NBSIR 74-544
Kerr Coefficients of Nitrobenzene and Water

Robert E. Hebner, Jr., Richard J. Sojka and Esther C. Cassidy

Electricity Division
Institute for Basic Standards
National Bureau of Standards
Washington, D. C. 20234

August 7, 1974

Prepared for
U. S. Air Force
Kirtland Air Force Base
Albuquerque, New Mexico 87117

NBSIR 74-544

KERR COEFFICIENTS OF NITROBENZENE AND WATER

Robert E. Hebner, Jr., Richard J. Sojka and Esther C. Cassidy

Electricity Division
Institute for Basic Standards
National Bureau of Standards
Washington, D. C. 20234

U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

TABLE OF CONTENTS

I. Introduction

The electro-optic Kerr effect is used routinely in a number of
laboratories throughout the world for the measurement of high voltage
pulses. Almost all work to date has used nitrobenzene as the
birefringent liquid. The primary reasons for the dominance of nitro-
benzene are that this fluid exhibits an approximately flat frequency
response from very low frequencies to about 10^8 Hz, and it has a larger
Kerr coefficient than any other liquid possessing a suitable frequency
response. There are a number of properties of nitrobenzene that
preclude its use as an insulant in conventional high voltage apparatus.
Primary among these is the fact that it is a good solvent. In addition
the resistivity of nitrobenzene is reduced by orders of magnitude by
impurities. For these reasons when it is used for voltage measurement
it is usually sealed in a cell constructed of glass, or other material
impervious to nitrobenzene, and the cell is connected to the high
voltage circuitry. Measurement of the phase shift between two
orthogonal components of the linearly polarized light beam incident
upon the calibrated cell provides the information necessary to measure
the pulse shape and/or the peak value of the applied pulse. This
optical coupling between the high voltage and detection circuits provides
both high noise immunity and can prevent the transfer of any high voltage
or high current surges between the pulse generator and sensitive
detection circuitry.

This report is directed toward an improvement of pulsed-voltage
measurement accuracy through a measurement of the temperature and
wavelength dependence of the Kerr coefficients of nitrobenzene and
water. Accurate values for magnitudes of these coefficients are
significant because knowledge of the cell geometry and the Kerr
coefficient of the birefringent fluid permits measurement of voltage
with an uncertainty of a few percent. This is useful in cases in which
it is impractical to calibrate the Kerr system against another measuring
device. The main disadvantage of this approach has been the large
uncertainty in the value of the Kerr coefficient. For example, a large
number of measurements of the Kerr coefficient of nitrobenzene have been
made. At a given temperature and wavelength, these values differ from
the average by ±40%. For water only one careful determination of the
Kerr coefficient was available in the literature. In presenting that
work, however, the authors made no estimate of the measurement error.
In this report the Kerr coefficient of nitrobenzene was measured with
an estimated uncertainty of ±6% and the measurements in water had an
uncertainty of ±8%.

The measurement of the temperature dependence of the Kerr coefficient
is even more significant for accurate voltage measurement because the
cell calibration is temperature dependent. Calibration of a Kerr cell
for high voltage measurement consists of applying a known voltage,
measuring the phase shift between two components of the polarized light
beam, and calculating the voltage necessary to cause a phase shift of

1

π radians. This voltage is called the cell constant and depends only on the cell geometry and the Kerr coefficient of the birefringent fluid. Accurate measurements of the temperature dependence of the Kerr coefficient permit correction of the cell calibration. The temperature dependence of the Kerr coefficients of both water and nitrobenzene are presented in this report.

The experimental approach was to repeat and refine the measurements previously made of the Kerr coefficient of nitrobenzene. Measurements in nitrobenzene would serve to calibrate the apparatus used for the measurement in water. Furthermore this redetermination of the Kerr coefficient of nitrobenzene would identify any systematic errors which may have arisen. Using the same cells used in the nitrobenzene study, the ratio of the Kerr coefficient of water to the Kerr coefficient of nitrobenzene was determined. To verify the accuracy of these measurements, the Kerr coefficient of water was determined independently from measurements of phase shift, cell geometry and voltage.

