFHIGH}}$ was obtained by extrapolation of the 45° line.
The value of $I_{\text{SCATT}}$ can be easily determined when the sample absorbance is so large that it absorbs most of the light incident on the sample cell. However, when the sample pressure and/or sample extinction coefficient are not high enough to produce flattening, another approach is feasible: one may determine $I_{\text{SCATT}}$ by comparing the absorbance spectra at low and high pressures, as done in Figure 5.19 for the 198 nm absorption peak, and as described by

$$A_{\text{EXPLOW}}(\lambda) = \log \frac{I_{0,\text{LOW}}}{I_{\text{LOW}}(\lambda)} = \log \frac{I_{0,\text{HIGH}}}{I_{\text{HIGH}}(\lambda) - I_{\text{SCATT}}} = K_e A_{\text{EXPHIGH}}(\lambda)$$

The effect of different sample concentrations, as incorporated in $K_e$, can be eliminated if both the experimental low-pressure and the adjusted high-pressure peaks are expanded to the same height and their shapes compared. This method was used to estimate $I_{\text{SCATT}}$ when the CD of Figure 5.4 was adjusted.

5.5.1 Scattering and CD

If the model of Eq. 5.28 is correct, it must also explain the behavior of CD at high pressures. The wavelength-dependent CD is given by the $\lambda$-dependent version of Eq. 3.22, namely

$$CD(\lambda) = \frac{I_{\text{RCP}}(\lambda) - I_{\text{LCP}}(\lambda)}{I_{\text{RCP}}(\lambda) + I_{\text{LCP}}(\lambda)}$$

5.30

where the LCP and RCP contributions may be obtained either from the average time-resolved profiles or windowing. Unfortunately, both $I_{\text{LCP}}$ and $I_{\text{RCP}}$ may include scattering components.

If one assumes that these components are equal (i.e., that they do not depend on the polarization of the light), substitution of Eq. 5.28 into Eq. 5.30, leads to

$$CD_{\text{EXP}}(\lambda) = \frac{1}{2.303} \frac{I_0 10^{-A_{\text{RCP}}(\lambda)} - I_0 10^{-A_{\text{LCP}}(\lambda)}}{I_0 10^{-A_{\text{RCP}}(\lambda)} + I_0 10^{-A_{\text{LCP}}(\lambda)} + 2I_{\text{SCATT}}}$$

5.31

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where cancellation of the scattering contributions occurs in the numerator. Because of the retention of the scattering term in the denominator, Eq. 5.31 and Eq. 3.5 are not equivalent, even in the ideal case $\Delta A \ll 1$. Instead, the curves of Figure 5.20, which depict the average of LCP and RCP absorptivities, as given by Eq. 5.28, and the corresponding CD, as given by Eq. 5.31 as a function of a "true" A, may be used to explain the anomalous behavior.

![Figure 5.19](image)

**Figure 5.19** Effect of scattering on the absorbance profile: a demonstration of the manner in which the scattering component was estimated. The experimental parameters are given in Table 5-1. In both figures, the absorbance values on the y-axis are for the low pressure spectrum.

(a) 198.73 nm absorbance peak for (+)-3-methylcyclopentanone at low (solid line) and high (dashed line) pressure. The high pressure peak is adjusted using the procedures described in the text.

(b) The scattering correction process: the solid curve is the low-pressure profile and the dotted curve, difficult to discriminate because of overlap with the solid curve, represents the high-pressure profile after correction for scattering. The unadjusted high-pressure peak (dashed line) is also shown in order to demonstrate the effects of the adjustment process.
For lower values of $A (I_{\text{PMT}} / I_0 > 0.05)$, the observed absorbance and CD increase linearly with "true" absorbance. Once scattering becomes important (i.e., when the observed absorbance curve starts to flatten), the CD maximizes and, thereafter, decreases. Finally, when $A$ is so large that only scattered light emerges from the sample, the denominator of Eq. 5.31 dominates and the CD drops toward zero.

![Graph](image)

Figure 5.20 Experimental absorbance and CD as a function of true absorbance with and without the presence of scattering. The experimental absorbance is the solid curve and the experimental CD is the dashed curve. The slanted lines show the ideal absorbance (solid) and ideal CD (dashed) in the absence of scattering. The horizontal solid line is the maximum value of the experimental absorbance. The value $I_0 / I_{\text{SCATT}} = 100$ was used. The CD y-scale is arbitrary.

The experimental validation of the CD-scattering model of Eq. 5.31 is provided in Figure 5.21. The results of Figure 5.21 were obtained by a procedure identical to that described for Figure 5.18. The agreement of theory and experiment is excellent.

Once $I_{\text{SCATT}}$ is known, the CD can be corrected by subtracting $2I_{\text{SCATT}}$ from the denominator of Eq. 5.31, as shown in Figure 5.4. $I_{\text{SCATT}}$, as estimated by comparison of low and high pressure absorbance spectra of Figure 5.18, is $I_{\text{SCATT}} = 0.01xI_0(205 \text{ nm})$. Similar comparisons using the non-smoothed absorbance of Figure 5.5 in the interval $197.5 \leq \lambda \leq 200$ nm yields $I_{\text{SCATT}} = 0.013xI_0(200 \text{ nm})$. The adjustments of Figure 5.4 were performed using the

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Figure 5.21 Comparison of model and experiment for both CD and absorbance as influenced by scattering.

