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MAGNETICALLY INDUCED LINEAR DICHROISM IN LIQUID SOLUTIONS

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MAGNETICALLY INDUCED LINEAR DICHROISM IN LIQUID SOLUTIONS

by

DAVID ZELMANOVIC

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Abstract

MAGNETICALLY INDUCED LINEAR DICHROISM IN LIQUID SOLUTIONS

by

David Zelmanovic

Adviser: Professor Raymond L. Disch

We have developed an instrument capable of measuring differences in absorption coefficients as small as 10^{-5} optical density units. Greatly enhanced S/N is achieved by including the light source in an opto-electronic feedback network. Additionally, use of a tunable dye laser increases light intensity and open-loop gain by two orders of magnitude relative to other light sources. This stabilizes closed-loop gain by making it more nearly independent of changes in open-loop gain parameters.

We have developed The Theory of Magnetically Induced Linear Dichroism (MLD) in Liquid Solutions. The MLD is expressed as a function of the applied static magnetic field tensor, H''_{α}, by expanding it in a Maclaurin series in H''_{α}. Included are the dependences on H''_{α} of the line shape function, S^{LK} the oscillator strength tensor, $\mu^{LK}_{\alpha\beta}$, and the probability function, Ω. It is shown that the coefficient of $H''_{\alpha}H''_{\beta}$ is the first nonzero term in the expansion.

The general predictions of the theory are outlined and the major features of the MLD spectra of liquid solutions of various lanthanide ions and metal porphyrins are discussed in light of these predictions. The spectrum of horse heart ferrocytochrome c is analyzed in detail and the results compared with results obtained from Magnetic Optical Rotatory Dispersion (MORD) spectra. They are in excellent agreement. Information concerning the anisotropy of the diamagnetic susceptibility of the MLD spectrum. This information is not obtainable through MORD or other techniques.

Acknowledgements

I thank Professor Raymond L. Disch for allowing me to share in his wisdom and insight and for his patience and kindness.

I thank Paul Schaedler of the Queens College Physics Department Machine Shop for his time and for designing, among other things, a motorized monochromator drive, a mount for a photo-acoustic modulator, a Faraday Cell housing and numerous mirror mounts.

I thank my wife, Elaine for enduring me during my times of turmoil and for sharing our happiness with me.

Table of Contents

Diagrams

Introduction

Consider a medium whose optic axis is parallel to the lab y-axis. Linearly polarized light whose propagation vector is in the z-direction is incident upon it. If the x-polarized light is absorbed more (or less) than the y-polarized light, the medium is linearly dichroic. Uniaxial crystals are naturally linearly dichroic. Isotropic crystals can be made linearly dichroic by compression, the direction of compression becoming the optic axis. They can also be made linearly dichroic by application of a magnetic field. Macroscopic samples of liquids and gases are not naturally linearly dichroic even though individual molecules may be highly anisotropic because thermal motion makes all molecular orientations equally probable. Therefore, light traversing a fluid will sample all molecular orientations equally. Fluids can also be made linearly dichroic by applying a magnetic field.

In a macroscopically isotropic medium, odd rank tensors describing macroscopic properties are equal to zero. Tensors of even rank have only one independent component. Anisotropic media, on the other hand, are described by tensors having more than one independent component [34]. In a linearly dichroic medium for example, the absorption coefficient is a 2nd rank tensor $\alpha_{\alpha\beta}$ whose principle values are not the same in all directions (by definition). Since, as we shall see, Magnetic Linear Dichroism (MLD) is quadratic in the field, measurements of MLD yield information about the anisotropy of second rank tensors such as $\chi_{\alpha\beta}$, the diamagnetic susceptibility tensor and second rank tensors that arise as outer products of the first rank tensor, such as $m_\alpha m_\beta$, the outer product of the magnetic moment tensor with itself. Magnetic Circular Dichroism (MCD) on the other hand, is linear in the applied field and as a result a measurement of MCD will give information on the anisotropy of first rank tensors only.

To date, only a few measurements of MLD have been made on solids and only one measurement [1] has ever been reported for liquid solutions. MLD is much easier to measure in solids than in liquids because absorption band widths are much narrower in solids at low temperatures so that first and second derivative MLD peaks are much larger in solids. MLD is an extremely feeble effect in either case. In solids the field is competing with the lattice energy and in fact the major source of MLD in solids is due to perturbation of the electronic state. In liquids the field competes with the thermal motion of the liquid.

We have succeeded in measuring the MLD of systems much less amenable to detection than those previously studied. Our innovation is in the area of optimization of signal to noise ratio (S/N) and involves the use of an opto-electronic feedback network which will be described in the experimental section of this dissertation. Our technique does not require the use of cryogenic equipment and as such is relatively economical and simple to carry out.

In the following sections we will:

1. Describe the polarimetric spectrodichrometer, including

details of its construction, and compare its properties to those of other dichrometers.

2. Carry out the Jones Calculus matrix analysis of the dichrometer.
3. Develop the theory of MLD in fluids <u>in detail</u> and give illustrative examples of predictions of the theory.
4. Analyze actual MLD spectra and point out the kind of information obtainable from these measurements.
5. Discuss various applications of the techniques.

Chapter 1

The polarimetric method is best appreciated by contrasting it to other existing methods.

The simplest way to measure LD [2] is to determine the absorption coefficient for x-polarized light and then for y-polarized light and to take their difference.

A modification of this method [3] involves insertion of a depolarizer between polarizer and sample (see figure #9). Measurements are made with and without the depolarizer and the difference is related to a dichroic ratio.

A double beam technique eliminates problems associated with duplication of light source intensity.

These two methods are only useful for measuring large linear dichroism signals such as those in anisotropic solids or stretched films. Small signals are deeply buried in 1/f noise.

An elegant way to avoid taking multiple spectra or double beaming was devised by Jaffe, Jaffe and Rosenheck [4] and independently by Rehovoth [5]. A thick wave plate with optic axis at 45° to the electric vector of polarized light is placed between polarizer and sample. The plate acts as a linear retarder. The relative retardance is related to wavelength according to the equation:

$$\phi (\lambda) = 2 \pi \Delta n(\lambda) T/\lambda$$

where

ϕ is in radians

Δn is the difference in refractive index along the two axes

T is the thickness of the plate in cm

λ is the wavelength in cm

therefore, when $nT/ = 1/2, 3/2, 5/2, \ldots$

$\phi = \pi, \pi 3, \pi 5, \ldots$

and as a Jones Analysis will show, light that was originally x-polarized has become y-polarized. For arbitrary values of nT/λ x-polarized light becomes elliptically polarized. A wavelength scan will cause a periodic swing between x and y polarization states. If the medium is dichroic the difference in absorption coefficient will appear as a modulation on an absorption spectrum (see figure #10). This technique has the added virtue of displaying the dichroism and absorption spectrum simultaneously. It is still limited in its accuracy by low frequency (1/f) noise even though the signal is not D.C. since the modulation is usually below 20 Hz.

An important refinement in measuring technique is the conversion of D.C. (or slowly varying A.C.) signals to A.C. signals of at least a few hundred Hz to avoid the effects of 1/f noise. Additionally, an A.C. signal can be separated from much larger noise by comparing it to a suitably chosen reference signal of the same frequency and phase. This process is called autocorrelation of phase-sensitive detection.

These techniques are employed in the Modified Grosjean-Legrand Dichrometer described by Disch and Sverdlik [6] and Mandel and Holzwarth [7]. The Grosjean-Legrand Circular Dichrometer (CD) is shown in figure #3. Linearly polarized light passes through a Pockels Modulator whose fast axis is at 45° to the plane of polarization of light. For circular dichroism (CD) measurements, the relative retardance sinusoidally changes from + to - 90°, which results in a periodic change of the polarization state from right to left circularity. For LD measurements an achromatic quarter wave plate, with its optic axis at 45° to that of the original polarization state of the light, is inserted between the modulator and sample cell. This modulates the light periodically from x to y polarization states. C.D. to L.D. conversion can also be achieved by applying a D.C. to the Pockels Cell that gives a relative retardance of 90° or by simply allowing the relative retardance to go from + to -180°. A linearly dichroic medium generates an intensity modulation at twice the frequency of the Pockels Cell modulation. The intensity-modulated beam is converted to voltage which is sent simultaneously to two filter networks. One passes only the A.C. component through a blocking capacitor. This A.C. is passed to a tuned amplifier and a phase-sensitive detector. The other network is a low-pass filter. The rectified A.C. and mean D.C. are then passed to a divider module whose output voltage is proportional to their ratio. The purpose of "ratioing" is to cancel effects of gradual changes such as those occuring in light source intensity during a wavelength scan. In practice it is found that the two filtering networks do not respond in the same way to various forms of noise. Consequently, it is advantageous to devise a method of detection that effectively reduces noise but does not require ratioing. The polarimetric spectrodichrometer does this by using an opto-electronic feedback mechanism whose principles of operation will now be explained.

Figure 1 is a representation of a polarimetric dichrometer. We will first describe each component separately and then the operation of the dichrometer as a unit.

The pump laser is a Spectra Physics 164 Argon Ion Laser. All spectral lines were used to pump the Coherent Model 590 Dye Laser. We used Rhodamine 6-G (565-635 nm) and Sodium Fluoroscein (540-580 nm) as our dyes. The prism monochromator is driven by a stepping motor connected to its michrometer dial-wavelength selector.

The polarizer, mounted with its fast axis at a 45° angle to the lab x-axis (a horizontal axis), is of the internal reflection type and is manufactured by Carl Lambrecht, Inc.

The sample cell is mounted between the pole faces of an Alpha Scientific Model 4600 Electromagnet that is capable of producing a maximum field of 22 kilo-gauss at the pole gap used (1.2 cm).

A soft-iron (ferromagnetic) box houses the Faraday Cell. The box keeps any stray flux from the electromagnet from generating an optical rotation in addition to that of the desired Faraday Effect. The Faraday Cell consists of approximately 45,000 turns of 30-guage enamel-insulated copper wire wound around a hollow brass bobbin whose outer diameter is 20 mm. Within the bobbin is a cylindrical glass slug whose outer diameter is 18 mm, inner diameter is 17 mm and whose length is 18 cm. The slug filled with carbon tetrachloride. In order to avoid problems associated with reflection and birefringence, the edges of the slug were made parallel to each other using the position of reflected laser light as an indicator of parallelism (see figure #2) and the windows used were of optically flat fused silica, which is transparent into the near Ultra-Violet.

The analyzer is of the same type as the polarizer and is crossed with respect to the polarizer.

The photomultiplier is an EMl Model 9558 (trialkili cathode).

The desired signal passes through a tuned amp (see figure #4) and then to a phase-sensitive detector (see figure #5) where it is multiplied by the reference signal from a 450 cycle oscillator (see figure #6).

The phase-detected output then goes to a Philbrick Researches P66A Op-Amp which serves as part of an opto-electronic feedback loop whose operation will be explained shortly. The output of this op-amp goes to one end of the Faraday Cell and to an integrator, which serves to smooth the D.C. signal (see figure #7). The other end of the Faraday Cell is connected to a signal from our 450 cycle oscillator that has first been amplified by a McIntosh 40 Audio Amplifier and send through a 40/1 step-up transformer.

Notice, in figure #1, the way in which the A.C. and D.C. are both on the Faraday Cell. The D.C. cannot be input through the transformer, of course. At the same time we want to establish a path to ground for the A.C. signal (and we want to avoid feeding back our A.C. signal). For this reason a large capacitance is placed in the feedback loop.

Finally, the smoothed signal is fed to the y-axis of a Houston Instruments Model 2000 X-Y Recorder. The input to the x-axis is a voltage linearly related to the wavelength setting on the dye laser.

The entire apparatus is mounted on marble slabs which are placed on sand-filled tables, to minimize effects of low frequency vibrations.

In considering the operation of the dichrometer, imagine that the medium is not made dichroic by the applied field. Light of frequency ν, linearly polarized at 45° to the lab x-axis, passes through the absorbing sample with its x and y components equally attenuated. The plane of polarization is therefore unchanged and the light has its plane of polarization at 450 Hz about its 45° axis. This modulation results in a 900 Hz <u>intensity</u>-modulated beam exitting the analyzer, which is at -45° to the lab x-axis (see figure #8 for explanation). Since the amplifier is tuned to 450 Hz, no signal appears on the recorder.

If the medium is made dichroic the x- and y-polarized components are no longer absorbed to the same extent and light exitting the sample cell has had its plane of polarization rotated from its original 45° orientation. This rotation, when coupled with the Faraday Cell modulation results in a 450 Hz intensity modulation of light exitting the analyzer (see Jones Analysis). The 450 Hz signal is a direct measure of optical rotation induced by the MLD. This signal is transduced by the photomultiplier, sent through a tuned amplifier and phase-sensitive detected (and rectified).

So far, we have processed our signal in the same way as Mandel and Holzworth, except that we did not need a depolarizer, since the analyzer passed only one polarization state, albeit of periodically varying intensity. We now feed back a fraction of the rectified signal negatively to the Faraday Cell. The current through the latter causes a rotation of the light in a direction opposite to that due to the dichroism. This negative-feedback loop makes the overall "closed-loop" gain of the signal, that is the amplification of the signal, dependent only on the feedback ratio, which is the fraction of signal fed back from output to input as illustrated in figure #1 and independent of the actual open loop gain parameters, if the open loop gain is large enough. In our apparatus the major gain factors include the light source intensity, photomultiplier, induction in the photomultiplier op-amp, and feedback op-amp. This is a well known principle in operational-amplifier electronics [16, 17]. Mathematically:

$$A_{C.L.} = \frac{A_{O.L.}}{1+BA_{O.L.}}$$

where

$A_{C.L.}$ = closed-loop gain

$A_{O.L.}$ = open-loop gain

B = feedback ratio

V_{in} = input voltage

V_{out} = output voltage

When $A_{O.L.} >> 1$ the equation reduces to $A_{C.L.} = 1/\beta$. The innovative use of this principle is the inclusion of the light source in the open loop gain. Under conditions of large open loop gain, greatly enhanced with laser sources, overall signal amplification is effectively independent of changes in source intensity due to frequency changes or plasma fluctuations in the gas laser. In practice, this negative feedback allows detection of rotations as small as 0.0005°.

Before using the polarimetric method, we tried two versions of an alternative detection scheme which also use opto-electronic feedback. This scheme is closely related to that of Disch and Sverdlik [6]. In the first version, horizontally polarized light goes through a Pockels Cell oriented with its fast axis at 45° to the horizontal axis. Its relative retardation is varied periodically at (450 Hz) from -180° to +180°. This causes initially horizontally polarized light to become elliptically polarized and, in the extreme + or - 180° relative retardation, to become vertically polarized. As before, imagine that the medium is not dichroic. The polarization-modulated beam enters an analyzer whose transmission axis is oriented at 45° to the transmission axis of the (horizontal) polarizer. As the Jones analysis shows, the exitting light is not intensity-modulated, since the analyzer "sees" the same intensity of light along its transmission axis at all times. If the medium is dichroic, light exitting the sample cell is <u>intensity</u>-modulated at 900 Hz, twice the modulation frequency (see Jones Analysis). The analyzer would be superfluous in this case if we did not introduce negative feedback. We do, of course, and a D.C. current proportional to the dichroism is fed back to the Faraday Cell (which no longer needs an A.C. modulation is already taken care of by the Pockels Cell). This current causes an optical rotation which opposes changes in polarization state due to the linear dichroism. The effect is to rotate the light so that the analyzer sees the same intensity of light along its transmission axis at all times.

In principle this method should succeed. In practice, however, Pockels Modulators are found to crack too readily under the strain of the impressed electric field. (We broke two of these expensive cells in this manner.) This may be due in part to the fact that we require a relative retardance of ±180° which requires a higher voltage, for a given wavelength, than does a relative retardance of ±90°.

In a variation of the above scheme, a Morvue Electronic Systems Photoelastic Modulator modulated the plane of polarized light at 50 KHz. This attempt to measure MLD was unsuccessful because we were unable to eliminate a large spurious 100 KHz signal that was nearly 90° out of phase with the desired signal. While we are unaware of the nature of this spurious signal we have determined that it originates at the photoacoustic modulator and increases rapidly with the temperature of the latter.

When dealing with polarized light it is necessary to minimize undesired effects of stray reflection, birefringence and optical components. If the front and back faces of the sample cell or of the Faraday Cell are not parallel, the x-polarized component of the light will be reflected to a different extent than the y-polarized component, resulting in a spurious dichroism.

The effects of birefringence differ according to the detection scheme used. For convenience we call the polarimetric method "#1" and the other method "#2." In #1 birefringence due to strain in the glass serves in the first approximation to degrade S/N by reducing the ability to determine the major axis orientation, since some light exits the analyzer at all times. This reduces the fraction of light incident on the photomultiplier cathode solely due to modulation.

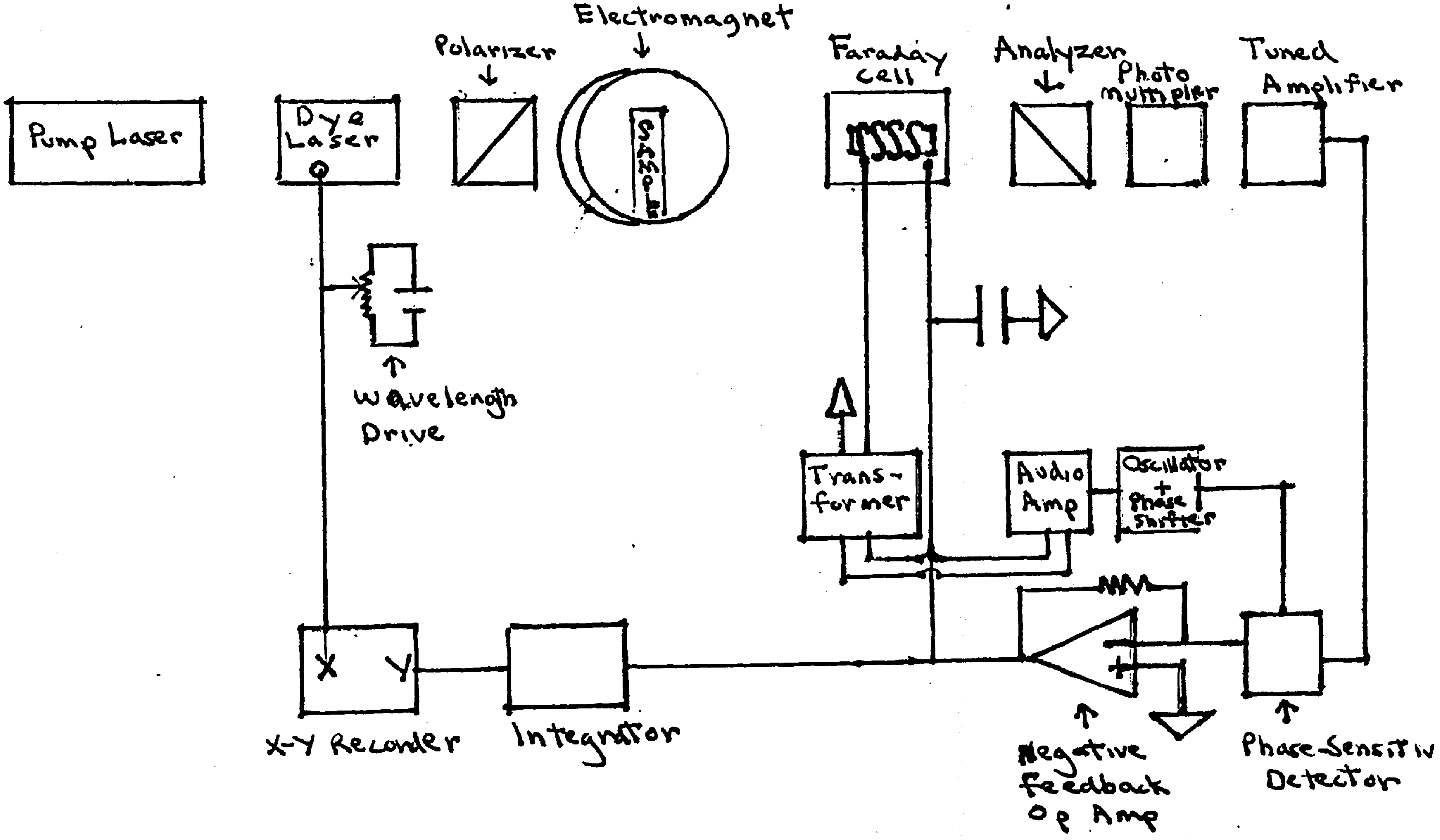
In #2 birefringence due to the glass adds to that from the modulators, effectively causing a modulation of $180° + 0$. Since this birefringence is, of course, wavelength dependent it is not constant during the course of a wavelength scan.