A description of the apparatus used in the course of these measurements is presented in Section II. The various techniques used in voltage measurement and the necessary equations for data reduction and error analysis are presented in Section III. Section IV presents the results of this investigation and compares them to those obtained by other workers. The report is summarized in Section V.

II. Apparatus

     The purpose of this section is to provide a detailed report of the apparatus and measurement techniques used. The apparatus is shown schematically in Fig. 1. The high voltage pulse generator was a Marx-type generator, i.e., capacitors charged in parallel, discharged in series, with appropriate wave shaping inductors to yield an approximately rectangular pulse with rise and fall times of approximately 1 μs and a duration of about 10 μs. The peak output voltage was approximately 65 kV. The Kerr cells used had spacing as small as 0.25 cm. This resulted in the ability to generate field strengths of order 250 kV/cm which was sufficient to cause electrical breakdown in the cells used.

The high voltage divider was a resistive divider, total resistance nominally 500 Ω. In addition to serving as a method of measuring the maximum pulse voltage, the divider is used to define the burden for the pulse generator. It should be noted, however, that with the largest capacitance water cell the RC time constant of the burden approached the designed risetime of the pulse generator. This was demonstrated experimentally by a lengthening of the pulse rise and fall times to about 2 μs. Conventional practice is to insure accurate pulse voltage measurement by using both a calibrated Kerr cell and the pulse divider to measure the voltage pulse. For most of the data presented in this report this practice was followed. In cases when measurements using both devices were obviously superfluous, e.g., when a large number of
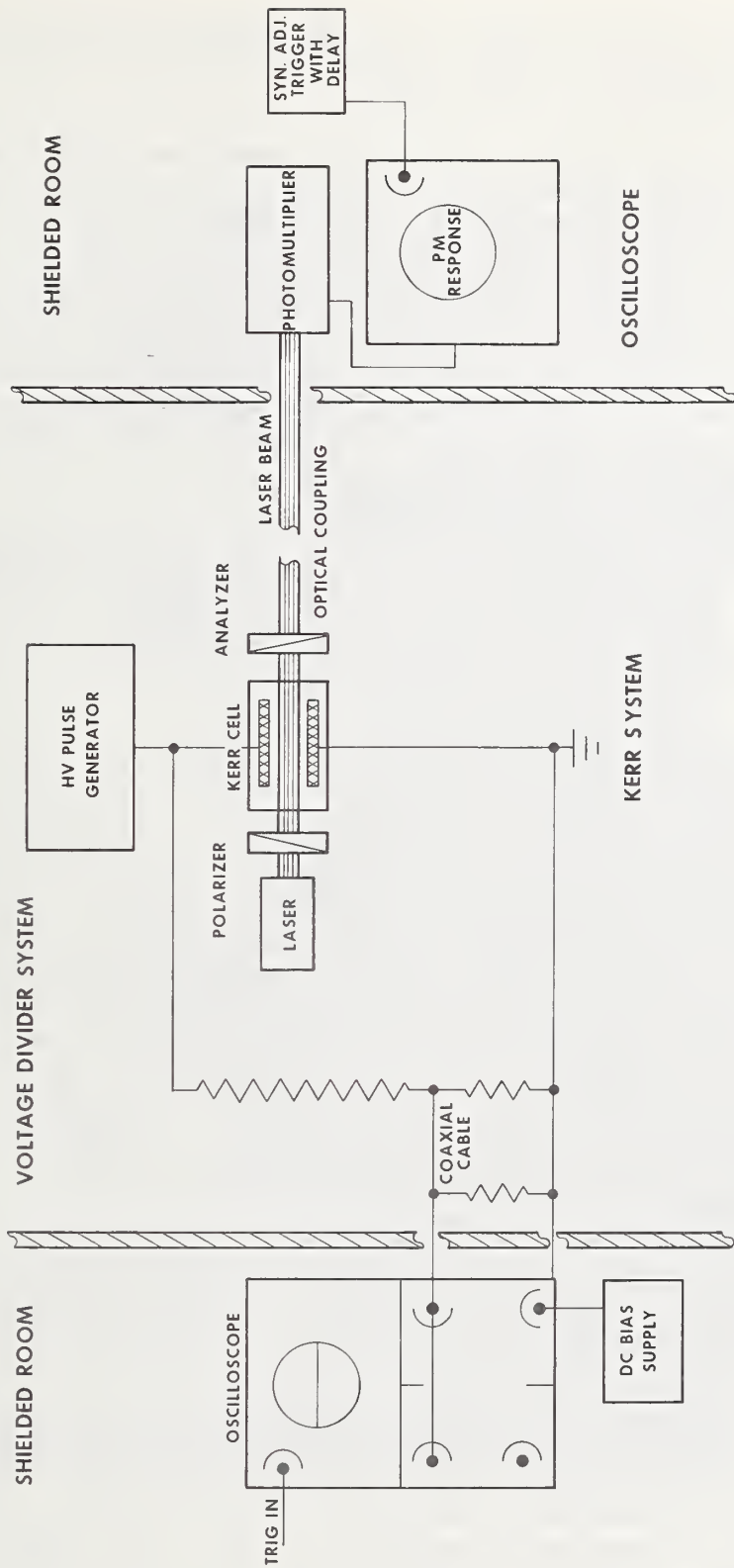
2