(a) The experimental high pressure absorbance and CD spectra. High pressure CD is shown by the dash-dot-dash line, high-pressure absorbance is the solid line, and the low-pressure absorbance curve is the dashed line. The low pressure curve was obtained from the non-smoothed absorbance curve of Figure 5.5. The absorbances are shown relative to that at 199.5 nm. The CD scale is arbitrary.

(b) $A_{\text{EXP}}$ and CD vs. $A$, obtained from data shown in part (a) by the procedure outlined with regards to Figure 5.18 and $\lambda_{\text{REF}} = 199.5$ nm (solid line). $K_c$ and $A_{\text{REFHIGH}}$ were estimated to be 4.7 and 0.1, respectively. The estimate for $A_{\text{REFHIGH}}$ was obtained from the low-pressure absorption curve and the assumption that sample absorbance at $\lambda = 200$ nm is 0. The theoretical curves (dashed line) were calculated$^{82}$ for $I_0/I_{\text{SCATT}} = 61.5$ and CD = 1.001. The experimental curve for CD terminates at $A_{\text{REFHIGH}}$: large oscillations inhibited extraction of line slope from the profile.

$^{82}$ The shape of the theoretical curve does not depend on the value of the CD.
latter value because it was obtained over a wider wavelength range and because the influence of $I_{\text{SCATT}}$ on the "low-pressure" spectra of Figure 5.4 could not be estimated. After correction, the relative heights of the two major peaks in the high-pressure CD spectra are essentially identical to those in the low pressure spectrum.

Based on these observations, one may predict the occurrence of other spurious structures. In the high $A(\lambda)$ region, for example at the 198.7 nm peak of (+)-3-methylcyclopentanone, the absorbance may be large enough to cause a CD dip at the peak maximum. However, once the maximum is traversed in either direction, $A(\lambda)$ will drop again and the CD will recover. This predicted dip, a depression in the center of $A_\lambda(\text{max})$, has been observed experimentally. It is shown in Figure 5.22 and Figure 5.23.

![Diagram](image.png)

Figure 5.22 The depression (i.e., dip) induced by scattering in the 198.7 nm CD peak of (+)-3-methylcyclopentanone. The lower pressure CD is shown in curves (a) and (b): (a) the CD observed at 600±30 mTorr; (b) the CD at ~600 mTorr after correction for scattering. As the pressure is increased to 1050 mTorr, a dip develops in the 198.7 nm peak, as shown in curves (c) and (d): (c) the CD observed at 1050±53 mTorr; (d) the CD for 1110 mTorr computed from that at ~600 mTorr (i.e., from curve (a)). The experimental parameters are given in Table 5-1. The theoretical curves were obtained using Eq. 5.33.
Figure 5.23 The depression induced by scattering in the 198.7 nm CD peak of (+)-3-methylcyclopentanone at intermediate pressures. The lower pressure CD observed at 600±30 mTorr is shown in curve (a). As the pressure is increased to 800 mTorr, a dip develops in the 198.7 nm peak, as shown in curves (b) and (c): (b) the CD observed at 800±45 mTorr; (c) the CD for 800 mTorr as calculated from that at ~600 mTorr (i.e., from curve (a)). The experimental parameters are given in Table 5-1. The theoretical curves were calculated using Eq. 5.33.

Figure 5.22 and Figure 5.23 also contain the theoretically predicted high-pressure CD spectrum that should be observed in the presence of scattering. These computations used the following procedures to minimize the errors caused by uncertainties in I₀: suppose that the CD at some pressure is given by Eq. 5.31. If this pressure is increased m times, Eq. 5.31 becomes

\[ CD = \frac{1}{2.303} \frac{I₀ 10^{-mLCP} - I₀ 10^{-mLCP}}{I₀ 10^{-mRCP} - I₀ 10^{-mLCP} + 2I_{SCATT}} \]

5.32

If both numerator and denominator are multiplied by I₀ \(^{(m-1)}\), Eq. 5.32 becomes

\[ CD = \frac{1}{2.303} \frac{I₀^m 10^{-mLCP} - I₀^m 10^{-mLCP}}{I₀^m 10^{-mRCP} - I₀^m 10^{-mLCP} + 2I_{SCATT}I₀^{m-1}} \]

or

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Therefore, if \( I_0, I_{SCATT}, I_{LCP} \) and \( I_{RCP} \) are known at any one pressure, Eq. 5.33 may be used to estimate the CD at any other pressure provided, that is, that \( I_{SCATT} \) remains relatively constant.

While the match of the theoretical and experimental profiles of Figure 5.22 and Figure 5.23 is not excellent, the generalized shapes are nonetheless quite similar, and they do support the contention that "false" dips can occur in the experimental CD spectrum. Thus, the observed occurrence of these "dips" is attributable to scattering.
6. CONCLUSION

The SDI, as shown experimentally and theoretically in this work, is a new type of instrument that generates data sets not previously available. It provides a very efficient means for collecting polarization-selective data in modulation spectroscopy, one that overcomes most problems confronted by MPS-PMT experiments. The advantages of the SDI, when compared to existing MPS-PMT methods, are:

--- It provides the average-time resolved profile of a modulated signal.

--- It eliminates errors when modulated signals depart from sinusoidal.

--- It offers separate measurements of parts of the signal associated with various phases of the modulation cycle.

--- It enables simultaneous measurement of absorption, CD and LD spectra.