Optical rotation has the same effect upon both methods, that it produces a spurious signal. In #1 the polarimeter has no way of distinguishing between a rotation due to any other factor.

In #2 a rotation has the effect of changing the 45° relative orientation of the polarizer-analyzer pair, although it does so in a different manner from the dichroism.

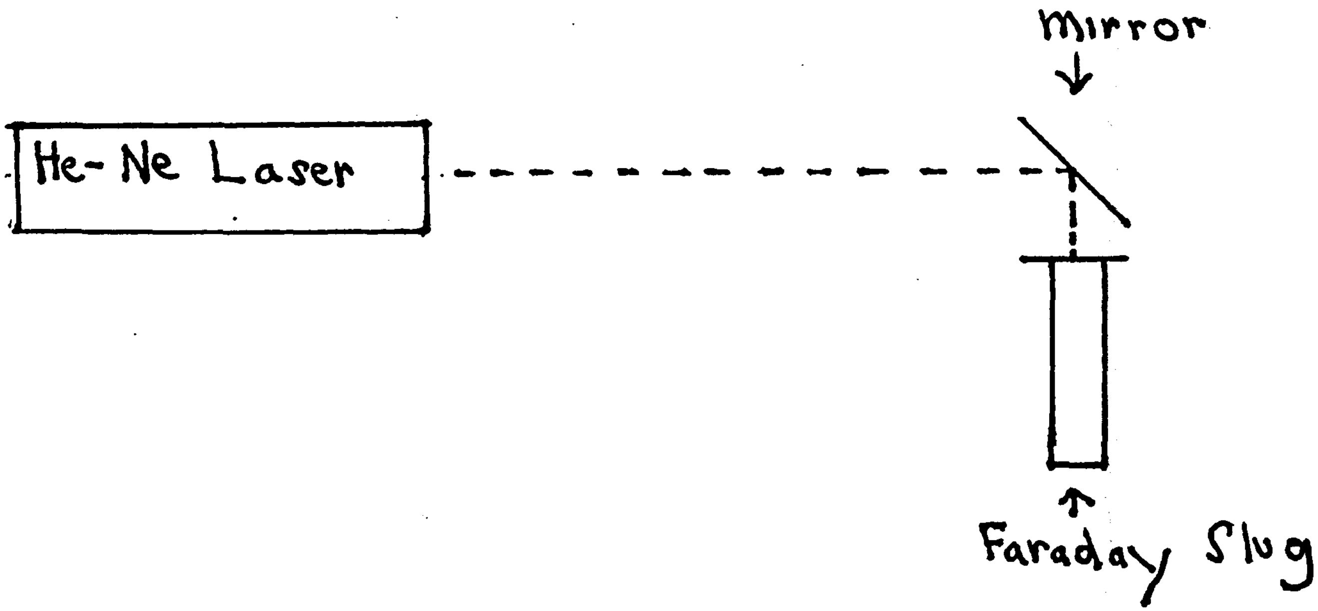
Ideally, we would eliminate all optical surfaces which serve only to hold samples in places. We considered having the sample jet across the path of the light beam instead of placing it in a cuvet (1cm x 1cm x 5cm) but this would make it difficult to keep the sample path length uniform and could introduce streaming dichroism. We also considered building our own sample cells, thereby eliminating strain caused by fusion of glass surfaces but found that it would be difficult to assure that the two pairs of faces would be parallel. We were forced to use commerical cuvets which <u>were</u> designed with parallel faces but not with serious regard to strain birefringence or optical rotation. We tested a large number of cells (720) before we found one that was suitable.

As we stated, our Faraday Cell has a glass tube filled with CCl_4, <u>not</u> the convential cylindrical glass rod. The glass rod would cause a large relative retardation due to the long path length. We have already described how we parallelized the ends of the tube.



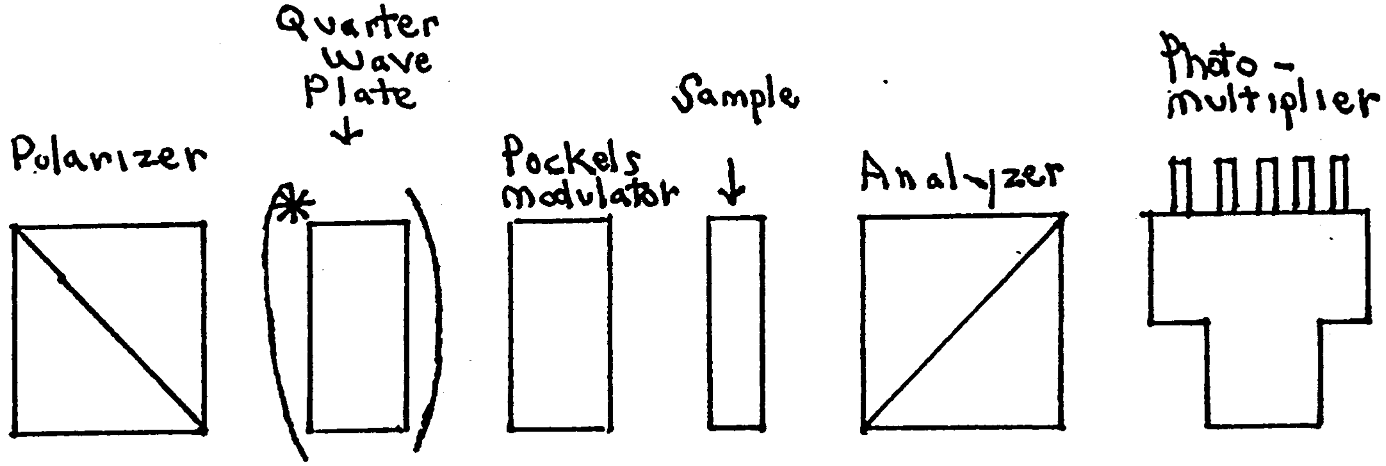
Polarimetric Linear Dichroism Detector

figure 1.



Parallelization of ends of Faraday Tube

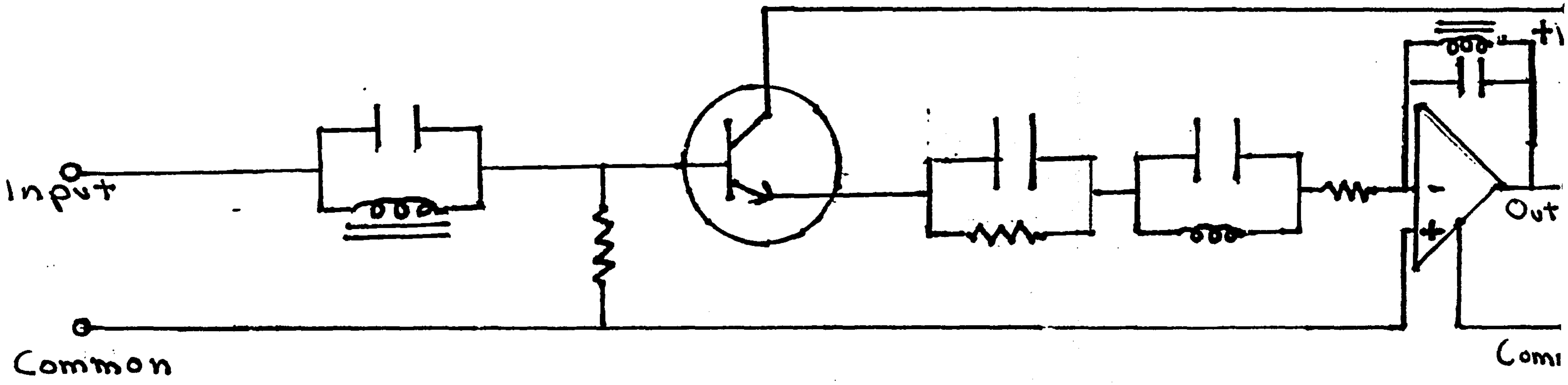
figure 2.



Circular Dichrometer

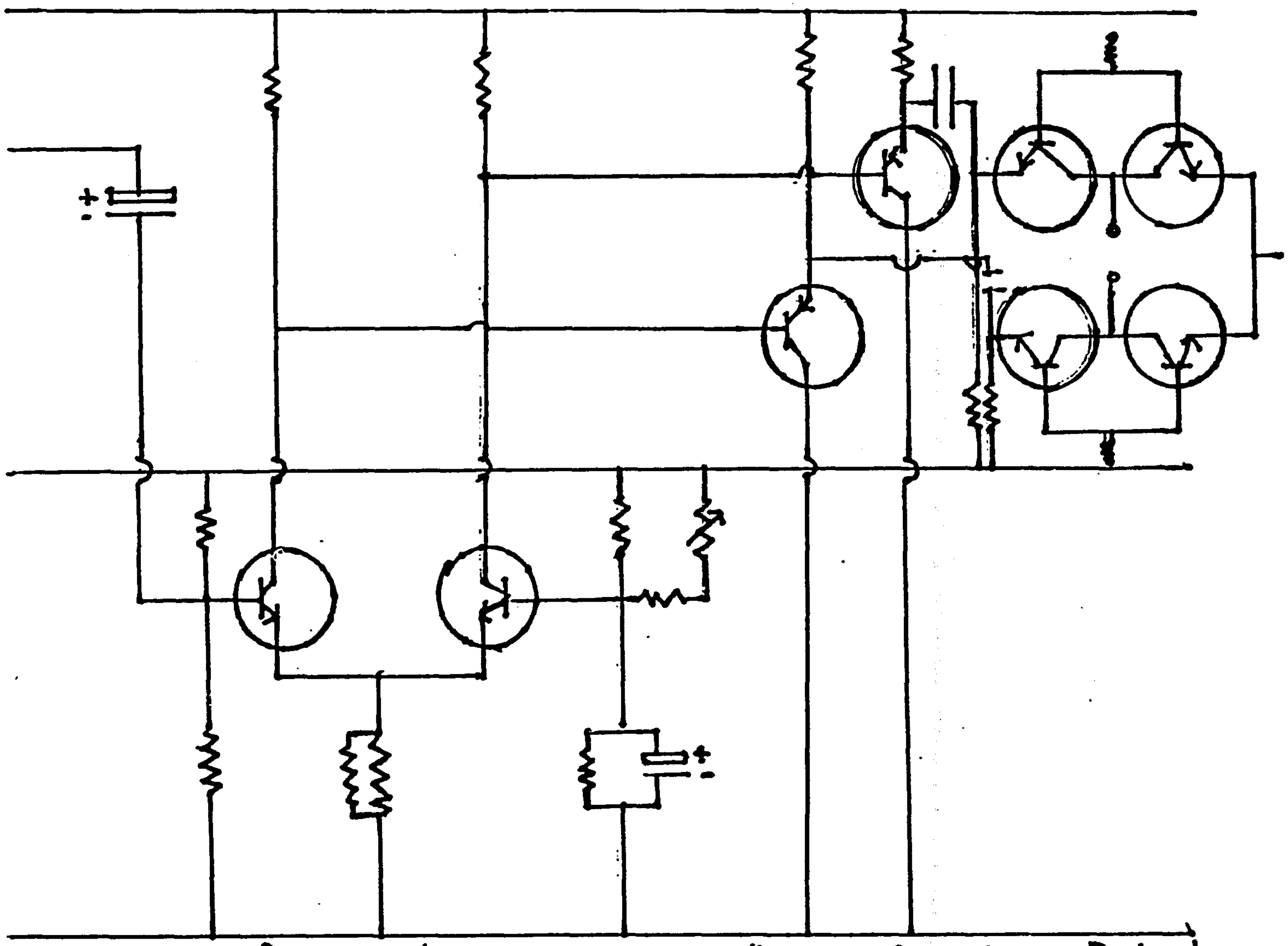
* Insertion of quarter wave plate converts CD to LD

figure 10



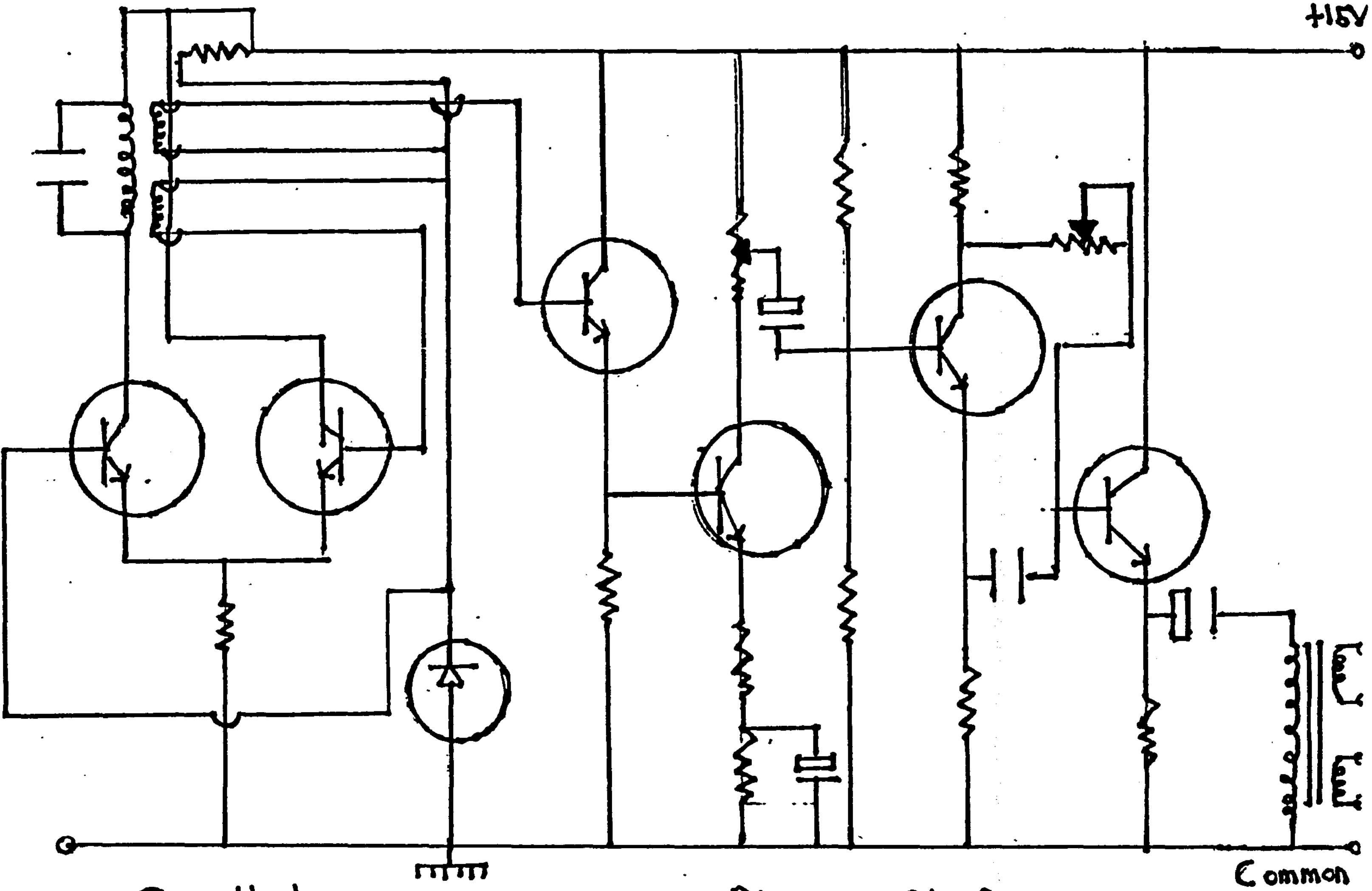
Tuned Amplifier

figure 4.



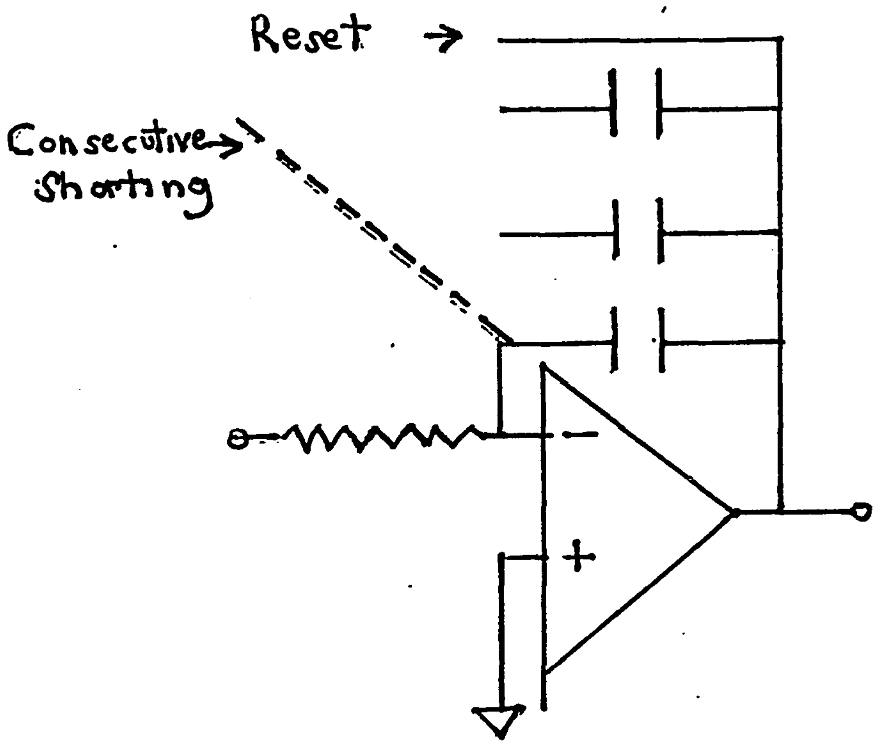
Phase Inverter + Phase Sensitive Detector

figure 5.