Fig. 1 Schematic diagram of the apparatus used in the determination of the Kerr coefficients of water and nitrobenzene.

3

observations were made using exactly the same set-up, only the divider measurement was recorded. In these cases the divider performance was verified before each series of data runs.

The light sources used for this study were a HeNe laser (632.8 nm) and an argon laser. A wavelength selector at the output of the argon laser permitted measurements at 514.5, 496.5, 488.0 and 476.5 nm.

Four different Kerr cells were used during the course of this study. These are shown in Fig. 2-4. Two of the cells, which have been discussed previously, were constructed to be, except for the length of the plates, geometrically identical. The plates in each cell were made of stainless steel, were electro-polished after cell construction, and were 4 cm wide and spaced 0.5 cm apart. The length of the plates in one cell was 12 cm, while the other had plates that were 24 cm long.

The third cell, also previously discussed, was designed so that the birefringent liquid was confined to a central volume well removed from electrode edges. In this cell, the liquid volume had dimensions: width 1 cm, thickness 1 cm, length 4 cm. The electrodes were stainless steel with dimensions: width 5 cm, length 14 cm and thickness 0.75 cm.

The fourth cell, which was used only for measurements in water, was specially constructed for this investigation. While the other cells were constructed of glass, this was made from polymethylmethacrylate. In order to provide an acceptable light path circular (diameter ≃ 5.5 cm) holes were cut in the end faces of the plastic box. Strain-free glass was then cemented over these holes. The spacing between the aluminum electrodes (4 cm wide, 30 cm long) was adjustable between 0.25 and 1 cm. The top plate of the cell was removable. When the cell was in use, it was filled so that the birefringent liquid covered the entire upper electrode. The upper electrode then served as the grounded electrode, and the high voltage pulse was applied to the lower electrode. The air space between the top of the liquid and the cover of the box served as a compressable volume so that the shock wave caused by electrical breakdown would not rupture the glass end plates. During the course of these investigations, a large number of electrical breakdowns occurred. In no case was the cell damaged.

During most of this study, a photomultiplier tube (1P21) was used to detect the modulated light beam. The output from the photomultiplier was displayed on a conventional oscilloscope and the data was recorded by photographing the oscilloscope trace whose sweep was synchronized with the high voltage pulse.