--- It facilitates 3-D absorbance measurements.

--- It has a wide dynamic range.

--- It offers a constant S/N ratio mode of operation.

--- It eliminates any PMT voltage feedback requirement.

--- It offers faster scanning speeds.

The time-resolution, selectivity, wide dynamic range and constant S/N ratio capabilities are useful for other MS experiments. Finally, pulse height distribution and time-resolved pulse counting experiments may benefit from the on-the-fly data processing capability, in the sense of significant overhead reduction.

Future work will proceed in three directions: the improvement of the SDI device itself, the interpretation of new experimental results obtained with the MPS-SDI method, and extensions of the technology to measurements of other physical quantities.
The SDI device can be improved by using faster components. However, the prototype described here fits all the needs of MPS-SDI studies, and is a compromise between price, performance, and hardware minimization. As a result, no external RAM's and ROM's are present. Only TTL logic has been used and, consequently, hardware for interfacing different technologies is not needed. An improved SDI version will be constructed using professional tools to reduce noise levels so that faster ADC's with better resolution (more bits) can be employed in order to increase the number of collected data-points. It will also include more user-friendly interfacing (e.g., digital display), external on-board RAM that will enable the DSP to perform the entire experiment without any computer assistance; on-board ROM for basic DSP programs; hardware that will perform high-photon-count time-resolved experiments (more than $2 \times 10^5$ photons/s); a new reference interface module; and better data acquisition software. These changes will result in better resolution, accuracy and faster processing, all of which are important for MPS-SDI investigations.

The MPS-SDI method should provide new information about the ground and excited electronic structures of molecules, about molecular orientations, and about molecular dynamics. Work in progress concerns MPS-SDI studies of several molecular systems, the investigations of molecular layers, particularly ones constituted from molecules of biological interest, and the development of detailed theoretical models for the interpretation of MPS-SDI measurements.
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APPENDIX A: OPTICAL CALCULI

The analysis of polarized light/matter interaction was pioneered by R. Clark Jones [32, 33]. Jones showed that the state of arbitrarily polarized light moving along the z-axis, after it has passed through matter can, be described by

\[
\vec{E}(z) = \begin{bmatrix} E_x(z) \\ E_y(z) \end{bmatrix} = \overline{M}(z) \begin{bmatrix} E_x(0) \\ E_y(0) \end{bmatrix}
\]

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 \(\overline{M}(z)\) is a complex 2x2 matrix given by

\[
\overline{M}(z) = \exp(zN)
\]

The matrix \(N\) is obtained as a weighted linear superposition of eight 2x2 matrices

\[
N = -\eta \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix} - \kappa \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} + \omega \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} + \delta \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} + g_0 \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} + p_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} + g_{45} \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} + p_{45} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}
\]

or, more compactly,

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

where the constants, in order of appearance in Eq. A.1, represent the following properties of the material through which the light has propagated:

\(\eta = 2\pi n/\lambda\), the phase retardation (PR) per unit length; \(n\) is the index of refraction
\(\kappa = 2\pi\varepsilon/\lambda\), the absorption coefficient (ABS) per unit length; \(\varepsilon\) is the extinction coefficient
\(\omega = 1/2(\eta_+ - \eta_-)\), the circular birefringence (CB) per unit length
\(\delta = 1/2(\kappa_+ - \kappa_-)\), the circular dichroism (CD) per unit length
\[ g_0 = \frac{1}{2}(\eta_\alpha - \eta_\beta), \text{ the linear birefringence (LB) per unit length} \]

\[ p_0 = \frac{1}{2}(\kappa_\alpha - \kappa_\beta), \text{ the linear dichroism (LB) per unit length} \]

\[ g_{45} = \frac{1}{2}(\eta_{45} - \eta_{135}), \text{ the (45°/135°) linear birefringence (LB') per unit length} \]

\[ p_{45} = \frac{1}{2}(\kappa_{45} - \kappa_{135}), \text{ the (45°/135°) linear dichroism (LD') per unit length} \]

The letter mnemonic notation of Jensen [34] is given in parentheses.

However, prior to any analysis of the polarization-dependent intensity of the light transmitted through a sample, the analysis of interest here because it is this intensity (i.e., the average power carried by the EM wave) that is measured by the apparatus of Figure 2.1, it will be shown that the matrix \( N \) can be obtained directly in terms of transition matrix elements from a semi-classical treatment of light-matter interaction. To our knowledge, such a derivation of the Jones' matrix \( N \) has not been given previously. Photons will be viewed as oscillations of the classical electromagnetic field, whereas the interactions between photon and molecule will be treated quantum-mechanically.

The electric field of an EM wave propagating in vacuum along the \( z \)-axis, the default direction if not otherwise stated, can be written [15] as

\[ \vec{E}(t, z) = E_0 \vec{\Pi} \exp[i(\omega t - kz)] \]

where \( \vec{\Pi} \) is a polarization vector in the \( xy \) plane, \( E_0 \) is a wave amplitude, \( \omega = 2\pi v \) is the angular frequency and \( k \) is the wave vector \((2\pi/\lambda)\). The corresponding magnetic field is obtained from Maxwell's equations [15] as

\[ \nabla \times \vec{E}(z,t) = \frac{1}{\mu} \frac{\partial \vec{H}(z,t)}{\partial t} \]

where \( \mu \) is the magnetic permeability. The power in the wave is given by a time average of the Poynting vector \( \vec{S} \) [15] as
where \( c \) is the speed of light.