Oscillator + Phase Shifter

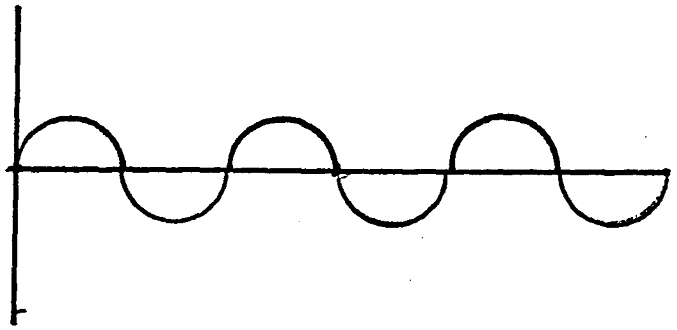
figure 6.



Integrator

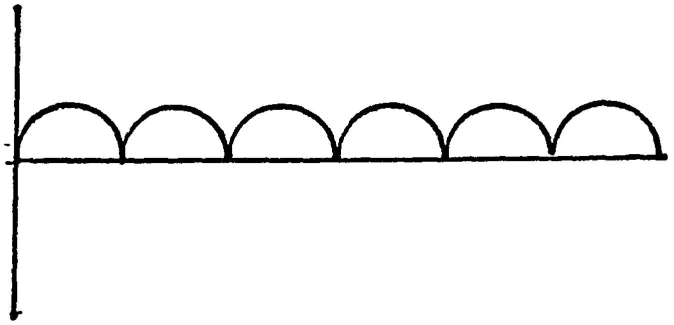
figure 7.

A.



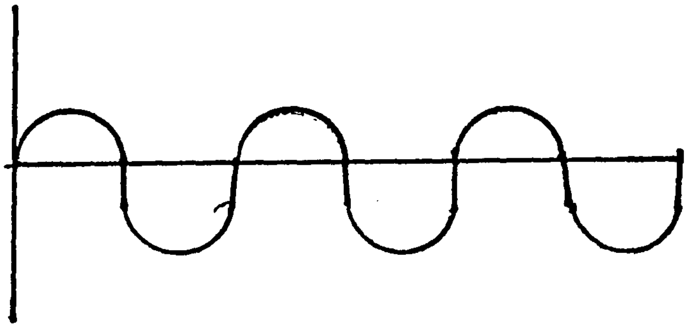
No MLD, Amplitude Modulation

B.



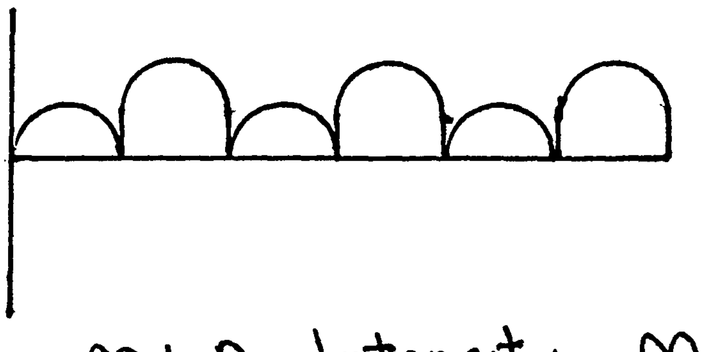
No MLD, Intensity Modulation

C.



MLD, Amplitude Modulation

D.



MLD, Intensity Modulation

figure 8

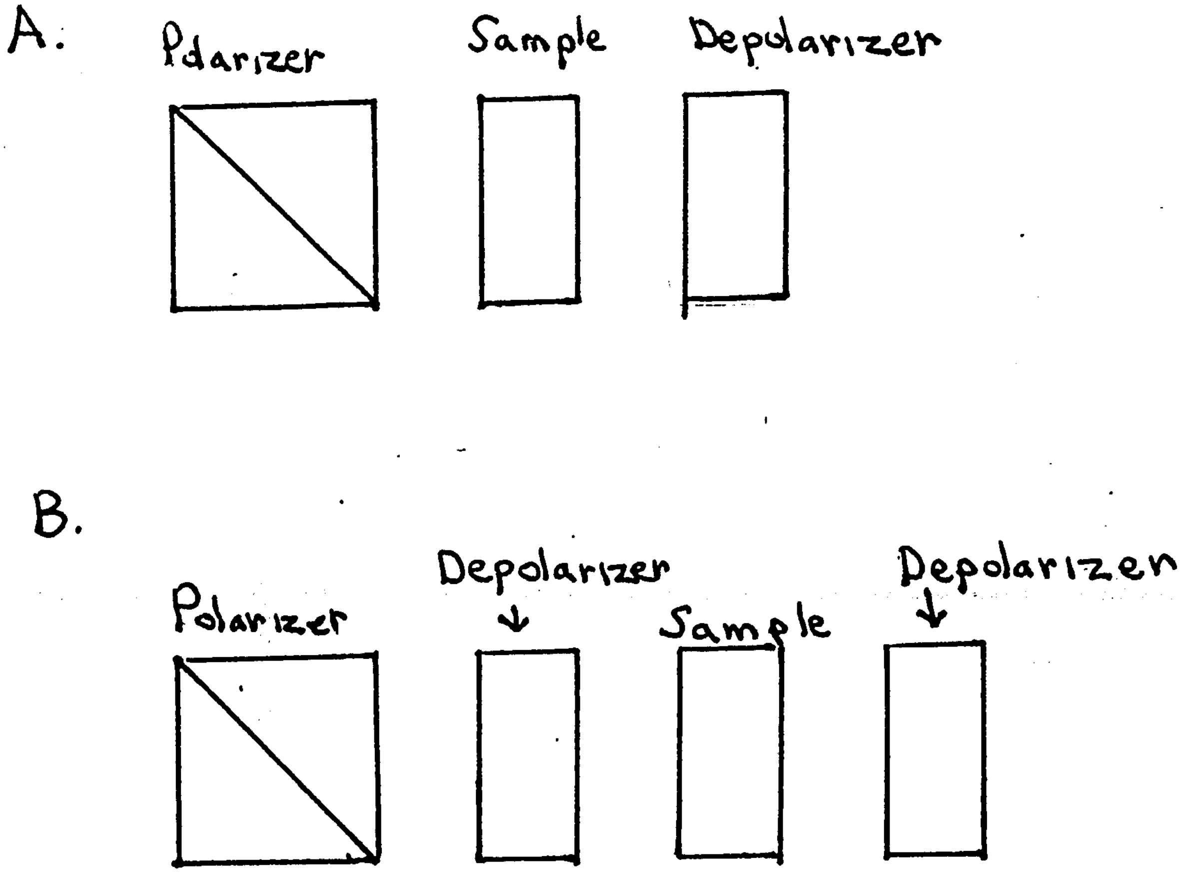


Figure 9.

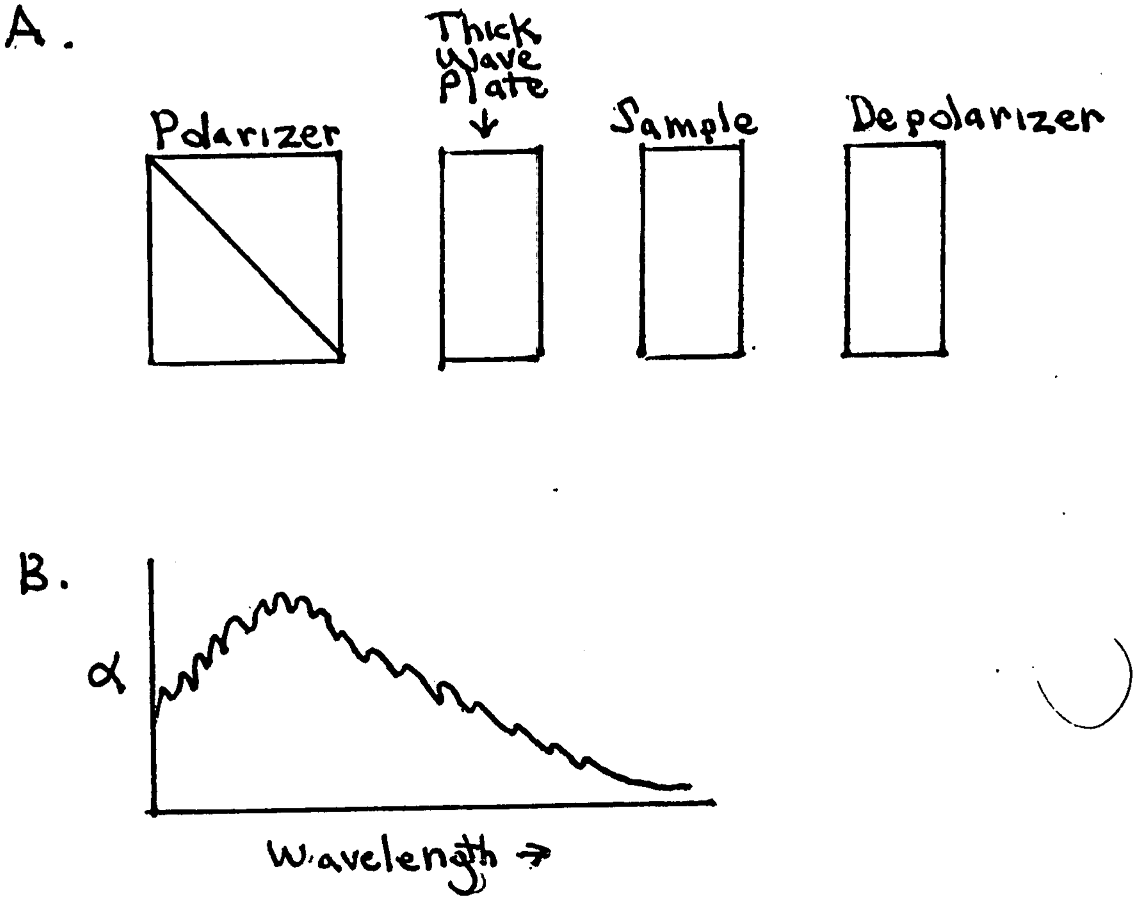


Figure 3.

Chapter 2

The x and y components of the electric vector of a plane light wave travelling in the z-direction are [18].

$$E_x = R(E_{ox}\exp(i\ (\omega t - (\omega/c)n_x z)))$$

$$E_y = R(E_{oy}\exp(i\ (\omega t - (\omega/c)n_y z)))$$

where

E_o = amplitude of electric field (V/cm)

ω = angular frequency (s^{-1})

t = time

z = distance travelled through medium (cm)

$\hat{n}$ = $n - ik$ = complex refractive index

n = c/u = real part of refractive index

k = extinction coefficient cm^{-1} (not the same as the ordinary extinction coefficient)

c = velocity of light in vacuo = 299×10^{-10} cm/s

u = phase velocity of electric vector (cm/s)

i = $\sqrt{-1}$

Expanding $\hat{n}$ in the above equations gives:

$$E_x = R(E_{ox}\exp(i\ (\omega t - (\omega/c)n_x z))\exp(-(\omega/c)k_x z))$$

$$E_y = R(E_{oy}\exp(i\ (\omega t - (\omega/c)n_y z))\exp(-(\omega/c)k_y z))$$

These equations show that the effect of a birefringent medium ($n_x \neq n_y$) representing the electric vector of light incident on the medium which is represented by the column vector

$$\begin{vmatrix} E_{ox}\exp(i\varepsilon x) \\ E_{oy}\exp(i\varepsilon y) \end{vmatrix}$$

is given by the 2 x 2 matrix:

$$\begin{vmatrix} \exp(iA) & 0 \\ 0 & \exp(-iA) \end{vmatrix}$$

<u>where</u>

$A = \pi z/\lambda$ (radians)

$\lambda =$ vacuum wavelength of radiation

$\varepsilon x,\ \varepsilon y =$ phase angles (radians)

These equations also show that the effect of a dichroic medium on the same electric vector is given by:

$$\begin{vmatrix} \exp(-K_x z) & 0 \\ 0 & \exp(-K_y z) \end{vmatrix}$$

We will now carry out a Jones Analysis [8,19] on methods #1 and #2 and discuss the results of each analysis,

Glossary of Terms for Both Methods

E_{ox} = amplitude of electric vector of light (V/cm)

$A = \delta_o \sin\omega t$ = relative retardation (radian)

$\delta_o = \pi$ (radian)

ε_x = phase angle (radian)

I_o = intensity of light entering sample cell (W)

I = intensity of light exitting sample cell (W)

$K_x \cdot z$, $K_y \cdot z$ = extinction coefficients

z = distance (cm) = length of sample cell

cf, sf = cosf, sinf

f = total Faraday Cell rotation (method #1)

$= g(\sin\omega t)th$ (radian)

g = peak amplitude of periodic Faraday Cell alternating half-shade rotation (radian)

ω = frequency of half shade rotation = 450 Hz

h = d.c. Faraday Cell rotation (method #1) (radian)

f_1 = Faraday Cell rotation (method #2) (radian)

ω_1 = frequency of Pockels Cell modulation = 450 Hz

Method #1

Optical Devices

1. Polarizer, with transmission axis at 45° to horizontal axis

$$\frac{1}{2}\begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix}$$

2. Linearly Dichroic Medium

$$\begin{vmatrix} \exp(-K_x z) & 0 \\ 0 & \exp(-K_y z) \end{vmatrix}$$

3. Faraday Rotator

$$\begin{vmatrix} cf & -sf \\ sf & cf \end{vmatrix}$$

4. Analyzer, crossed with respect to polarizer

$$\tfrac{1}{2}\begin{vmatrix} 1 & -1 \\ -1 & 1 \end{vmatrix}$$

These optical devices operate on horizontally polarized light given by the column vector

$$\begin{vmatrix} \exp(i\varepsilon_x) \\ 0 \end{vmatrix}$$

$$\tfrac{1}{2}\begin{vmatrix} 1 & -1 \\ -1 & 1 \end{vmatrix} \begin{vmatrix} cf & -sf \\ sf & cf \end{vmatrix} \begin{vmatrix} \exp(-K_x z) & 0 \\ 0 & \exp(-K_y z) \end{vmatrix} \tfrac{1}{2}\begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix} \begin{vmatrix} \exp(i\varepsilon_x) \\ 0 \end{vmatrix}$$

The resultant column vector is

$$\tfrac{1}{4}\, E_{ox}\exp(i\varepsilon_x) \left| \begin{array}{l} \exp(K_x z)\cdot cf - \exp(-K_y z)\cdot sf \\ -\exp(-K_x z)\cdot sf - \exp(-K_y z)\cdot cf \\ \\ \exp(-K_y z)\cdot sf - \exp(-K_x z)\cdot cf \\ \exp(-K_y z)\cdot cf + \exp(-K_x z)\cdot sf \end{array} \right|$$

The intensity of the resultant light is

$$I = 1/16\ (E_{ox})^2 \left| \begin{array}{l} cf\cdot(\exp(-K_x z - \exp(-K_y z)) \\ -sf\cdot(\exp(-K_x z) + \exp(-K_y z)) \end{array} \right|^2 + \left| \begin{array}{l} cf\cdot(\exp(-K_x z) + \exp(K_y z)) \\ -cf\cdot(\exp(-K_x z) - \exp(K_y z)) \end{array} \right|^2$$

$$I = 1/8\ (E_{ox})^2 \left| \begin{array}{l} (\exp(-K_x z) - \exp(-K_y z))cf \\ -(\exp(-K_x z) + \exp(-K_y z))sf \end{array} \right|^2$$

Since $f \ll 1$ $cf \approx 1$ and $sf \approx f$

Therefore

$$I = 1/8\ (E_{ox})^2 \left| \begin{array}{l} (\exp(-K_x z) - \exp(-K_y z)) \\ -(\exp(-K_x z) + \exp(-K_y z)\cdot f \end{array} \right|^2$$

We can rewrite $\exp(-K_x z) - \exp(-K_y z)$

as

$$\frac{1}{2} \left| \begin{array}{l} \exp(-K_x z) \;\; (1-\exp(K_x z) \;\; \exp(-K_y z)) \\ +\exp(-K_y z) \;\; (\exp(K_y z) \;\; \exp(-K_x z)-1)) \end{array} \right|$$

or as

$$\frac{1}{2} \left| \begin{array}{l} \exp(-K_x z) \;\; (1-\exp \;\; (-\delta) \\ \qquad\qquad + \\ \exp(-K_y z) \;\; (\exp(+\delta) \;\; -1) \end{array} \right|$$

where

$$\delta = z(K_y - K_x)$$

Since $\delta << 1$

$$\exp(\delta) \quad 1 + \delta$$

Therefore $\frac{1}{2} \left| \begin{array}{l} \exp(-K_x z) \;\; (1-\exp(-\delta) \\ +\exp(-K_y z) \;\; (\exp(\delta) \;\; -1 \end{array} \right| =$

$$\delta/2 \;\; (\exp(-K_x z) + \exp(-K_y z))$$

Substituting this result in the expression for I gives:

$$I = 1/8 \;\; (E_{ox})^2((\exp(\exp(-K_x z)+\exp(-K_y z))((\delta/2)-f))^2$$

Consider the following cases:

1. No linear dichroism present

$$\exp(-K_x z) = \exp(-K_y z)$$

and $\delta/2 = h$ (not f!) $= 0$

therefore $I = \frac{1}{4}(E_{ox})^2 \exp(-2K_x z)\ (g\sin\omega t)^2$

This expression contains terms in 2ω, not ω

since $\sin^2\omega t = \frac{1}{2}(1-\mathrm{co}2\omega t)$

and not 450 Hz signal will be detected.

2. Linear dichroism present

$\delta/2$ opposes h and the expression for I does contain a term in ω since

$$\begin{aligned} f^2 &= (g\sin\omega t + h)^2 \\ &= g^2\sin^2\ t + \underline{2gh\sin\omega t} \end{aligned}$$

The maximum Faraday rotation possible in our apparatus is

$\pm$ .045°/57.3°/radian = $\pm\ 7.86 \times 10^{-4}$ radians

As we shall see when we analyze MLD spectra, the minimum detectable signal is $\leq .2\%$ of the maximum at a 1 second time constant or $\pm 1.57 \times 10^{-6}$ radian. Our intensity expression shows that $/\delta/ = 2/h/$ when negative feedback is applied. The minimum δ detectable is thus 3.14×10^{-6}. Since

$$I/I_o = \exp(-2Kz) \text{ and } A = \log_{10} I_o/I = 2KiZ/2.303 = \alpha' z$$

$\delta = 3.14 \times 10^{-6}$ corresponds to a difference of 2.73×10^{-6} Optical Density Units (O.D.)

Optical Devices

1. Pockels Modulator oriented with optic axis at 45° to the horizontal axis:

$$\begin{vmatrix} 1/\sqrt{2} & -1/\sqrt{2} \\ 1/\sqrt{2} & 1/\sqrt{2} \end{vmatrix} \begin{vmatrix} \exp(iA) & 0 \\ 0 & \exp(iA) \end{vmatrix} \begin{vmatrix} 1/\sqrt{2} & 1/\sqrt{2} \\ -1/\sqrt{2} & 1/\sqrt{2} \end{vmatrix} = \begin{vmatrix} \cos A & i\sin A \\ i\sin A & \cos A \end{vmatrix}$$

2. Linearly Dichroic Medium:

$$\begin{vmatrix} \exp(-K_x z) & 0 \\ 0 & \exp(-K_y z) \end{vmatrix}$$

3. Faraday Rotation:

$$\begin{matrix} cf_1 & -sf_1 \\ sf_1 & cf_1 \end{matrix}$$

4. Analyzer having azinuith of its transmission axis oriented at 45° to the horizontal axis:

$$\begin{matrix} 1 & 1 \\ 1 & 1 \end{matrix}$$

These devices operate on horizontally polarized light:

$$\tfrac{1}{2}\begin{vmatrix} 1 & 1 \\ 1 & 1 \end{vmatrix} \begin{vmatrix} cf_1 & -sf_1 \\ sf_1 & cf_1 \end{vmatrix} \begin{vmatrix} \exp(-K_x z) & 0 \\ 0 & \exp(-K_y z) \end{vmatrix} \begin{vmatrix} \cos A & i\sin A \\ i\sin A & \cos A \end{vmatrix} \begin{vmatrix} E_{ox}\exp(iEx) \\ 0 \end{vmatrix}$$

The resultant column vector is:

$$\tfrac{1}{2}E_{ox}\begin{vmatrix} \exp(-K_x z)\cos\varepsilon_x\cos A(cf_1+sf_1)-\exp(-K_y z)\sin\varepsilon_x\sin A(cf_1-sf_1) \\ +i(\exp(-K_x z)\sin\varepsilon_x\cos A(cf_1+sf_1)-\exp(-K_y z)\cos\varepsilon_x\sin A(cf_1-sf_1)) \\ \text{"} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{"} \\ \text{"} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{"} \end{vmatrix}$$

The light intensity is obtained as $\vec{E}\cdot\vec{E}^*$;

$$I = (E_{ox})^2/2 \left| \begin{array}{c} \exp(-2K_x z)\cos^{2A}(cf_1+sf_1)^2 \\ + \\ \exp(-2K_y z)\sin^2 A(cf_1-sf_1)^2 \end{array} \right|$$

$$I = (E_{ox})^2/2 \left| \begin{array}{l} \exp(-2K_x z)(1+2f_1) \\ \qquad + \\ \sin^2 A \;\; (\exp(-2K_y z)-\exp(-2K_x z) \\ \qquad -2f(\exp(-2K_x z)+\exp(-2K_y z)) \end{array} \right|$$

since $f_1 << 1$

using the same arguments as in the previous analysis we arrive at the following:

$$I = (E_{ox})^2/2 \left| \begin{array}{c} (\delta-2f_1)(\exp(-2K_x z)+\exp(-2K_y z))\sin^2 A \\ + \\ \exp(-2K_x z)(1 + 2f_1) \end{array} \right|$$

Consider the following cases:

1. No linear dichroism present

<u>then</u> $\delta=2f=0$

$$I = (E_{ox})^2/2 \cdot \exp(-2K_x z)$$
$$I_o = (E_{ox})^2$$

and $I/I_o = \exp(-2K_xz)/2$

The factor of ½ results from the 45° relative orientation of polarizer and analyzer.

2. Linear Dichroism present:

In this case δ and 2f oppose each other and I contains a term in $\sin^2 A$ as well as in $\exp(-2K_xz)$. Note that:

since $\quad A = \gamma_o \sin\omega_1 t$

then $\quad \sin^2 A = (\sin(\gamma_o \sin\omega_1 t))^2$

is a series of Bessel Functions of integer order [20].

$$(\sin(\gamma_o \sin\ {}_1t))^2 = \left| \begin{array}{l} 2J_1(\gamma_o)\sin\omega_1 t + 2J_3(\gamma_o)\sin 3\omega_1 t) \\ \\ +2J_5(\gamma_o)\sin 5\omega_1 t + \ldots \qquad\qquad) \end{array} \right|^2$$

$$(\sin(\gamma_o \sin\omega_1 t))^2 = 2(J_1^2(\gamma_o)\sin^2\ {}_1t + J_3^2(\gamma_o)\sin^2 3\omega_1 t + \ldots)$$

$$+4(J_1J_3\sin\omega_1 t\sin 3\omega_1 t + \ldots\_$$

$J_1(\gamma_o) = .5668$

$J_3(\gamma_o) = .0691$

$J_5(\gamma_o) = .0022$

$J_1J_3 = .0392$

$J_1^2(\gamma_o) = .3213$

It is obvious that we need only consider terms in $J_1^2(\gamma_o)$ and $J_1(\gamma_o)$ and $J_1(\gamma_o)J_3(\gamma_o)$

Now

$$\sin^2{}_{\omega 1}t = \tfrac{1}{2}(1-\cos 2\omega_1 t)$$

$$\sin\omega_1 t \ \sin 3\omega_1 t = \tfrac{1}{2}(\cos 2\omega_1 t-\cos 4\omega_1 t)$$

We save only the $2\omega_1 t$ terms. Thus:

$$(\sin(\gamma_o \sin\omega_1 t))^2 = (\cos 2\omega t)(.6426)+(\cos 2\omega_1 t)(.1568)$$

$$\approx - .486 \cos 2\omega_1 t$$

Finally:

$$I = (E_{ox})^2 /2 \left| \begin{array}{l} (\delta-2f_1)(\exp(-2K_x z)+\exp(-2K_y z))(-.486(052\omega_1 t) \\ +\exp(-2K_x z)(1+2f_1) \end{array} \right|$$

Chapter 3

The most appropriate treatment of liquid solutions at room temperature is a semiclassical one [9]; Rotational states are assumed to be a classical continuum while vibrational and electronic states are considered to be discrete and are treated quantum mechanically.

The molecular hamiltonian H is the sum of three parts; H_o, H_1, and H_2. H_o is the hamiltonian of the molecule unperturbed by magneto static field or radiation field [21].

$$H_o = \sum_i (\tfrac{1}{2}m_i)(-h\hat{\nabla}_i^{\,2}) + V = \sum_i (\tfrac{1}{2}m_i^{\,2} \cdot c^2)(s \cdot (\hat{\nabla} V x \hat{p}_i))$$

$$+ \sum_{i<j} (e_i e_j / m_i m_j c^2)(\hat{s}_i \cdot \hat{s}_j / r_i{}^3 j) - 3(\hat{s}_i \cdot \hat{r}_{ij})(\hat{s}_j \cdot \hat{r}_{ij}) / r_{ij}^{\,5}))$$

<u>where</u>

Summations are over electrons and nucleii except for spin-dependent terms which are only over electrons.

m_i = mass of ith particle

$\hat{\nabla}_i$ = Laplacian operator of ith particle

V = potential energy of interaction of particles i and j (in pairs) = $\Sigma e_i \cdot e_j / r_{ij}$

e_i = coulombic charge on ith particle

r_{ij} = distance between particles i and j

c = velocity of light

$\hat{p}_i$ = linear momentum operator of ith particle

$\hat{s}_i$ = spin operator of ith particle

The first and second terms are the kinetic and potential energy operators. The third term is the spin-orbit coupling operator and the fourth term the spin-spin coupling operator.

Application of a static magnetic field perpendicular to the director of propagation of light (Zeeman effect) is represented by the perturbation H_i.

$$H_i = (\tfrac{1}{2}m_i)\ ((e_i/c)\ (\hat{A}_{1i}\cdot\hat{p}_i) + (e_i/c)^2\ (\hat{A}_{1i}\cdot\hat{A}_{1i})$$

$$\sum_i + (e_i/m_ic)\ (\hat{s}_i\cdot\hat{\nabla}_i x\hat{A}_{1i})$$

$$+ (\tfrac{1}{2}m_i{}^2c^2)\ (\hat{s}_i\cdot(\hat{\nabla}_i Vx(-e_i/c)\hat{A}_{1i}))$$

<u>where</u>

A_{1i} = vector potential at particle i of the static magnetic field.

The first term leads to the first order orbital Zeeman effect. The second term loads to the Larmor part of the Zeeman energy, quadratic in the static magnetic field. The third term represents the interaction between spin and $\mathcal{H}_1$. The fourth term represents perturbation of the spin-orbit coupling by $\mathcal{H}_1$.

Finally, the system H_o+H_1, is perturbed by light.

$$H_2 = \sum_i (e_i/2m_ic)(\hat{A}_{2i}\cdot\hat{p}_i)-(e_i/m_ic)(\hat{s}_i\cdot\hat{\nabla}xA_{2i})$$

$$+(e_i/2m^2c^3)(\hat{s}_i(\hat{\nabla}_iVx\hat{A}_{2i}))-(e_i/m_ic)(A_{1i}\cdot A_{2i})$$

where

A_{2i} = vector potential of the electromagnetic radiation at particle i.

The first term leads to the primary interaction of the periodic electromagnetic field with the electronic charge distribution. The second term represents interaction of spin with the periodic field. The third term represents perturbation of the spin-orbit coupling by the periodic field and the fourth term the interaction of the static and periodic fields through the electronic charge distribution. The overall hamiltonian is $H = H_o + H_1 + H_2$

The total hamiltonian H is of the same form as the one given by P.J. Stephens [10] on MCD, except that we must include terms quadratic in $\mathcal{H}_1$, in the perturbation development in order to account for MLD. The static magnetic field perturbation contains a term quadratic in $\mathcal{H}_1$. As a result, we must include, to second order, perturbation terms that are linear in $\mathcal{H}_1$. The first order term is:

$$(e_i/2m_i c^2)\hat{A}_{1i} \cdot \hat{A}_{1i} = (\tfrac{1}{4})(\hat{\mathcal{H}}_{1i} x \hat{r}_i) \cdot (\hat{\mathcal{H}}_{1i} \hat{x} r_i)$$

where

r_i = position of particle i

Using the vector identity:

$$(A x B) \cdot (A x B) = (A \cdot A)\ (B \cdot B) - (A \cdot B)\ (A \cdot B)$$

we have:

$$(e_i/8m_i c^2)\ (|\hat{\mathcal{H}}_{1i}|^2 |\hat{r}_i|^2 - (\hat{r}_i \cdot \hat{\mathcal{H}}_{1i})\ (\hat{r}_i \cdot \hat{\mathcal{H}}_{1i}))$$

or, in cartesian tensor notation [22] repeated Greek subscripts denote summation)

$$(e_i/8m_i c^2)\ (\mathcal{H}_{1i\alpha}\mathcal{H}_{1i\alpha} r_\beta r_\beta - \mathcal{H}_{1i\alpha}\mathcal{H}_{1i\beta} r_\alpha r_\beta)$$

The second-order (Van Vleck) term is:

$$\sum_{K \neq L} < \psi_{OK}|H^1|\psi_{OL}> <\psi_{OK}|H^1|\psi_{OL}>^* / (E_{OL} - E_{OK})$$

where

ψ_{OK}, ψ_{OL} = eigenfunctions of H_0 (K and L labelling states)

H^1 = $(e_i/2m_i c)\ H_{1i\alpha} \cdot (\hat{r}_i x \hat{p}_i + 2\hat{s}_i)_\alpha$

E_{OL}, E_{OK} = eigenvalues of $H_{OL}\psi_{OL}$, $H_O\psi_{OK}$

As Stephens [10] points out, it is necessary to include terms representing perturbation of the spin-orbit coupling in order to obtain the correct expression for H_2. This allows us to transform matrix elements of the generalized momentum into electric dipole matrix elements by equating u to the $(H_0+H_1, \hat{\mu})$ commutator.

$$\hat{u} = (i/hc)(((H_0+H_1),\ \hat{\mu}))$$

therefore

$$<\psi_K/\hat{u}/\ _K\ = (i\omega_{KL}/c)\quad _K/\hat{\mu}/\psi_L$$

where

$$u = \sum_i (e_i/m_i c)\ (\hat{p}_i + (\tfrac{1}{2}m_i c^2)\hat{s}_i x \hat{\nabla}_i v - (e_i/c)\hat{A}_{1i})$$

$h = h/2\pi$

$m = {}_i e_i \hat{r}_i$

$\omega_{KL} = \omega_K - \omega_L$

ψ_K, ψ_L = eigenfunctions of $\hat{H}_o+\hat{H}_1$

Consider a liquid solution through which linearly polarized light passes. In general the molar extinction coefficient of the sample, α, is independent of the polarization state of the light. However, if a static magnetic field is applied across the solution in the lab z-direction, α becomes a function of the polarization state of the light. In particular, if the light is incident on the sample in a direction transverse to the applied magnetic field and is x-polarized, the sample may absorb a different amount of light than if the light were y-polarized. If it does, it is displaying magnetic linear dichroism (MLD).

The general expression for α is [24,25,26]:

$$\alpha = (A/Q \sum_{K,L} \int_{\tau} S^{LK} \mu^{LK}_{\alpha\beta} \exp(-U(\tau)/kT)d\tau) e_\alpha e_\beta$$

<u>where</u>

Q = partition function = $\sum_K \int \exp(-U^K(\tau)/kT)d\tau$

$A = (8\pi^3 N_\nu/hc \times 10^3)$

N = Avogadro's number = 6.02×10^{23}

h = Planck's constant = 6.63×10^{-27} erg.s

c = velocity of light = 2.99×10^{10} cm/s

ν = frequency of electromagnetic radiation (S^{-1})

K,L = initial, final vibronic states

S^{LK} = line shape function

$\mu^{LK}_{\alpha\beta}$ = oscillator strength tensor = $\langle K|\overset{+}{\mu}_\alpha|L\rangle\langle K|\mu_\beta|L\rangle^*$(debye^2)

$\mu_\alpha = \acute{e}r$; $\acute{e}$ = electronic charge = 4.8×10^{-10}esu

r_α = position tensor

$*$ = complex conjugation

U^K = energy of state K (ergs)

= position and orientation variable

e_α = unit tensor

k = Boltzman constant = 1.38×10^{-16}erg K^{-1}

T = temperature (^oK)

α is a function of $\Omega_K d\tau$ is the probability that a molecule is in a quantum state K with orientation τ and energy $U^K(\tau)$

$$\Omega_K = \exp(-U^K(\tau)/kT)/\sum_K \int_\tau \exp(-U^K(\tau)/kT)d\tau$$

S^{LK} is the line shape function. It accounts for the fact that the electronic transitions are not infinitely sharp. In this thesis we use the rigid-shift approximation whereby the Zeeman effect serves simply to shift the center frequency of the transition without changing the form of the line shape function. We use the Lorentzian line shape function which is of the form [11]:

$$S^{LK} = Nb/(\Delta\nu^2(H) + b^2)$$

where

b = halfwidth at half height (s^{-1})

$\Delta\nu = \nu - \nu_o$ (s^{-1})

$\nu_o = (U^L - U^K)/h = \Delta U^{LK}/h$ = center frequency

N = normalizing constant

$\mu_{\alpha\beta}$ is a 2nd rank tensor (see Appendix V) related to the probability of an electric dipole transition state K to state L.

We now define Δ, the molar MLD:

$$\Delta = (A\int_\tau S^{LK}(H)\mu_{\alpha\beta}(H)\exp(-U^K(\tau,H)/kT)d\tau/Q\tau,(H))e''_\alpha e''_\beta - e^\perp_\alpha e^\perp_\beta$$

$$= \overline{S^{LK}\mu_{\alpha\beta}}\cdot(e''_\alpha e''_\beta - e^\perp_\alpha e^\perp_\beta)$$

(The bar signifies an average)

where

$e''_\alpha, e^\perp_\alpha$ = unit tensors in the directions parallel and perpendicular, respectively, to the static magnetic field direction.