When the EM wave enters a medium, interaction between radiation and matter occurs. That interaction is manifested through 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

\[
N(\omega) = n(\omega) - \frac{i}{2k} \alpha(\omega)
\]

Manipulation of the first-order perturbation theory solution of the time-dependent Schrödinger equation (Einstein's absorption coefficients [3, 18], Fermi's Golden Rule [35], retention of terms to the level of electric dipole, magnetic dipole and electric quadrupole, and the assumptions of a single active transition and total orientation of the molecular sample, yields [3]

\[
N(\omega) = 1 - \frac{in'\hbar}{2hc} \left| \vec{M}(0f) \cdot \vec{P} + \vec{M}(0f') \cdot (\vec{z} \times \vec{P}) + i \frac{\omega}{2c} \cdot \vec{z} \cdot \vec{Q}(0f) \vec{P} \right|^2 \left[ g_{\text{abs}}(\omega) - ig_{\text{disp}}(\omega) \right]
\]

where \( n' \) 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 initial and final state(s), respectively, and \( g_{\text{disp}}(\omega) \) and \( g_{\text{abs}}(\omega) \) are dispersion and absorption curves, respectively [3, 15]. The last expression can be rewritten as

\[
N(\omega) = 1 - \left| M_f(\vec{P}) \right|^2 g_f(\omega)
\]

by defining a vector operator \( M_f \).
\[ M_f(\vec{v}) = \sqrt{\frac{n^2}{hc}} \left[ \vec{M}(0f) \cdot \vec{v} + \vec{M}(0f) \cdot (\hat{z} \times \vec{v}) + i \frac{\omega}{2c} \hat{z} \cdot \vec{Q}(0f) \cdot \vec{v} \right] \]  

A.7

or, more compactly

\[ M_f(\vec{v}) = M_f(\vec{v}) + M_{-f}(\vec{v}) + Q_f(\vec{v}) \]

and combining the absorption and dispersion shape curves into an imaginary shape function \( g_f(\omega) \). The \( \omega \) dependence of 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 cases in which more than one transition from the same initial state can be induced by light of frequency \( \omega \).

Simple insertion of Eq. A.7 into Eq. A.2 to obtain

\[ \vec{E}(\tau, z) = E_0 \vec{P} \exp \left\{ i \left[ \omega \tau - N(\omega)kz \right] \right\} \]  

A.8

is incorrect even though Eq. A.8 has the correct vacuum limit (i.e., for \( N = 1 \) it yields Eq. A.2). The problem with Eq. A.8 is that it implies that matter cannot change the polarization of light, which is obviously wrong. For example, a sugar solution rotates the plane of polarization of linearly polarized light. This problem can be "fixed" by decomposing the incoming wave into two orthogonally-polarized components which then propagate through the material with their own complex indices of refraction according to Eq. A.8: if their absorption coefficients are different, the two components will be absorbed to different degrees and, when combined after passage through the sample, they will produce a polarization different from that of the incident light. The same will hold true if the phasing (real refraction) is altered differentially. However, the result obtained for the power loss is a function of the choice of the orthogonal polarization

\[ ^{83} \text{All two-dimensional complex vectors can be described as a superposition of two complex two-dimensional, non-collinear vectors that constitute a basis set [19].} \]
pair; thus, in order for Eq. A.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 orthogonal characteristic polarizations for which the electric field vector obeys Eq. A.8 must be found. One obvious candidate, denoted $\Pi_2$, 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

$$M_f(\Pi_2) = 0 \quad \text{A.9}$$

If $\Pi_2$ is split into $x$ and $y$ components, $\Pi_x$ and $\Pi_y$, respectively, and the linear property of $M_f$ is used

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

Eq. A.9 becomes

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

The obvious solution of Eq. A.11 is

$$\Pi_{2x} = M_{fy} \quad \Pi_{2y} = -M_{fx} \quad \text{A.12}$$

Therefore, the normalized polarization vector $\tilde{\Pi}_2$ is given by

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

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

---

84 Since the electric vector is two-dimensional, a 2x2 complex matrix should describe its interaction with matter. If this matrix can be written as a linear combination of Hermitian and identity matrices it will have two orthogonal eigen-vectors [32, 33] (i.e., light with polarization the same as one of the eigen-vectors will exhibit only absorption and no polarization changes). It will be shown that this supposition holds only when all active transitions have identical wavelength-dependent profiles $g(\omega)$. 

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\[ \Pi_1 \cdot \Pi_2^* = \Pi_2 \cdot \Pi_1^* = 0 \quad \text{A.14} \]

as

\[ \Pi_1 = \frac{1}{\sqrt{|M_{fx}|^2 + |M_{fy}|^2}} \left( M_{fx}^* \hat{x} + M_{fy}^* \hat{y} \right) \quad \text{A.15} \]

Inserting A.15 into A.7 yields

\[ M(\Pi_1) = \sqrt{|M_{fx}|^2 + |M_{fy}|^2} \quad \text{A.16} \]

In the case when only the electric dipole term is present in A.7, \( M_{\alpha} \) and \( M_{\beta} \) are real and Eq's. A.15 and A.16 correctly imply that light, when linearly polarized at an angle determined by the ratio of \( M_{\alpha} / M_{\beta} \), propagates with no polarization change and an absorptivity that is related to the dipole moment vector length, whereas the orthogonal linear component, \( \Pi_2 \), propagates with no changes at all.