Note that S^{LK}, $\mu_{\alpha\beta}$ and U^K are explicit functions of H. We now expand Δ, $\mu_{\alpha\beta}$, U^K and S^{LK} in power series in H about H = 0 (Mclaurin Series) [23]:

$$\Delta = ((\overline{S^{LK}\mu^{LK}_{\alpha\beta}})_o + (\partial\overline{S^{LK}\mu^{LK}_{\alpha\beta}}/\partial H_\gamma)_o He''_\gamma$$

$$+ \tfrac{1}{2}(\partial^2 S^{LK}\mu_{\alpha\beta}/\partial H_\gamma \partial H_\delta)_o H^2 e''_\gamma e''_\delta + \ldots)\cdot(e''_\alpha e''_\beta - e^\perp_\alpha e^\perp_\beta)$$

$$\mu_{\alpha\beta} = \mu^{o}_{\alpha\beta} + (\partial\mu_{\alpha\beta}/\partial H_{\gamma})_{o}He''_{\gamma} + \tfrac{1}{2}(\partial^{2}\mu_{\alpha\beta}/\partial H_{\gamma}\partial H\delta)^{2}_{o}He''_{\gamma}e''\delta + \ldots$$

$$U = U^{o} + (\partial U/\partial H_{\alpha})_{o}He''_{\alpha} + \tfrac{1}{2}(\partial^{2}U/\partial H_{\alpha}H_{\beta})_{o}H^{2}e''_{\alpha}e''_{\beta} + \ldots$$

$$= U^{o} - m_{\alpha}He''_{\alpha} - \tfrac{1}{2}\chi_{\alpha\beta}He''_{\alpha}e''_{\beta} + \ldots$$

$$S^{LK} = S^{oLK} + (\partial S^{LK}/\partial H_{\alpha})_{o}He''_{\alpha} + \tfrac{1}{2}(\partial^{2}S^{LK}/\partial H_{\alpha}\partial H_{\beta})_{o}e''_{\alpha}e''_{\beta} + \ldots$$

<u>where</u>

$H''_{\alpha} = He''_{\alpha}$ = static magnitic field tensor in the " direction.

m_{α} = magnetic dipole moment tensor

$\chi_{\alpha\beta}$ = diamagnetic susceptibility tensor

Now, $(S^{LK}\mu^{LK}_{\alpha\beta})_{o}(e''_{\alpha}e''_{\beta} - e^{\perp}_{\alpha}e^{\perp}_{\beta})$ is zero, of course, since the medium behaves isotropically in the absence of $H_{\alpha}\cdot\partial(S^{LK}\mu_{\alpha\beta}/\partial H_{\gamma})_{o}He''_{\gamma} \cdot (e''_{\alpha}e''_{\beta} - e^{\perp}_{\alpha}e^{\perp}_{\beta}) = 0$ as well. To show this we may consider the molecules to be fixed in space and average over all directions e''_{α}, $e^{\perp}_{\alpha}$. We find [9] that $\overline{(e''_{\alpha}e''_{\beta} - e^{\perp}_{\alpha}e^{\perp}_{\beta})e''_{\gamma}} = 0$. Therefore the leading term in Δ is in H^{2}. (and only this term is considered in this work) To evaluate this term we again fix the molecules in space and average over all possible directions. The result is [9]:

$$\overline{e''_{\alpha}e''_{\beta}e''_{\gamma}e''_{\delta}} = (1/15)\ (\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\gamma}\delta_{\beta\delta}\delta_{\gamma})$$

$$\overline{e''_{\alpha}e''_{\beta}e^{\perp}_{\gamma}e^{\perp}_{\delta}} = (1/30)\ (4\delta_{\alpha\beta}\delta_{\gamma\delta} - \delta_{\alpha\beta}\delta_{\beta\delta} - \delta_{\alpha\delta}\delta_{\beta\gamma})$$

where

$\delta_{\alpha\beta}$ = the Kronecker Delta, a second rank tensor which = 1 for $\alpha = \beta$ and = 0 for $\alpha \neq \beta$,

thus:

$$(\tfrac{1}{2})(\partial^2 S\overline{^{LK}\mu_{\alpha\beta}}/\partial H_\gamma \partial H_\delta)_o \cdot (e''_\alpha e''_\beta - e^\perp_\alpha e^\perp_\beta)(e''_\gamma e''_\delta) =$$

$$(S^o A/60)\left[\begin{array}{l} (3(\partial^2\mu_{\alpha\beta}/\partial H_\alpha \partial H_\beta)_o + 3(\partial^2\mu_{\alpha\beta}/\partial H_\beta \partial H_\alpha)_o - 2(\partial^2\mu_{\alpha\alpha}/\partial H_\beta \partial H_\beta)_o \\ +(1/kT)(3\mu^o{}_{\alpha\beta}\chi_{\alpha\beta} + 3\mu^o{}_{\alpha\beta}\chi_{\beta\alpha} - 2\mu^o{}_{\alpha\alpha}\chi_{\beta\beta}) \\ +(2/kT)(3(\partial\mu_{\alpha\beta}/\partial H_\alpha)_o m_\beta + 3(\partial\mu_{\alpha\beta}/\partial H_\beta)_o m_\alpha - 2(\partial\mu_{\alpha\alpha}/\partial H)_o m_\beta \\ +(1/kT)^2(3\mu^o{}_{\alpha\beta} m_\alpha m_\beta + 3\,\mu^o{}_{\alpha\beta} m_\beta m_\alpha - 2\,\mu^o{}_{\alpha\alpha} m_\beta m_\beta) \end{array}\right]$$

$$+ (S' A/60)\left[\begin{array}{l} (1/h)(3\mu^o{}_{\alpha\beta}\Delta\chi^{LK}_{\alpha\beta} + 3\,\mu^o{}_{\alpha\beta}\Delta\chi^{LK}_{\beta\alpha} - 2\,\mu^o{}_{\alpha\alpha}\Delta\chi^{LK}_{\beta\beta}) \\ +(2/h)(3(\partial\mu_{\alpha\beta}/\partial H_\alpha)_o\Delta m^{LK}_\beta + 3\,(\partial\mu_{\alpha\beta}/\partial H_\beta)_o\Delta m^{LK}_\beta - 2\,(\partial\mu_{\alpha\alpha}/2H_\beta)_o \\ \qquad \Delta m^{LK}_\beta) \\ +(2/kTH)(3\mu^o{}_{\alpha\beta} m_\alpha \Delta m^{LK}_\beta + 3\,\mu^o{}_{\alpha\beta} m_\beta \Delta m^{LK}_\alpha - 2\,\mu^o{}_{\alpha\alpha} m_\beta \Delta m^{LK}_\beta) \end{array}\right]$$

$$+ (S'' A/60)\left[3\mu^o{}_{\alpha\beta}\Delta m^{LK}_\alpha \Delta m^{LK}_\beta\, m^{LK}_\beta + 3\,\mu^o{}_{\alpha\beta}\Delta m^{LK}_\beta - 2\,\mu^o{}_{\alpha\alpha}\Delta m^{LK}_\beta \Delta m^{LK}_\beta\right]$$

(see appendix for details)

where

$S', S'' = \partial S^{LK}/\partial\nu,\ \partial^2 S^{LK}/\partial\nu^2$

$\Delta m_\alpha^{LK} = m_\alpha^L - m_\alpha^K$

$\Delta\chi_{\alpha\beta}^{LK} = \chi_{\alpha\beta}^L - \chi_{\alpha\beta}{}^K$

$m_\alpha, \chi_{\alpha\beta} = m_\alpha^K, \chi_{\alpha\beta}^K$

This expression has the form:

$$S^o(A_o + (B_o + C_o)/T + D_o/T^2) + S\ (A_1 + B_1 + C_1/T) + S(A_2)$$

We briefly outline the general predictions of the theory. For nondegenerate ground states C_o, D_o, and C_1 are zero since they involve m_α. If K and L are both nondegenerate B_1 and A_2 are also zero. If the MLD curve has the same shape as the absorption curve, we must deal only with the coefficients of S^o. If the ground state is nondegenerate, the temperature-dependence (orientation effect) is due entirely to B_o. Measurement of Δ at two different temperatures determines A_o and B_o. If the MLD curve has the shape of the first derivative of the absorption curve, we must deal only with the coefficients of S'. If K and L are nondegenerate Δ is due to A_1 and its measurement yields information about $\Delta\chi_{\alpha\beta}^{LK}$. If the MLD curve has the shape of the second derivative of the absorption curve, then at least one of the two vibronic levels is degenerate. As we shall see in the next section, the MLD curve can be a convolution of S^o, S', and S'' curves.

Chapter 4

We have recorded the MLD spectra of the following lanthanide ions [27,28,29]:

Nd^{3+}, Pr^{3+}, Er^{3+}, Ho^{3+}

We have also recorded the MLD spectra of the following porphyrins: [15,30,31,32,33]: ferrocytochrome c (horse heart), pyridine haemochrome, imidazole haemochrome. The actual spectra and the baseline-corrected spectra are shown in the following figures. In the case of ferrocytochrome c the deconvoluted spectrum is also shown. The lanthanides were obtained as chlorides from Professor Harry G. Brittain of Seton Hall University and the porphyrins were obtained from Dr. Thomas Strekas of Queens College, C.U.N.Y. The lanthanides were each dissolved in H_2O in the presence of .1M $HClO_4$ (to prevent oxide formation) and were between .5g/ml and 1g/ml in concentration. Ferrocytochrome c was prepared by reducing Ferrocytochrome c in the presence of dithionite. The haemochromes were prepared by reacting hemin with pyridine and imidazole, respectively, in the presence of dithionite. The porphyrins were in the 10^{-6} - 10^{-5} molar concentration range.

The lanthanide spectra will be discussed qualitatively only. The MLD spectrum of horse heart ferrocytochrome c will be discussed in detail and only the most general features of the two haemochromogen spectra will be pointed out.

The lanthanides were chosen for MLD analysis because of their relatively large permanent magnetic moments and because of the sharpness of their absorption bands. To the extent that the electronic orbital magnetic moment is quenched by the ligand field of the solvent, the magnetic moment m_{α}^{K} is due to electronic spin. The band sharpness enhances terms in S'' and S' relative to S^{o} since the bandwidth appears in S^{o}, S', S'' to the -1, -2, -3 powers respectively.

In each of the lanthanides analyzed the spectrum appears to be dominated by S' curves (Note also the S' curve at 622.5 nm in Nd^{3+}). However, as figure 16 shows, the sum of S' and S'' curves of similar magnitudes is a curve that looks similar to an S' curve. The major difference between S' and $S' + S''$ is the fact that the node appears at the center frequency in S' and higher than the center frequency in $S' + S''$. Assuming an S' curve, we expect B, to be small compared to C since the contribution from the mixing of states is expected to be small compared to the contribution from m_{α}. A, is also considered to be small compared to C, since in general, the contribution to the total magnetic susceptibility from $\chi_{\alpha\beta}$ is negligible in systems with permanent magnetic moments [12]. A large value of C, implies that Δm_{α}^{LK} is not small. However, the absence of S'' character indicates that it is not very large, either.

In analyzing the MLD spectrum of horse heart cytochrome c (and the spectra of the other two haemochromes) we initially assume that the molecule obeys D_4h symmetry, even though it contains a very large protein portion, since we know the $\pi \rightarrow \pi$ * transition to be localized in the ring system. We shall return to this point shortly. We therefore consider only the planar metalloporphyrin part of the molecule. The 18-center conjugated π system 13 spans the following irreducible representations:

$$2a_{1u} + 4a_{2u} + 3b_{1u} + 3b_{2u} + 6e_g$$

The Q-bands at 550.3 nm and 524 nm are each due to $a_{2u} \rightarrow e_g$ one electron transitions and the Sovet band at 413 nm to an $a_{1u} \rightarrow e_g$ electronic transition. The molecular symmetry of the ground state is A_{1g}, of the Q-bands is $a_{2u} \times e_g = E_u^Q$ and of the S band is $a_{1u} \times e_g = E_u$. We assume that these are the only states that contribute [14]. The actual MLD spectrum and the deconvoluted spectrum indicate that:

$$\Delta = A/60\ ((A_o + B_o/T)S^o + (A_1 + B_1)S' + A_2 S'')$$

We proceed with the tensor contraction. The z-axis is taken as the unique axis. Therefore [35], the only nonzero matrix elements involving m_α are in the z-direction. Additionally, use of a molecule-fixed axis system requires that $\chi_{\alpha\beta}(\alpha \neq \beta) = 0$. Also, xx = yy under D_{4h} symmetry. We choose the complex basis, x + iy, -(x-iy), z since this basis set diagonalizes m_z. The result is:

$$A_o = -4(\partial^2\mu_{xx}/\partial H_z^2)_o$$

$$B_o = (4/k)\ \mu^o{}_{xx}\ (\chi_{xx} - \chi_{zz})$$

$$A_1 = (8/h)(\partial\mu_{xx}/\partial H_z)_o m_z^L$$

$$B_1 = (4/h)^2\mu^o{}_{xx}(\Delta\chi_{xx}^{LK} - \Delta\chi_{zz}^{LK})$$

$$A_2 = -(4/h)^2\mu^o{}_{xx}(m_z^L)^2$$

As the computer plots indicate, the S'' term dominates.

$\Delta(S'')(545\text{nm}) = -2.51 \times 10^{-10}$ (cm^2/mol Gauss^2) (see appendix)

$S''(545\text{nm}) = 1.70 \times 10^{-39}$ (S^3)

$A/60 = 6.8 \times 10^{51}$ (s.erg.cm)$^{-1}$

$\mu^o{}_{xx} = 1.40 \times 10^{-36}$ (Debye^2)

$$m_z^L \text{ (erg/Gauss)} = \pm(2.51 \times 10^{-10}/4 \times 1.7 \times 10^{-39} \times 2.27 \times 10^{52} \times 6.8 \times 10^{51} \times 1.4 \times 10^{-36})^{\frac{1}{2}}$$

$m_z^L = 1.41\beta$

This value compares well with the value of 1.49β obtained using Magnetic Optical Rotatory Dispersion techniques (MORD). (see appendix)

The S^o term is smaller than the S'' term:

$\Delta(S^o)(\underline{550\text{nm}}) = 2.51 \times 10^{-10}$ (cm^2/mol Gauss^2)

$S^o(\underline{550\text{nm}}) = 8.5 \times 10^{-14}$ (S)

$\mu^o{}_{xx}(\underline{413\text{nm}}) \approx 7.5 \times 10^{-36}$ (Debye^2)

$U^Q - U^S \equiv \Delta U^{Q-S} = -1.2 \times 10^{-12}$(erg)

$T \approx 293$ (^{o}K)

$\langle Eu^Q|m_z|Eu^S\rangle \equiv b_{12} = 1.49 \times 10^{-20}$ erg/Gauss (see appendix)

$(S^oA/60)A_o = 5.57 \times 10^{-12}$ (cm^2/mol Gauss^2) $<<\Delta(S^o)$

Therefore, the S^o term is due almost entirely to B_o:

$\chi_{xx} - \chi_{zz} = -3.13 \times 10^{-27}$(erg/G^2)

We cannot attribute this result to the conjugated ring system since, in it $|\chi_{zz}|>>|\chi_{xx}|$ and $\chi_{xx} - \chi_{zz}$ is a positive quanity since χ_{zz} is negative, whereas analysis of the spectrum shows it to be a negative quanity. Therefore, we conclude that B_o is associated with the very large protein moiety and that $|\chi_{xx}|>|\chi_{zz}|$.

This conclusion is further supported by noting that the MLD spectra of the pyridine and imidazole haemochromes show little, if any, S^o character. This is in keeping with the fact that these molecules have no attached protein moiety. Under this new assumption, the molecular transition is still localized, but $\chi_{\alpha\beta}$ no longer has D_4h symmetry. Reevaluating B_o:

$$B_o = (6/k)\mu^o{}_{xx}(\chi_{tr} - \chi_{zz})$$

<u>where</u>

$$\chi_{tr} = (1/3)(\chi_{xx} + \chi_{yy} + \chi_{zz})$$

$$\mu^o{}_{xx} = 2.8 \times 10^{-36} \text{ (Debye}^2\text{)}$$

and

$$(\chi_{tr} - \chi_{zz}) = -4.04 \times 10^{-14} \times 2.51 \times 10^{-10}/8.5 \times 10^{-14} \times 6.8 \times 10^{51} \times 3 \times 2.8 \times 10^{-36}$$

$$= 2.08 \times 10^{-27} (\text{erg/Gauss}^2)$$

Note that in the above evaluation, we are using the real basis, x, y, z, instead of the complex basis since $\mu^o{}_{\alpha\beta}(\alpha \neq \beta) = 0$ in the real basis and this result simplifies the analysis. This seemingly arbitrary choice is legitimate since the resultant MLD is independent of basis set.

The S' term is the smallest term:

$$\Delta(S')(547 \text{ nm}) \simeq 7.5 \times 10^{-11} \text{ (cm}^2\text{/mol Gauss}^2\text{)}$$

$$S'(547 \text{ nm}) = 1.11 \times 10^{-26} (S^2)$$

if $(A/60)\ (B,S') = \Delta S'(547 \text{ nm})$

then $(\Delta\chi^{LK}_{tr} - \Delta\chi^{LK}_{zz}) = 7.32 \times 10^{-28} \text{erg/Gauss}^2$

and if $(A/60)(A,S') = \Delta S'(547 \text{ nm})$

then $b_{12} = 1.17 \times 10^{-20}$ erg/Gauss $= 1.26\beta$

but MORD analysis (see appendix) indicates that $b_{12} \simeq 1.60\beta$.

This implies that B_1 opposes A_1 and that it's actual value is approximately -1.5×10^{-28} (erg/Gauss^2). Since we have assumed the molecular transition to be localized in the ring, we can assign this value to the change in χ_{zz} of the ring system due to the transition.

As noted, the MLD spectra of the pyridine and imidazole haemochromes show predominantly S'' behavior, with virtually no S^o contribution. The imidazole haemochrome appears to have a larger S' term than the pyridine haemochrome.

In summary, MLD spectra, especially in conjunction with MORD of MCD (Magnetic Circular Dichroism) spectra, when accompanied by a comprehensive theoretical development yield information about ground and excited magnetic moments and diamagnetic susceptibilities, mixing-in of other states due to the Zeeman perturbation and polarization of transition moments.