Therefore, one may calculate the effect of matter on any polarized beam \( \Pi \) by decomposing it into the two characteristic components \( \Pi_1 \) and \( \Pi_2 \) of Eq's. A.13 and A.15, each of which then interacts according to Eq. A.8 with its own complex index of refraction. Finally, after transit through the sample, the two components are rejoined. This procedure can be described mathematically as

\[ E(t, z) = E_0 \exp(i\omega t) \times \left\{ \gamma_1 \Pi_1 \exp \left[ -ikz \left( 1 - i|M_f(\Pi_1)|^2 g_f(\omega) \right) \right] + \gamma_2 \Pi_2 \exp(-ikz) \right\} \quad \text{A.17} \]

where

\[ \gamma_i = \Pi_i \cdot \Pi_i^* \]
and Eq. A.9 has been used. Differentiation of Eq. A.17 and equating the x and y components on both sides, yields the two coupled differential equations

\[
\frac{\partial E_x(z,t)}{\partial z} = -AE_x(z,t) - B_1E_y(z,t) \\
\frac{\partial E_y(z,t)}{\partial z} = -B_2E_x(z,t) - CE_y(z,t)
\]

where

\[
A = k \left[ i + g_f(\omega) \right] M_{fx}^2 \\
B_1 = kg_f(\omega) M_{fx}^* M_{fy} \\
B_2 = kg_f(\omega) M_{fx} M_{fy}^* \\
C = k \left[ i + g_f(\omega) \right] M_{fy}^2
\]

In other words, the matrix

\[
N' = \begin{bmatrix} A & B_1 \\ B_2 & C \end{bmatrix}
\]

describes the effects of an infinitesimally thin slab of matter on the incident radiation. As such, it is equivalent to Jones' \(N\) matrix, and the two characteristic polarizations \(\vec{\Pi}_1\) and \(\vec{\Pi}_2\) of Eq's. A.13 and A.15, respectively, are the orthogonal eigen-vectors of \(N'\). The latter may be verified by inserting the definitions of Eq. A.19 into Eq. A.20 for the matrix \(N'\). One obtains

\[
N' = \begin{bmatrix} \left[ i k + kg_f(\omega) \right] M_{fx}^2 & kg_f(\omega) M_{fx}^* M_{fy} \\ kg_f(\omega) M_{fx} M_{fy}^* & \left[ i k + kg_f(\omega) \right] M_{fy}^2 \end{bmatrix}
\]

\[
= ik \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} + kg_f(\omega) \begin{bmatrix} \left| M_{fx} \right|^2 & M_{fx}^* M_{fy} \\ M_{fx} M_{fy}^* & \left| M_{fy} \right|^2 \end{bmatrix}
\]
Furthermore, Eq. A.21 demonstrates that the two characteristic polarizations remain orthogonal even when the molecular orientation is non-uniform: the only requirement is that all active transitions possess the same complex function $g_d(\omega)$ (i.e., the matrix $N'$ must a superposition of the Hermitian and identity matrices$^{44}$). Finally, when the relationships

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

and

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

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

The solution to the Eq. A.17, then, is

$$E_x(z,t) = \frac{\exp(-\beta_1 z)}{\beta_1 - \beta_2} \left[ E_{x0}\left(\beta_1 - C\right) + E_{y0}B_1 \right] - \frac{\exp(-\beta_2 z)}{\beta_1 - \beta_2} \left[ E_{x0}\left(\beta_2 - C\right) + E_{y0}B_1 \right]$$

$$E_y(z,t) = \frac{\exp(-\beta_1 z)}{\beta_1 - \beta_2} \left[ E_{x0}B_2 + E_{y0}\left(\beta_1 - A\right) \right] - \frac{\exp(-\beta_2 z)}{\beta_1 - \beta_2} \left[ E_{x0}B_2 + E_{y0}\left(\beta_2 - A\right) \right]$$

where

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

and

$$E_{x0} = E_x(0,t) = E_0 \Pi_x \exp(\omega t)$$

$$E_{y0} = E_y(0,t) = E_0 \Pi_y \exp(\omega t)$$

The $x$ and $y$ components of $\tilde{H}(z,t)$, as obtained from Eq. A.3, are given by
Finally, by combining Eq's. A.4 and A.24, the intensity of the light is found to be

\[
I = \langle S \rangle \cdot \tilde{z} = \frac{c}{8\pi k} \Re \left[ \frac{-i}{\mu} \left( E_x \frac{\partial E_y}{\partial z} + E_y \frac{\partial E_x}{\partial z} \right) \right]
\]

In the general case, \( \mu \) is a complex number. However, the analysis of Chapter 5 is done for non-magnetic materials and the value of \( \mu \) is set equal to 1.
APPENDIX B: SDI HARDWARE

The formal SDI description of Chapter 4 provided little technical detail concerning the block diagram of Figure 4.1. The purpose of this Appendix is to provide the missing information. Thus, an electronic schematic is shown and the signal path is discussed for each SDI block introduced in Chapter 4. An elementary knowledge of electronics, TTL logic circuitry, and computer interfacing is necessary to understand the discussion of this Appendix.