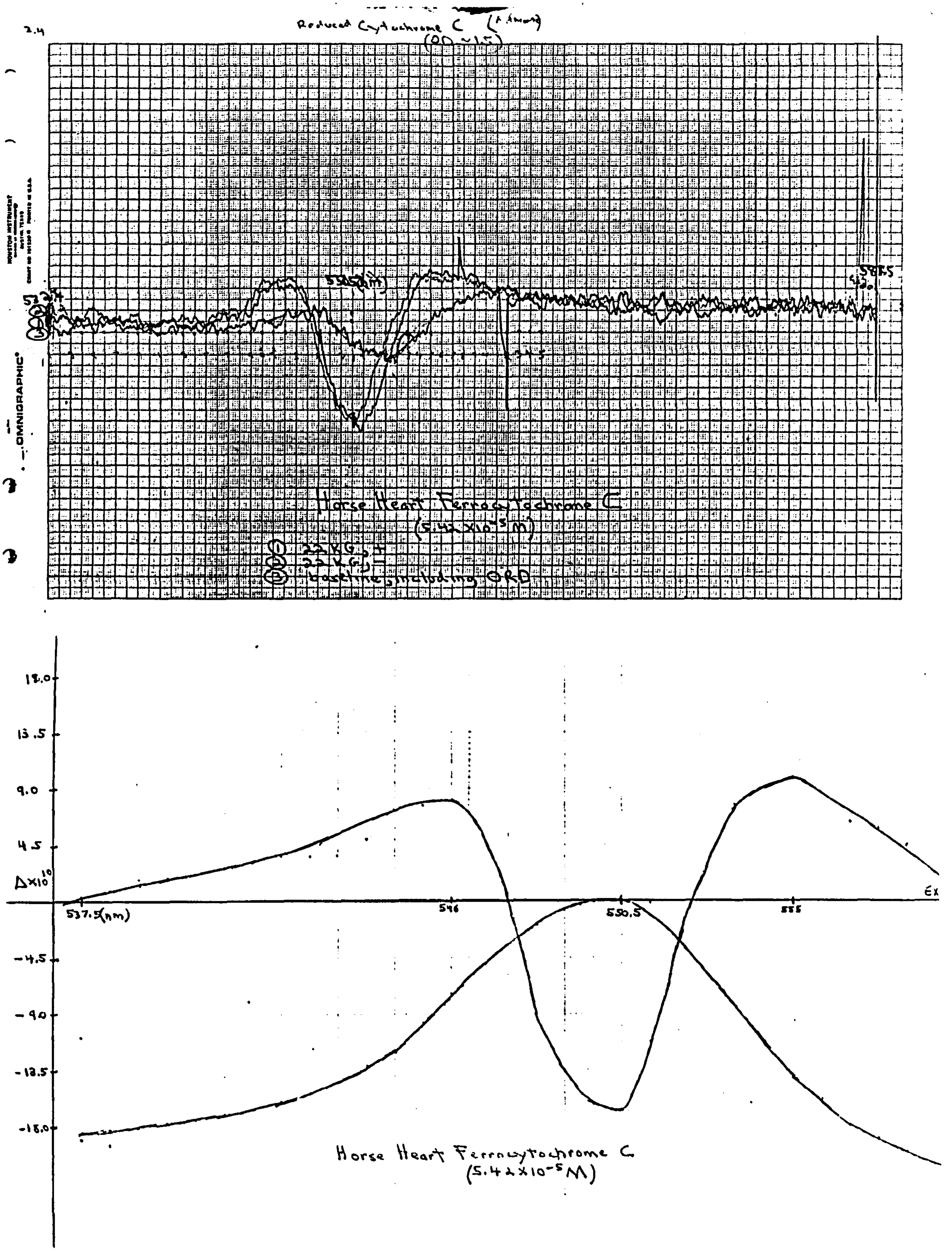

Reduced Cytochrome C
(OD ~1.5)
2.4
OMNIGRAPHIC
HOUSTON INSTRUMENT
550.5nm
537.4
558.5
Horse Heart Ferrocytochrome C
(5.42x10^-5 M)
① 22 KG, +
② 22 KG, −
③ baseline, including ORD
18.0
13.5
9.0
4.5
Δx10^10
−4.5
−9.0
−13.5
−18.0
537.5(nm)
546
550.5
555
Ex
Horse Heart Ferrocytochrome C
(5.42x10^-5 M)

Figure 11

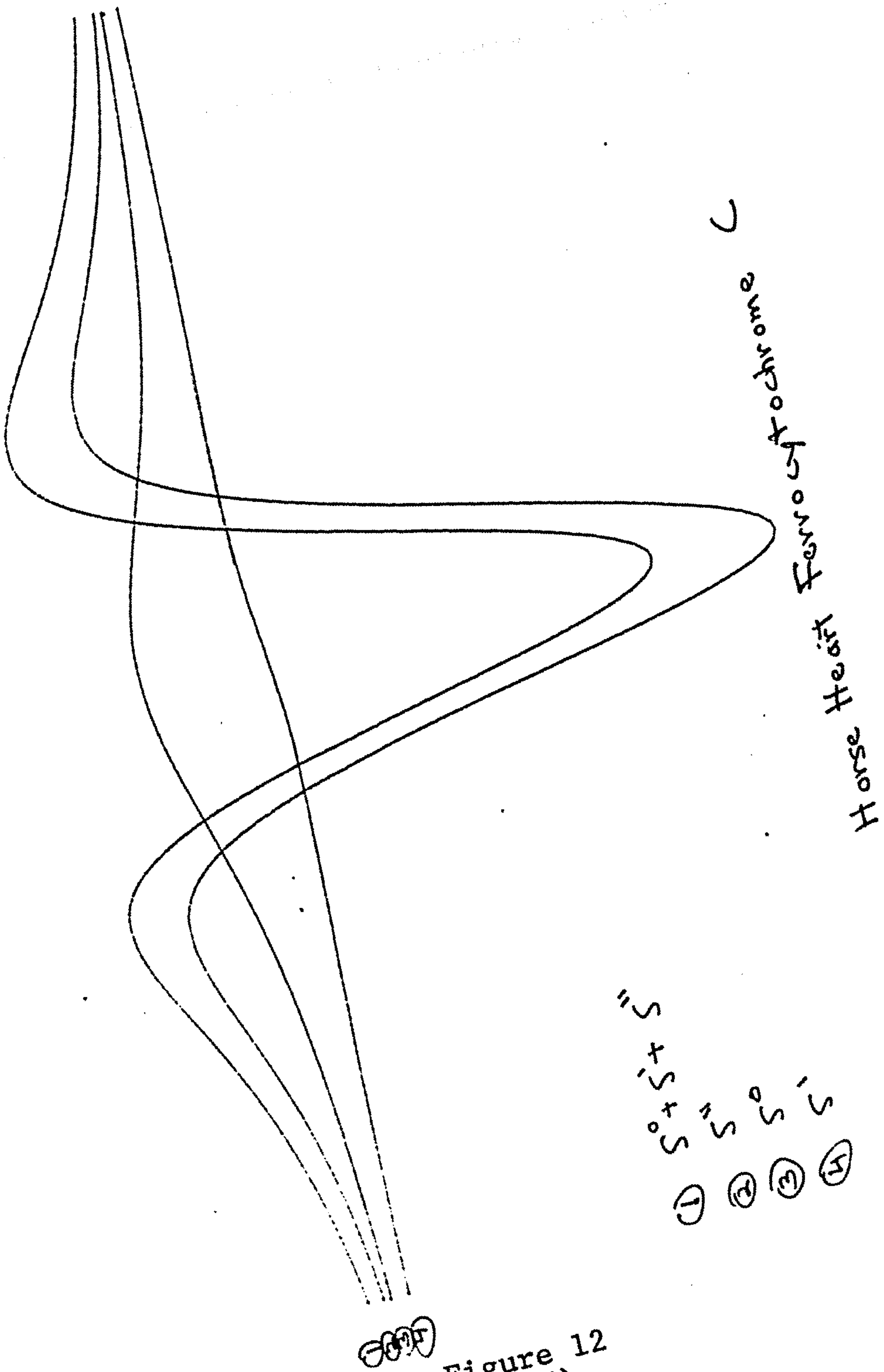


Figure 12

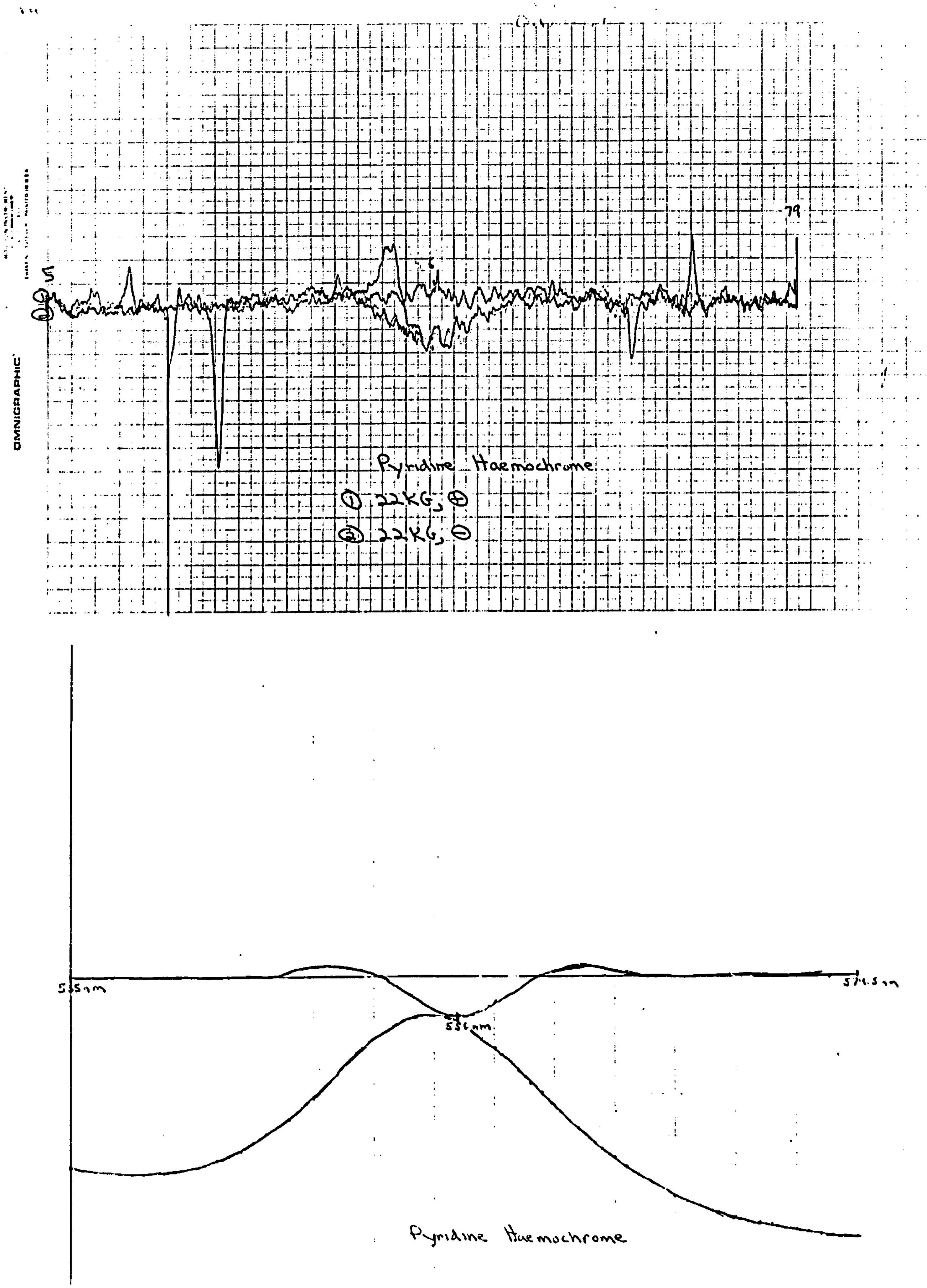
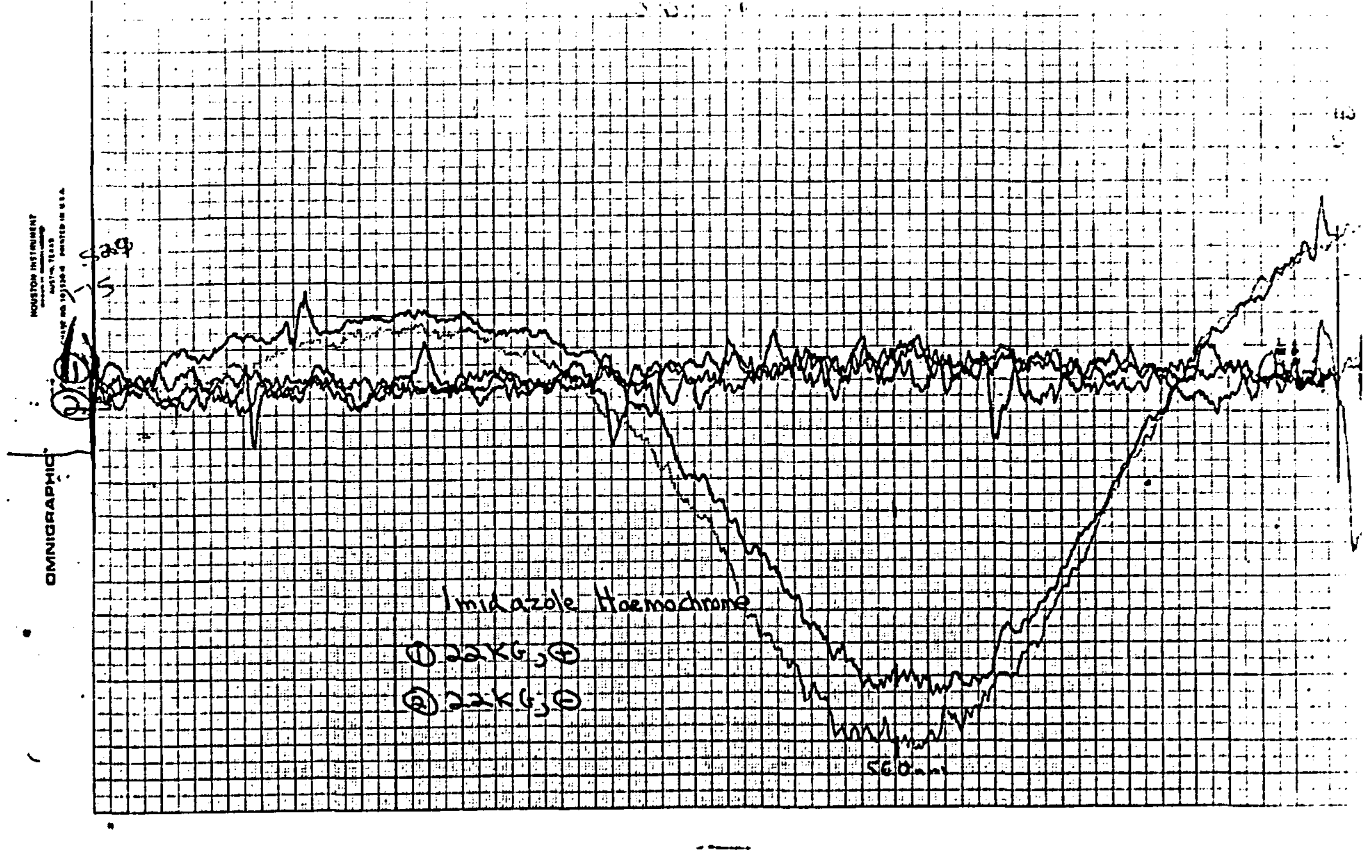

OMNIGRAPHIC
5
79
Pyridine Haemochrome
① 22KG, ⊕
② 22KG, ⊖
555nm
556nm
574.5nm
Pyridine Haemochrome

Figure 13


OMNIGRAPHIC
HOUSTON INSTRUMENT
529
1-5
①
②
Imidazole Haemochrome
① 22KG, ⊕
② 22KG, ⊖
560nm

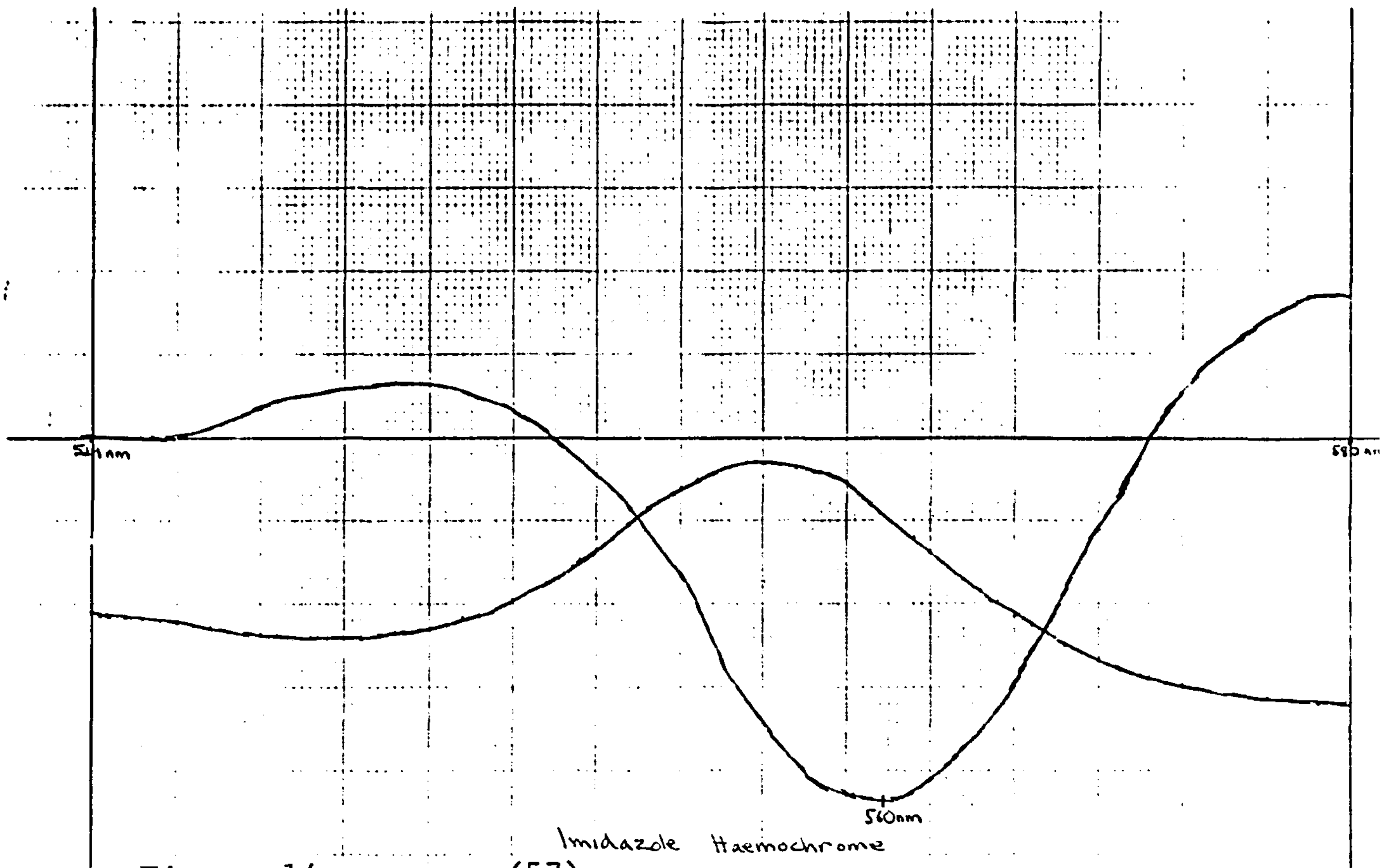
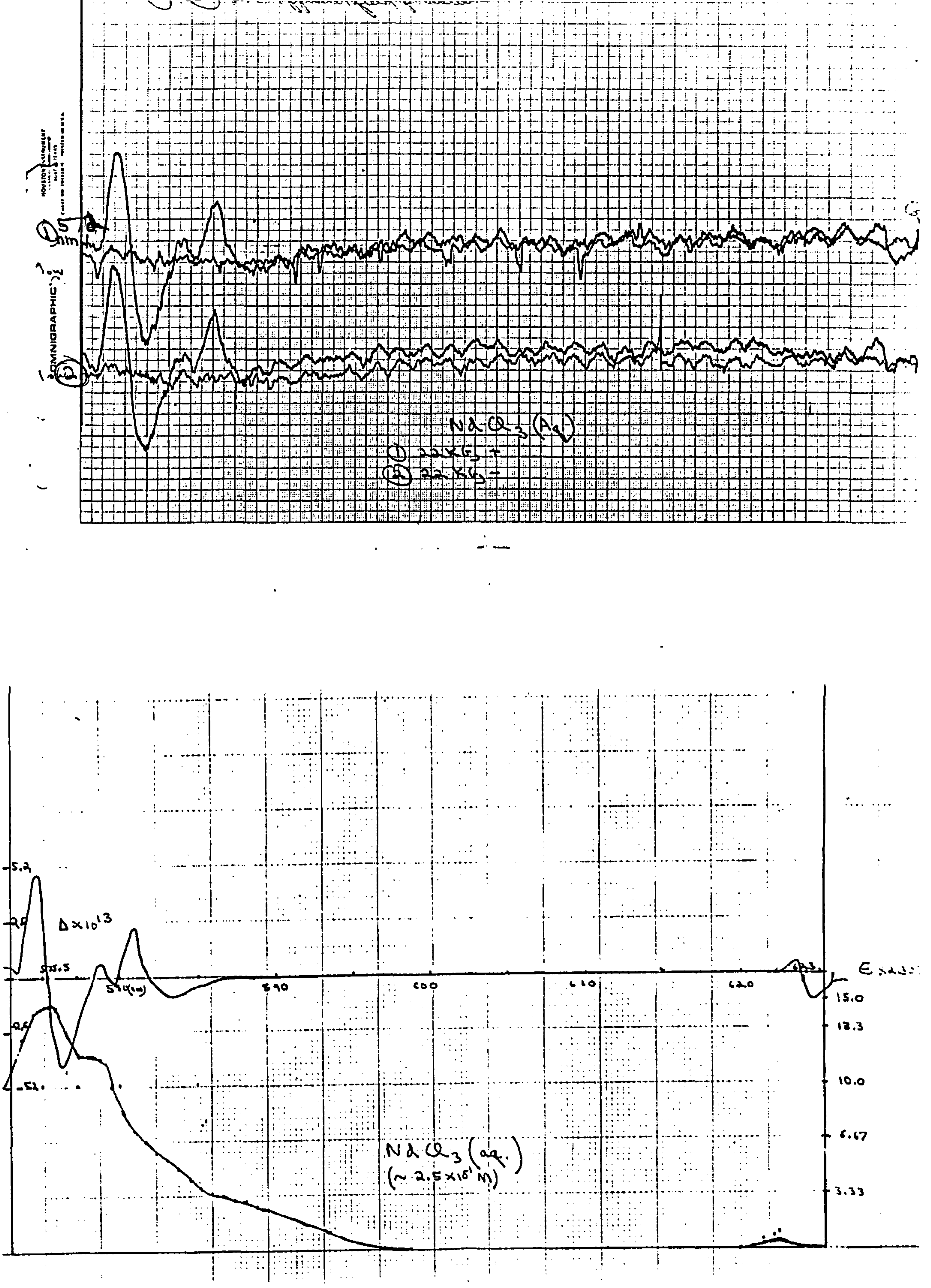