- The preamplifier

A detailed schematic of the preamplifier (PA) is given in Figure B.1. The PA consists of five stages. The first stage is constructed around an ultra-fast current feedback amplifier A1 (AD844AN) which converts input current pulses into voltage pulses. The conversion constant is determined by the \( R_2 + V_1 \) combination and ranges from \(-\times 120 \text{ V/A}\) to \(-\times 5120 \text{ V/A}\). The second stage is built around A2 (AD843JN) and merely provides more voltage amplification. The gain is determined by the \( R_8/(R_3+V_2) \) ratio and ranges from \(-\times 0.5\) to \(-\times 4.5\). The third stage, a peak widening stage, is built around A3 (AD712JN). The output of A2 is first scaled down by the \( V_3+R_4 \) and \( V_4 \) resistor network which also determines the charging and discharging RC constant for capacitor C5 (because A3 has a high input resistance). As a result of these time-constants, both of which equal the product of C5 and the parallel combination of \((V_3+R_4)\) and \( V_4 \), the pulses appearing on the output of A2 are widened. The voltage on C5 is then fed to the non-inverting input of one of the two amplifiers in A3 (pin 5) which is in the emitter-follower setup and serves as a signal buffer. In the fourth stage, the remaining amplifier of A3 is used for additional amplification and offset adjustment. The gain is determined by the \( R_5/(R_6+V_5) \) ratio and ranges from \(-\times 0.2\) to \(-\times 5.2\). The offset can be adjusted using a precise, 20 turn, \( V_7 \) trimmer. Finally, in the fifth stage, A4 (AD712JN) is used as an output buffer and limiter.
Limiting is achieved by lowering the positive supply voltage of A4 to ~2 V. This voltage causes the A4 output to saturate at ~1.8 V and protects the two ADC block converters (which can only handle input voltages of 2 V). The low positive supply voltage of A4 is controlled by the V6 trimmer whose output is buffered by A5 (SK3552) and filtered by capacitors C9 through C11.

Overall amplification is chosen so that most of the time (99%) the A4 output does not exceed 1.5 V, the upper range limit for the two SDI converters. All the operational amplifiers have 0.1 µF bypass capacitors on the power pins. In addition, the voltages supplied by the external power supply are filtered by C14-C15 and C16-C17 capacitor pairs. The capacitors C11-C14, although shown on the schematic, are not present in the existing pre-amplifier prototype because of space limitations. They will be included in future versions.

A printed circuit board will be designed for the PA in order to minimize the noise level (which, at this point, is sufficiently low not to exert any influence on the conversion process executed by the 8-bit converters). As a result, a better resolution ADC (12-bit) can be used in the ADC block. The PA will also be redesigned for computer control of the following parameters: gain control in the I/V stage (stage 1); gain control in the voltage amplifier stage (stage 2); peak shape control in the peak shaping stage (stage 3); offset and gain control in the second voltage amplification stage (stage 4); and maximum-amplitude control in the limiter stage (stage 5).

- The reference interface

The reference interface circuitry is shown in Figure B.2. The reference signal enters SDI through the BNC connector (J4) and is fed to the inverting input of voltage comparator A20 (SK3567A) where it is compared to the threshold voltage at the
non-inverting input. The SDI threshold point is set at 0 V (i.e., the non-inverting pin is hardwired to ground). When the voltage on the inverting input increases above threshold, the output of A20 goes negative; when the input falls below 0 V, the output goes positive. The comparator output, pulled up to +12 V by resistor R4, is then converted to a TTL signal by the T2-R6 combination. Output from T2 is further inverted by one of the Schmitt-trigger inverters of A19 (SN74AS14) in order to allow the DSP to use interrupt mode of operation initiated on both the rising and falling edges of the reference signal.

The existing version of the reference interface may run into difficulty when noise is superimposed on the incoming reference signal. If noise is present at the moment when the reference voltage is close to threshold, oscillations will occur at the output. These oscillations can be prevented by using a feedback capacitor (C50*) and inserting a small resistor (R13*) between the threshold voltage source and the inverting input as shown in Figure B.3: a negative/positive change on the comparator output, which corresponds to above/below the threshold state of the negative input, is transferred by the capacitor to the positive input. This transfer decreases/increases the threshold voltage and, in this way, creates a positive feedback loop to prevent oscillation and force the comparator to a stable state. Voltage recovery at the threshold input is determined by the C50xR13 time constant.

- The ADC Block

The ADC block is shown in Figure B.3 and Figure B.4. The signal enters the SDI through the BNC connector (J13), terminated through R9, and then fed to the non-inverting inputs of the two buffer amplifiers A5 (MC34002), each of which services one ADC. Both amplifiers are in the emitter-follower setup and no RC components exist in the feedback loop. The output from the first amplifier (A5 - pin 1) is connected to the input of converter A4. The output from the second amplifier is connected to the input of converter A6. Both
ADC's are MC10319. The ADC input range and linearity is determined by the voltage on the VRT, VRM and VRB pins. The VRB pin is hardwired to ground and the VRT voltage is supplied by 1.5 V reference circuitry built around a precise 2.5 V reference IC A1 (REF43) and operational amplifier A2 (MC34002)-transistor T1 combination. The output voltage of A1, filtered by capacitor C1, is decreased to 1.5 V by the R1/R2 1:1.5 resistor divider. The A2-T1 combination with R5 and C5 in the emitter-follower feedback loop provides temperature stabilization and noise filtering. Because R1 and R2 are both fixed, the reference voltage may not be exactly 1.5 V (which is not important in the present situation). Better linearity is achieved using the ten-turn precision trimmers V1 and V2 to set the VRM pins to a voltage exactly half way between those of the VRT and VRB.

This circuitry has the following power requirements: +12 V, -12 V, -5 V, and +5 V for the analog part, and +5 V for the ADC digital component. The -12 V, -5 V, and +12 V are provided by an external power supply through the J14, J12, and J15 connectors, respectively. For filtering purposes, J14 and J15 are bypassed to ground by capacitors C7 and C3, respectively. To reduce noise, the +5 V required for the ADC analog component is provided by the voltage regulator A3 (LM7805) and the filtering capacitor C7, instead by the +5 V power lines common to all digital IC's on the DSP board. All power pins on the amplifiers, the ADC's, and the IC's (except A23) are bypassed to ground with 0.1 μF ceramic capacitors. These capacitors are either shown in the schematic or are listed in the NOTES section of the drawing where the particular IC appears.

The 8-bit digital outputs of the two converters are added by an 8-bit adder. Three clocks are needed to perform this addition: CLK1, CLK2, and CLK3. All these clock signals are generated from the DSP clock (CLKOUT) by A12 (SN74AS04): CLK1 is the CLKOUT delayed by two NOT gates, CLK2 is the inverted CLKOUT delayed by three
NOT gates, and CLK3 is the CLKOUT delayed by four NOT gates. The conversion/addition operation, which requires two and a half DSP clock cycles, can be described, using these clocks, by the five steps shown on Figure B.5:

1) Converter A6 begins conversion on the falling edge of CLK3;

2) One half a clock cycle later, result from A6 becomes available (the rising edge of CLK3) and conversion in A4 is initiated (the falling edge of CLK2);

3) On the following rising edge of CLK2, the converter A6 output is loaded into the intermediate buffer A7 (SN74AS374) and the data on A4 become available;

4) The outputs of A4 and A7 are loaded into input buffers A8 and A9 (both SN74AS374) half a clock cycle later. These two 8-bit numbers are added by two 4-bit full-adders A11 and A10 (both MC54F283) during the next CLK1 cycle;

5) Finally, on the next rising edge of CLKOUT, the sum is transferred to the adder output buffer, which consists of A13 and A14 (both SN74AS374), where it can be accessed by the DSP.

Because the DSP needs to access only one external memory location, namely the adder output buffer, no address decoding circuitry is required. Thus, the RD* DSP pin can be connected directly to the high-impedance control pin on buffers A13 and A14. However, for safety, all software is written as if the adder output buffer were located at address 0x0000. The upper 7 bits of the adder output are padded with zeros (A14) because the DSP operates on 16-bit numbers.

This block offers considerable room for improvements. By lowering pre-amplifier noise, new ADC's with better resolution (12-bits) can be used. The manipulation of digital samples before reading into the DSP can proceed in two ways:
In the first approach, one fast converter, say 100 MHz, and one ECL adder can add four consecutive samples prior to reading into the DSP. The drawback of this approach lies in the resolution of the 100 MHz ADC that is limited to 8-10 bits. However, that may not be a problem since our current prototype uses the 8-bit ADC's successfully.

The other approach employs four 12-bit 25 MHz ADC's shifted 90° out of phase in combination with the three adder stages, and provides the sum of ADC outputs to the DSP in each of its clock cycles. This approach has advantage that only TTL technology can be used but it requires more hardware.

Further improvement can be achieved by incorporating circuitry for fast photon-counting and time-resolved photon detection. The former can be implemented with DSP-accessible counters, and the latter by fast discriminator whose state may be either added by the adder circuitry or directly read by the DSP. Even though the current version permits such experiments, the low light intensity conditions are necessary so that the widened pulses do not overlap. New circuitry can push those limits toward higher photon counts.

The DSP block

The existing DSP block contains only the clock and power interface circuitry shown in Figure B.2. Power required for normal operation of the SDI is supplied by an external power supply through the two connectors J10 and J11. Each connector has a pair of 10 μF and 0.1 μF capacitors between the +5 V and ground lines: C30 and C4 for J10, and C26 and C27 for J11, respectively. The DSP clock is generated by a 12.000 MHz processor-grade crystal (A21), with corresponding capacitors C36 and C37 connected to the DSP XTAL and CLKIN pins. All other oscillator components are already built into the processor.
Major hardware improvement of this block can be achieved in two ways:

- Added ROM, containing code for DSP boot-up and routines for program downloading through the serial port, will permit SDI use with computers that only have serial ports. Indeed, the new, faster serial communication standards now on the market (universal serial buss - USB, firewire - IEEE 1394) will enable serial interfaces to start compete speed-wise with parallel interfaces.

- A second improvement is the addition of external RAM memory to free the SDI from the limits imposed by the size of the DSP internal memory (which in the current processor version totals 4K-words) and to permit data collection for longer time periods without computer support. At the moment, data must be transferred to the computer in each wavelength step so that the DSP internal memory is freed for a new integration. Finally, a more user-friendly status display will be added to the existing apparatus.