541nm
580nm
560nm
Imidazole Haemochrome

Figure 14



HOUSTON INSTRUMENT
OMNIGRAPHIC
① 5 nm
②
NdCl3 (Aq)
① 22 KG +
② 22 KG −
5.2
2.6
Δ×10^13
575.5
580(nm)
590
600
610
620
623
ε ×
15.0
13.3
10.0
6.67
3.33
-2.6
-5.2
NdCl3 (aq.)
(~ 2.5×10⁻¹ M)

Figure 15

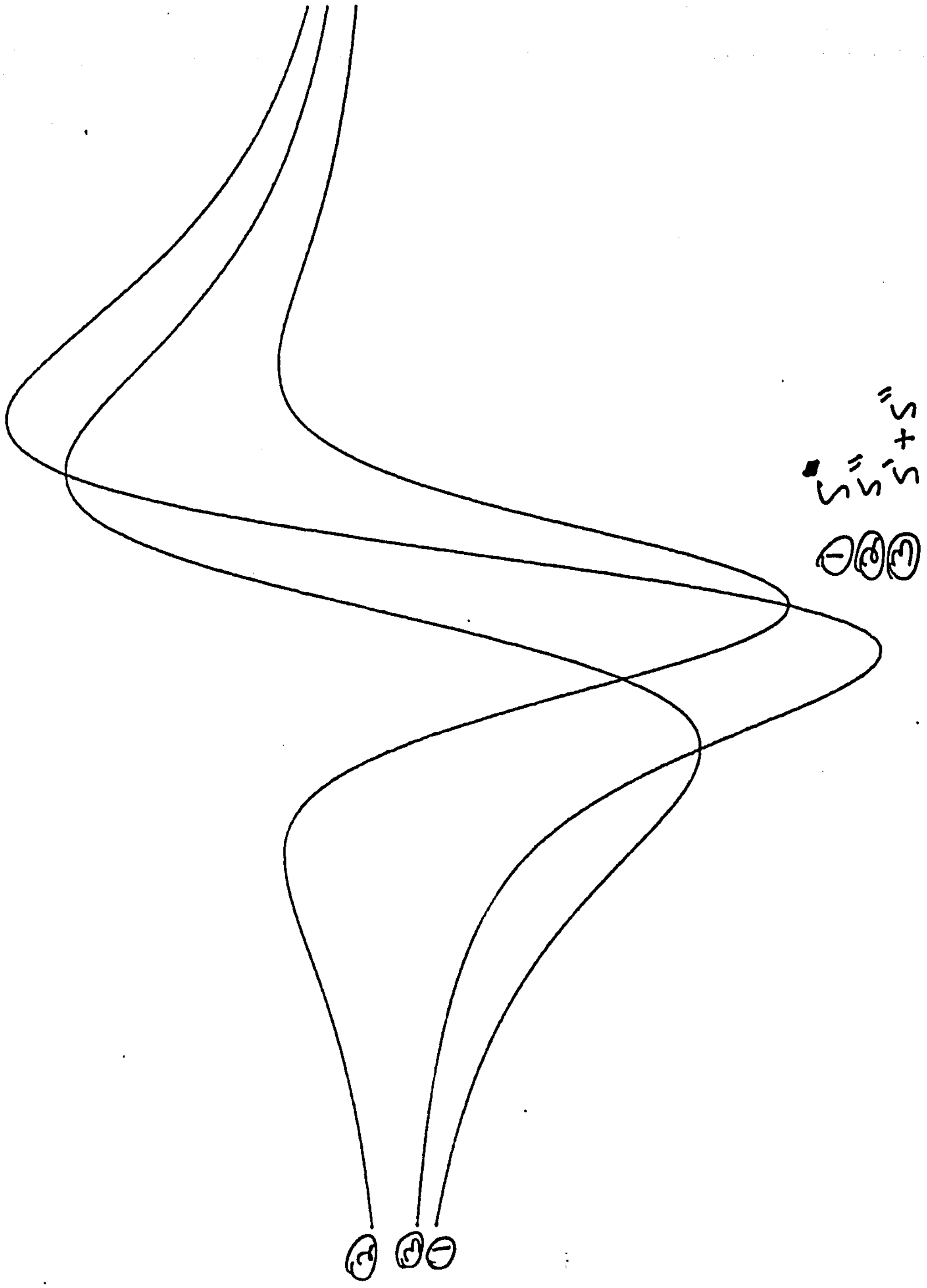
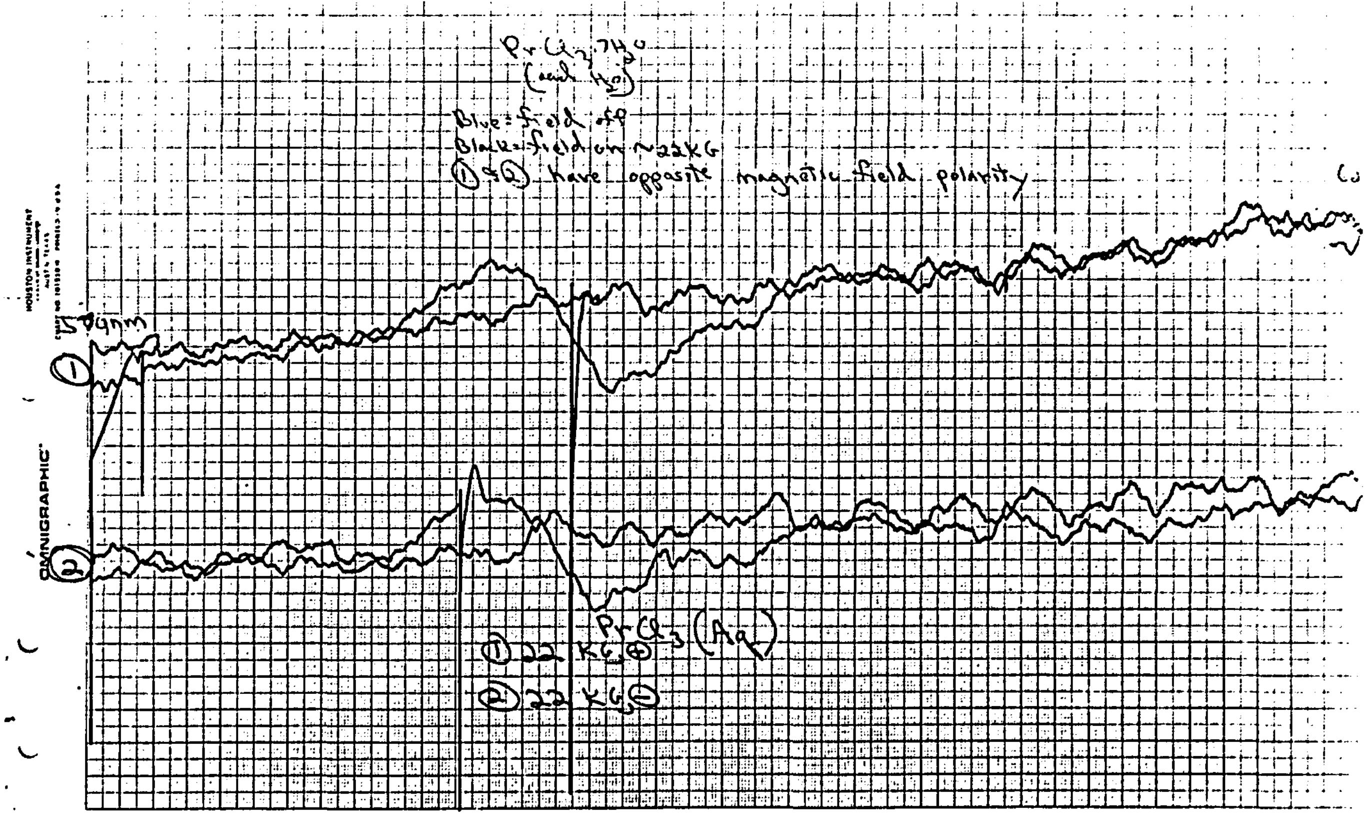


Figure 16


PrCl3·7H2O
(acid H2O)
Blue: field off
Black: field on ~22KG
①&② have opposite magnetic field polarity
589nm
①
②
PrCl3(Aq)
① 22 KG ⊕
② 22 KG ⊖
HOUSTON INSTRUMENT
OMNIGRAPHIC

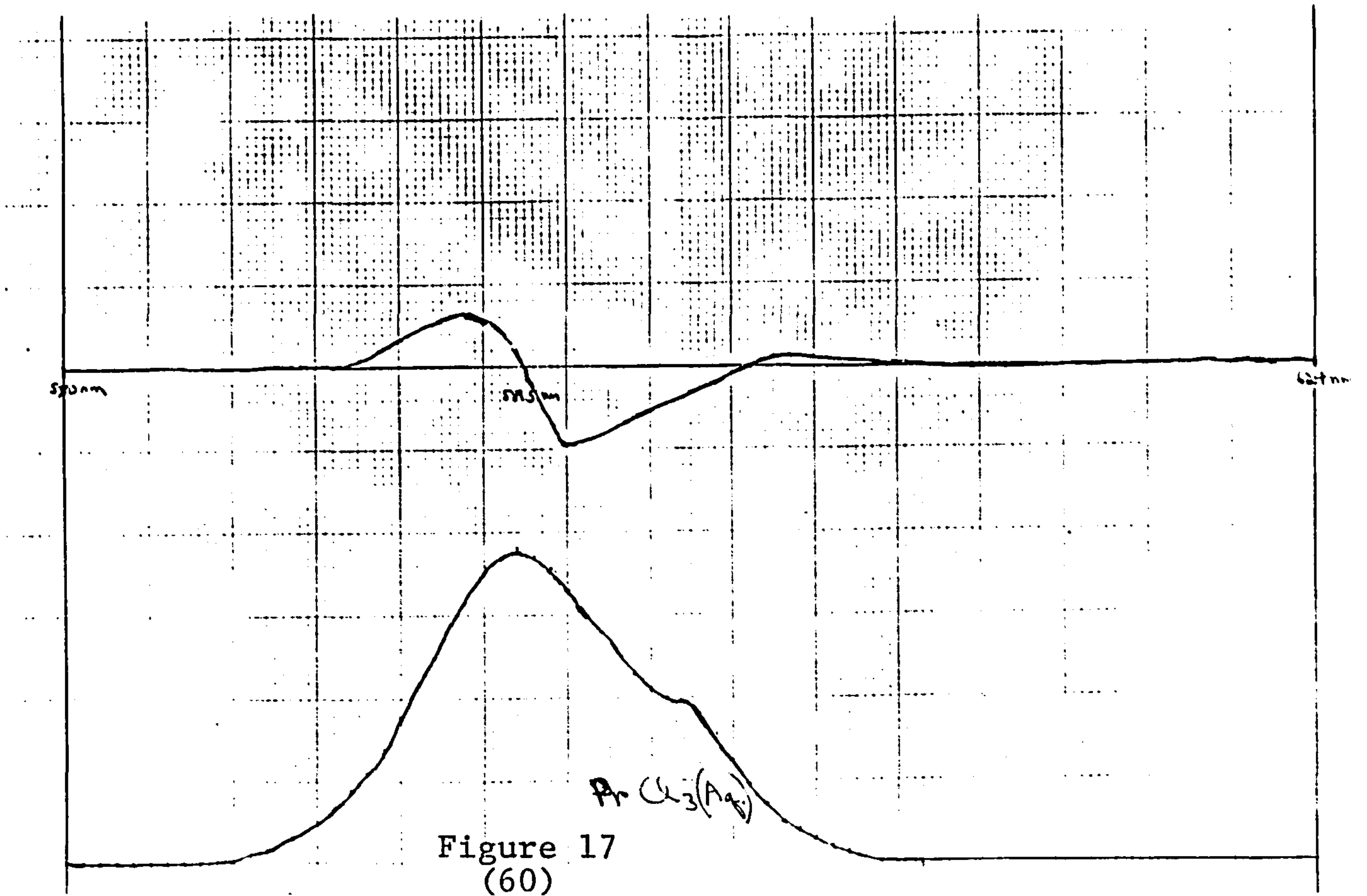
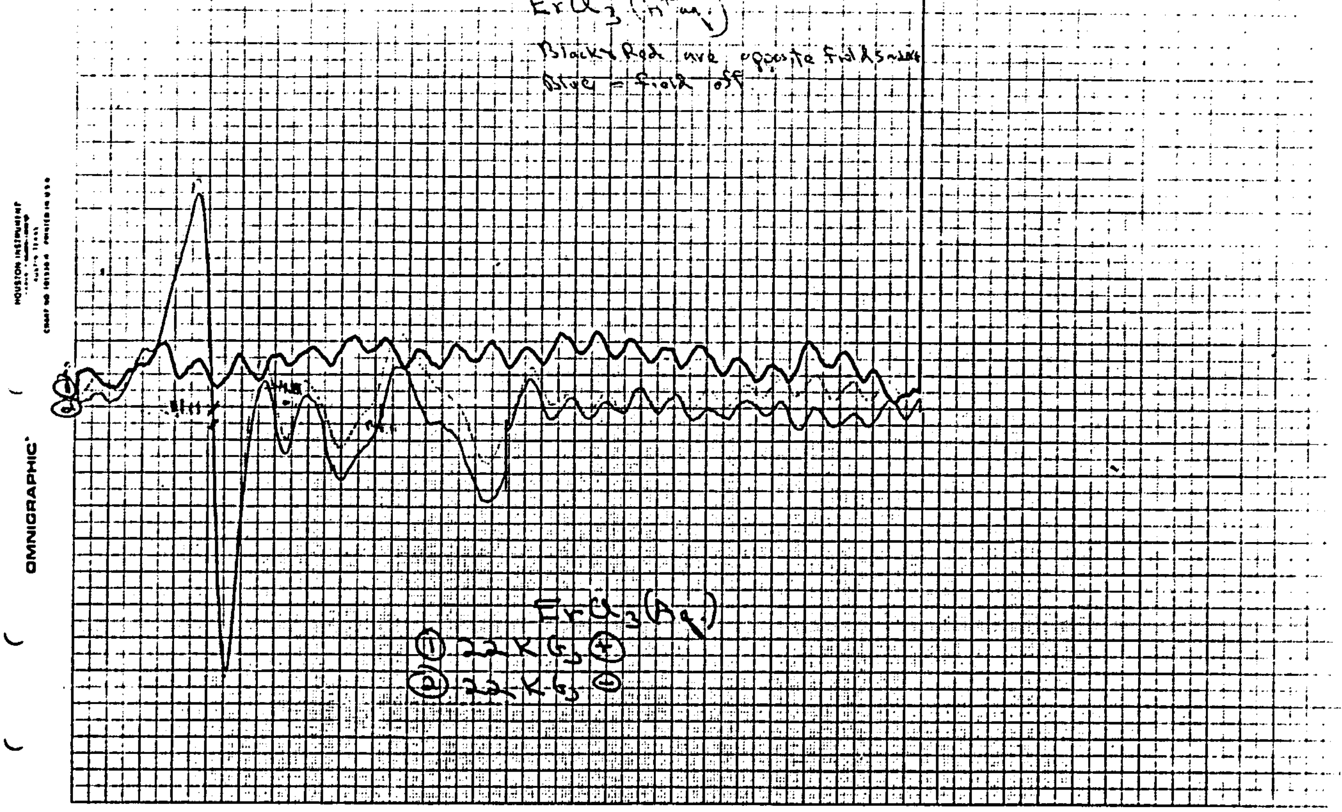

570nm
585nm
[illegible] nm
PrCl3(Aq)

Figure 17


$ErCl_3$ (in aq.)
Black & Red are opposite fields ~22K
Blue = field off
HOUSTON INSTRUMENT
OMNIGRAPHIC
$ErCl_3(Aq.)$
① 22 KG ⊕
② 22 KG ⊖