- The parallel interface

A detailed schematic of the parallel interface is shown in Figure B.6. The interface is built around the DSP Host Interface Port (HIP). To access the HIP registers, read and write timing sequences provided in the AD manual must be followed [27]. In all, a total of sixteen (8 data, 6 HIP control, and 3 general purpose) signals must be controlled through the parallel interface. In order to control 16 lines through the 8-bit printer port available on all computers, multiplexing is necessary. Logically, the lines are divided among three 6-bit registers. Data is read into the registers from the lower six bits of printer bus (J1), referred to as the external data bus, while the upper two bits, referred to as the external address bus, are used for register addressing through the one-out-of-eight demultiplexer A15 (SN74AS138). Address setting on the A and B inputs of A15 causes the corresponding demultiplexer output to go low. Therefore, to load data into any one of the three registers,
the following procedure must be followed: (i) data for loading must be put on the external data bus; (ii) simultaneously, the register address must appear on the external address bus - demultiplexer output goes low; (iii) without changing contents of the external data bus, the address must be changed to 11₂, which causes all demultiplexer outputs to go high and produces the positive edge that loads the registers with the contents of the data bus.

Physically, these sixteen lines are divided among two 6-bit and one 8-bit register, A16 (SN74AS174), A17 (SN74AS174), and A18 (SNAS841), respectively. A18 is a 10-bit three-state buffer of which two bits are not used. A17, address 01₂, is used to buffer all six HIP control lines. A16, address 00₂, stores the upper nibble of 8-bit data and the two general purpose control lines (RESET, interrupt request line). To read the 8-bit data into buffer A18, address 10₂, the upper four bits must first be loaded into A16. Then, by writing the lower four bits into A18, the upper nibble is automatically loaded from the output of A16. The reason for this particular sequence is the three state capabilities of A18 which are required because the same eight HIP lines are used for both input and output.

When the read/write line (HRW) is set for reading, the A18 buffer output is simultaneously set to high impedance through the OC* pin. The reset pins of A16 and A17 are connected to +5V through R11 and R10, respectively. For inverting the demultiplexer output required for control of A18, one NAND gate of A23 (SN74AS00) is used. Other A23 gates are used for generation of the PCNTL signal (power control). When the PCNTL signal is high, as shown in Figure B.2, the R12-T4 combination enables relay K1 which, in turn, disconnects power from the DSP. This feature can be used either to ensure that the RESET pin is set to low before power is applied to the DSP or for testing purposes. To set the PCNTL to high, a write to the A18 has to be initiated (NOT COMPLETED - step (i) only) with the upper-most bit of the data bus set to 0. In this way, both pins 3 and 11 of A23 are

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high and the AND combination (NAND+NAND) translates this to logical 1 on the PCNTL line. To prevent disconnection of the DSP power while writing data to buffer A18, THE MSB OF THE EXTERNAL DATA BUS MUST ALWAYS BE SET TO 1. The contents of the DSP HIP registers can be read through the 8-bit digital port on J2.

A major improvement of the parallel interface can be achieved by introducing a combined 8/16 bit version of the interface, which will enable faster exchange of data between SDI and computer. The reason for retention of compatibility with the 8-bit version is convenience: this bus size facilitates program downloading through the parallel 8-bit port available on almost every computer.

- The Serial Interface

The serial interface, as shown in Figure B.2, (up to 12 Mbauds), consist of two-plus-two Schmitt-trigger inverters of A19 (SN74AS14) inserted for DSP protection between the receive and transmit pins and J7 and J6 connectors, respectively. Two general purpose digital outputs controlled by the FO and FL2 DSP pins are available on the J8 and J9 connectors, respectively. Some of these pins are shared with DSP serial port #2 (SPORT2) and can be used only if appropriate flags are set in the DSP control register, as described in the AD manual [27].

Because the DSP contains all the necessary logic and control circuitry for implementation of a variety of serial protocols, no additional changes for this block are planned. It is possible, however, that this block will be adapted for serial communication with other processors in future multiprocessor versions of the instrument.

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Figure B.1 Electronic schematic of the Pre-Amplifier
Figure B.2 Electronic schematic of the DSP, Reference, and Serial Interface
Figure B.3 Electronic schematic of the ADC Block
Figure B.4 Electronic schematic of the ADC Block (Adder)
Figure B.5 Timing diagram of the ADC Block
Figure B.6  Electronic schematic of the Reference Interface
VITA

Aljosa Vrancic was born in Zagreb, Croatia. He graduated from High School for Mathematical and Computer Science Education in Zagreb during May, 1986. Because of his interest in electronics and computers, he decided to pursue a bachelor's degree in electrical engineering at the University of Zagreb, where he met and fell in love with Andreja, his future wife. In 1989, as a result of his interest in both electronics and scientific work in the area of quantum mechanics, he was awarded Scholarship from “Ruder Boskovic” Institute, Zagreb, the leading scientific research institution in Croatia. During his senior year he was also awarded the City of Zagreb Scholarship as one of the fifty best students at the university.

Immediately after completing his undergraduate degree in the Fall of 1991, Aljosa started to work at “Ruder Boskovic” Institute, which he left one year later to join Louisiana State University in order to pursue further education in the combined areas of physics, computer science, and computer engineering. He obtained a master of science degree in physics in 1995. He is a candidate for the doctor of philosophy degree in physics.

Aljosa and Andreja currently live in Austin, Texas, where he is working as a Software Engineer at National Instruments.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Aljosa Vrancic
Major Field: Physics

Title of Dissertation: The Selective Digital Integrator - A New Device for Modulated Polarization Spectroscopy

Approved:

[Signatures]

Major Professor and Chairman
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: September 16, 1997

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