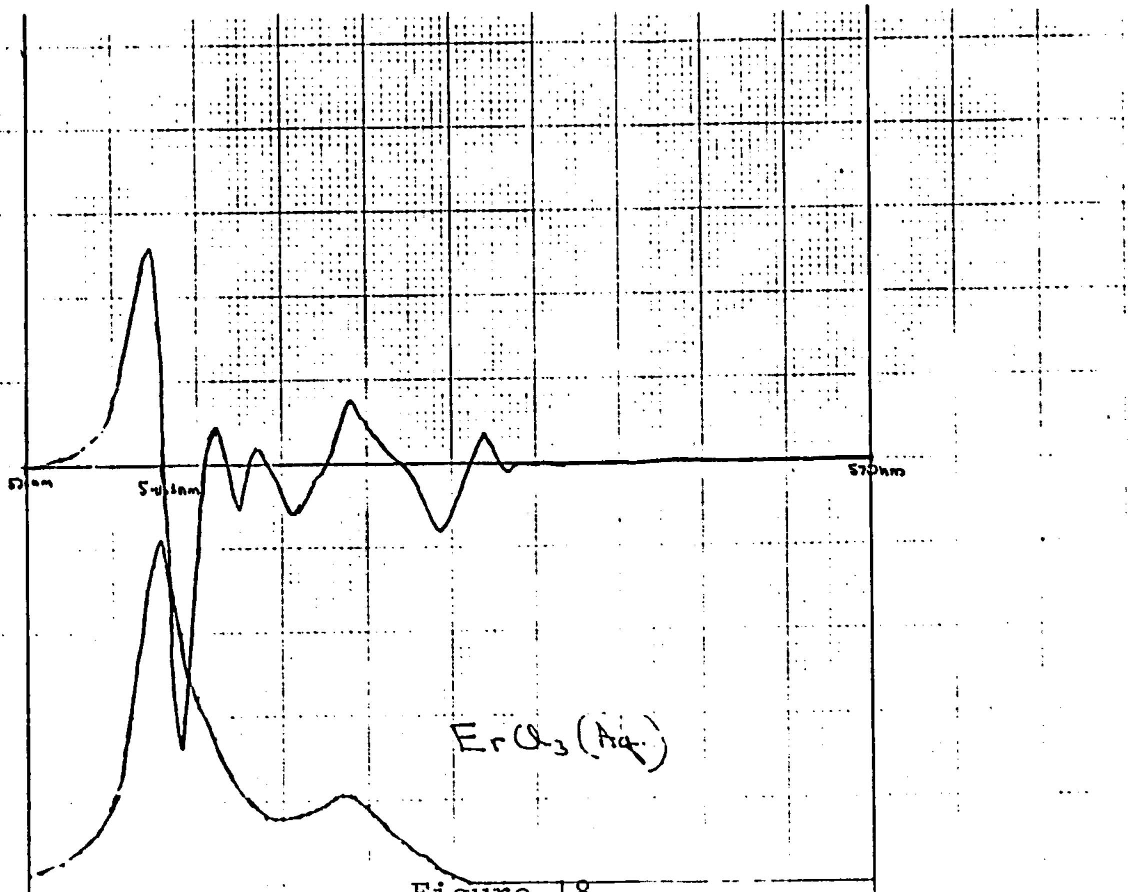

570nm
$ErCl_3(Aq.)$

Figure 18

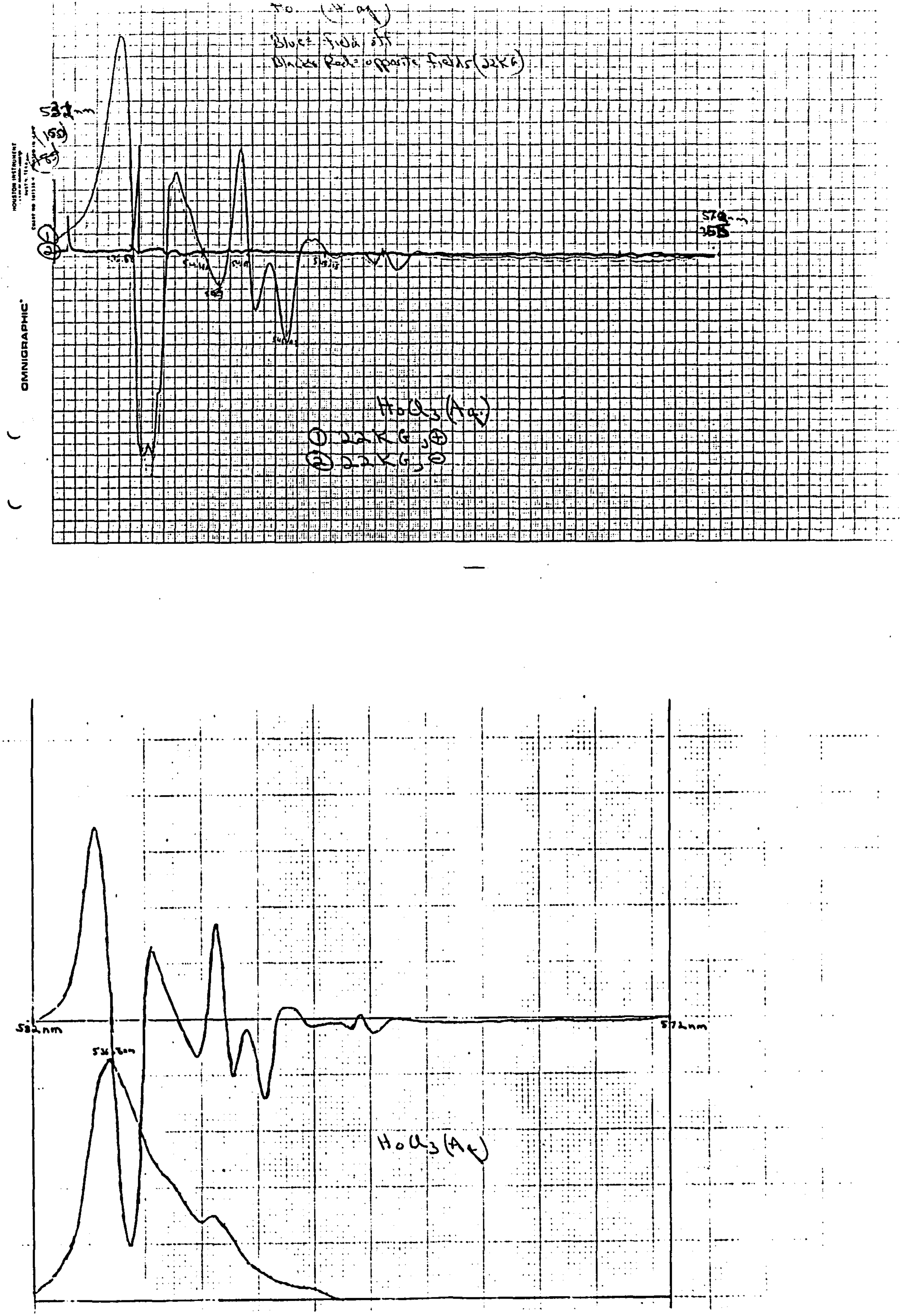

Blue: field off
Black & Red: opposite fields (22KG)
532nm
(150)
578nm
HOUSTON INSTRUMENT
OMNIGRAPHIC
HoCl3(Aq.)
① 22KG, ⊕
② 22KG, ⊖
532nm
572nm
536.3nm
HoCl3(Aq)

Figure 19

APPENDIX

I. $(\partial^2(S^{LK}\mu_{\alpha\beta}e^{-U/kt}/Q)/\partial H^2)_o$

$$(\partial^2(A(x)\cdot B(x)\cdot C(x))/\partial X^2)_o =$$

$$(ABC'' + AB''C + A''BC + 2AB'C' + 2A'B'C + 2A'BC')_o$$

<u>where</u>

$A', B', C' = \partial/\partial x\ (A,B,C)$

$A'', B'', C'' = \partial^2/\partial^2 X^2 (A,B,C,)$

$A = S^{LK} = Nb/(\Delta\nu^2(H) + b^2)$

<u>where</u>

$b =$ halfwidth at half height (S^{-1})

$\Delta\nu = \nu - \nu_o\ (S^{-1})$

$\nu_o = (U^L - U^K)/h = \Delta U^{LK}/h$

$N =$ normalizing constant

$(\partial S^{LK}/\partial H) = -2N\Delta\nu b/(\Delta\nu^2 + b^2)^2(\partial\Delta\nu/\partial H)$

$$(\partial^2 S^{LK}/\partial H) = N\begin{bmatrix} 8\Delta\nu^2 b/(\Delta\nu^2 + b^2)^3 - 2b/(\Delta\nu^2 + b^2)^2\ (\partial\Delta\nu/\partial H)^2 \\ -2\Delta V b/(\Delta V^2 + b^2)^2(\partial^2\Delta V/\partial H^2) \end{bmatrix}$$

$\partial\Delta\nu/\partial H = -\partial\nu_o/\partial H = -(1/h)(\partial\Delta U^{LK}/\partial H)$

$\partial^2\Delta\nu/\partial H^2 = -\partial^2\nu_o/\partial H^2 = -(1/h)(\partial^2\Delta U^{LK}/\partial H^2)$

$$\begin{aligned} \Delta U^{LK} &= \Delta U_o^{LK} + (\partial\Delta U^{LK}/\partial H)_o H + (1/2)(\partial^2\Delta U^{LK}/\partial H^2)_o H^2 +\ldots \\ &= \Delta U_o^{LK} - \Delta m^{LK}\cdot H - (1/2)\Delta\chi^{LK}H^2 +\ldots \end{aligned}$$

$(\partial S^{LK}/\partial\nu) = -2N\Delta\nu b/(\Delta\nu^2 + b^2)^2 \equiv S'$

$(\partial^2 S^{LK}/\partial\nu^2) = N\left[8\Delta\nu^2 b/(\Delta\nu^2 + b^2)^3 - 2b/(\Delta\nu^2 + b^2)^2\right] \equiv S''$

$S_o'^{LK} = S'\Delta m^{LK}/h$

$$S_o^{LK} = \begin{bmatrix} (1/h)^2 S'' \ (\Delta m^{LK})^2 \\ +(1/h) S' \Delta\chi^{LK} \end{bmatrix}$$

$$B = \mu_{\alpha\beta} = \langle K(H)|\vec{\mu}_\alpha|L(H)\rangle\langle K(H)|\vec{\mu}_\beta|LH\rangle^*$$

$$K(H_\alpha) = \Psi_o^K + (\sum_{J\neq K}(\langle\Psi_o^J|m_\alpha|\Psi_o^K\rangle\Psi_o^J, \Delta U^{KJ}))_o H_\alpha + \ldots$$

We choose, as an example, the $A_1g \rightarrow E_u^Q$ transition in ferrocytochrome c. We use a basis set that diagonalizes M_z; that is, we use $(1/\sqrt{2})(x + iy)$, $-(1/\sqrt{2})(x - iy)$, $z(+, -, o)$ we assume that the only wavefunctions mixed are E_u^Q and $E_u^{(S)}$ [14]. Note that under D_4h only m_z matrix elements are nonzero. Also, although μ_{xy}, μ_{yx} are nonzero in this basis, their sum is zero and as such they do not contribute to the oscillator strength;

(A_1g has the symmetry properties of z^2 in D_4h

$$\langle z^2|x|E_{u\pm}^Q\rangle\langle z^2|y|E_{u\pm}^Q\rangle^* = \int_\tau z^2x(x + iy)d\tau\int_\tau z^2y(x - iy)d\tau$$

$$= -i\int z^2 \ X^2 d\tau\int z^2y^2 d\tau \quad \text{since } \int_\tau xy d\tau = 0$$

$$\text{but} \quad z^2|y|E_{u\pm}^Q\rangle\langle z^2|x|E_{u\pm}^Q\rangle \overset{*}{=} i\int_\tau z^2x^2 d\tau\int_\tau z^2y^2 d\tau$$

$$= - z^2|x|E_{u\pm}^Q\rangle\langle z^2|y|E_{u\pm}^Q\rangle^*$$

Additionally, the contributions of μ_{xy}, μ_{yx} to $\partial\mu_{\alpha\beta}\partial H_\alpha$ cancel since (in this basis):

$\langle E_{u\pm}^S/Lz/E_{u\pm}^Q\rangle = \pm mK$

Therefore we need only evaluate

$((\partial\mu_{xx} + \partial\mu_{yy})/\partial H_z)_o$:

$$= 2(\partial\mu_{xx}/\partial H_z)_o$$

$$= 4\langle A,g\,|x\,|E_u\overset{2}{\pm}\rangle\langle A,g\,|x\,|E_u\overset{S}{\pm}\rangle\langle E_u\overset{S}{\pm}\,|\vec{L}_z\,|E_u\overset{Q}{\pm}\rangle/\,\Delta U^{Q-S}$$

$$= 4(\mu^o{}_{xx}{}^Q)^{\frac{1}{2}}(\mu^o{}_{xx}{}^S)^{\frac{1}{2}}b_{12}/\,\Delta U^{Q-S}$$

$$(\partial^2\mu_{\alpha\beta}/\partial H\ \ \partial H\delta)_o = 2(\partial^2\ {}_{xx}/\,\partial H_z^2)_o$$

$$= 4\mu^o{}_{xx}{}^S\ (b_{12})^2/(\Delta U^{Q-S})^2$$

Note that we have neglected the second-order correction to the wavefunction.

$$C = \exp(-U(\tau,H)/kT)/Q = X/Q$$

where $\quad x = \exp(-U(\tau,H)/kT)$

$$\partial C/\ H = (x'Q - Q'x)/Q^2$$

$$= x'/Q - Q'x/Q^2 = x'/Q$$

$$\partial^2 C/\partial H^2 = (Qx'' - Q'x')/Q^2 - ((Q^2(Q'x)' - (Q\ x)Q^2)'/Q^4)$$

$$= X''/Q$$

Note that the remaining terms each equal zero [9].

$$x_o' = (\partial \exp(-U(\tau\,,H)/kT)/\partial H)_o = (1/kT)m$$

$$x_o'' = (1/kT)^2m^2 + (1/kT)X$$

II. Determination of Oscillator Strength

A. $$\int \alpha(\nu)\, d\nu = \frac{8\ N\nu}{3hc \times 10^3}\, \Sigma\, |\langle K|\mu|L\rangle|^2$$

$$D = \sum_{+,-} \left| \langle A\ g \middle| \mu \middle| E_u^Q \rangle \right|^2 = \frac{7.68 \times 10^{17} \times 9 \times 10^{13} \times 6.63 \times 10^{-27}}{8 \times 31 \times 6 \times 10^{23} \times 5.454 \times 10^{14}} D^2$$

$$= 5.62 \times 10^{-36}\ D^2$$

B. $$2.77 \times 10^4 \times 2.303\ (\mathrm{cm}^2/\mathrm{mol}) = \frac{8^3 N\nu}{3hc \times 10^3}\, D^Q S^o$$

$$S^o(550\mathrm{nm}) = \frac{2.77 \times 10^4 \times 2.303 \times 9 \times 10^{13} \times 6.63 \times 10^{-27}}{8 \times 31 \times 6 \times 10^{23} \times 5.454 \times 10^{14} \times 5.62 \times 10^{-36}}\ (S)$$

$$S^o(550\mathrm{nm}) = 8.52 \times 10^{-14}\ (S)$$

S^o is of the <u>form</u> . $2b/[(\Delta\nu^2 + b^2)]$

$b = 5 \times 10^{12}\ S^{-1}$

$S_o^o = 1.27 \times 10^{-13}\ S$

$S_o = S^o/1.49\ S$

Note that in A. $\int S^o(\nu)\, d\nu \equiv 1$ and is therefore not included in the calculation.

III

Calculation of Δ

$$\Delta/\mathrm{cm} = \frac{4h(\mathrm{cm}^{-1})}{c(\mathrm{mol/L})H^2(\mathrm{Gauss})}$$

$h(550\mathrm{nm}) = (7.85\mathrm{x}10^{-6}\mathrm{cm}^{-1}/\mathrm{in.\ chart\ paper}) \cdot .21\ \mathrm{in} = 1.65\mathrm{x}10^{-6}\mathrm{cm}^{-1}$

$c = 5.42 \times 10^{-5} (\mathrm{mol/L})$

$H = 2.2 \times 10^{4} (\mathrm{G})$

$\Delta = 2.51 \times 10^{-10}\ (\mathrm{cm}^2/\mathrm{mol\ G}^2)$

The observed h is due to <u>two</u> degenerate transitions A,g $E^{Q}_{u+,-}$ and equals $5.02 \times 10^{-10} (\mathrm{cm}^2/\mathrm{mol\ G}^2)$.

IV MORD CALCULATIONS [14,15]

$$\emptyset m(\text{degcm}^2/\text{decimol}) = -(24NH/hc)\ (Af_1) + (B + C/kT)f_2$$

The A term arises from Zeeman splitting of the K-L transition, the B term from mixing of states into K and L by H, and the C term from the change in population of the component states of ground state K as a result of Zeeman splitting. C = 0 for nondegenerate ground states. f_1, f_2 are line shape functions.

For the cytochrome c $A\ g \rightarrow E^{Q}_{u+,-}$ transition:

$$\Delta m_z^{LK} = m_z^{L} = 2A/D = (1.49b^2 htc/6\nu NHD)_{\emptyset m\ 550nm} = 1.49\beta$$

<u>where</u>

$$D = 2\sum_{+,-} |\langle A\ g|\mu x|E^{Q}_{u}\rangle|^2 = 5.62 \times 10^{-36}\ (\text{Debye}^2)$$

$$H = 10^4\ \text{Gauss}$$

$$\emptyset_{m\ 550nm} = 1.93 \times 10^5\ (\text{deg cm}^2/\text{decimol})\ [14,15]$$

$$b_{12} = (B/D)(\Delta U^{Q-S})\ D(S)/\Sigma D(Q,)^{-\frac{1}{2}} = 1.60\beta$$

<u>where</u>

$D(S)$ = D of the Soret band $\simeq 3 \times 10^{-35}$ (Debye^2)

$D(550nm) + D(524nm)$

$\sum_{+,-} D(Q) = \simeq 10^{-35}(\text{Debye}^2)$

$B = (1.49 \times 4\ bhc/24NH\nu)\emptyset_m(546nm)$

Note that since the rotation due to B is so much smaller than that due to A, the assigned value is only an approximation.

V

Tensor Notation [22]

Repeated suffixes imply summation:

e.g. $\mu_{\alpha\beta}m_\alpha m_\beta \qquad (\alpha,\beta = x,y,z)$

$= \quad \mu_{xx}m_x^2$

$+\mu_{yy}m_y{}^2$

$+\mu_{zz}m_z{}^2$

$+\mu_{xy}m_x m_y$

$+\mu_{xz}m_x m_z$

$+\mu_{yx}m_y m_x$

$+\mu_{yz}m_y m_z$

$+\mu_{zx}m_z m_x$

$+\mu_{zy}m_z m_y$

Note that μ_{xy} does not necessarily equal μ_{yx} as was demonstrated in appendix I, where it was shown that $\mu_{xy} = -\mu_{yx}$ (in the complex basis). Those familiar with tensors will also note that all the tensors in this work are subscripted regardless of whether they are covariant or contravariant. This is a legitimate practice in standard three-space, in which such distinctions are meaningless.

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