The temperature of the cell was controlled through a control of the temperature of the oil bath in which the cell was immersed. The heating-cooling unit was a commercially-available thermostated unit. The temperature range covered was from 280 K to 322 K. Upon changing the selected temperature, the system was given about three hours to stabilize. For the temperature increments used, no change in the cell temperature as

4
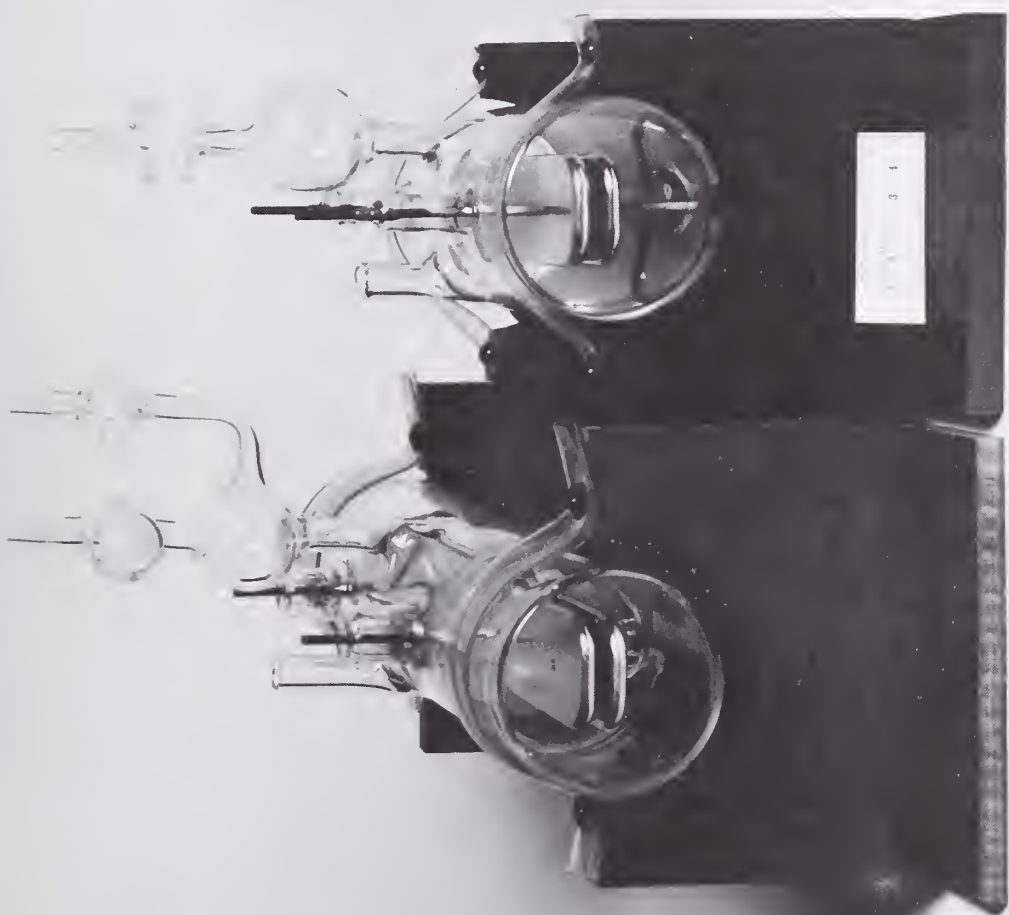
Fig. 2 Kerr cells used for the determination of the Kerr coefficients of both nitrobenzene and water. The cells were designed to be geometrically identical except that the plates in one cell were twice as long as they were in the other.

5

Fig. 3 Kerr cell used in the determination of the Kerr constant of
nitrobenzene. The birefringent liquid is confined to a volume
well removed from the electrode edges.

Fig. 4 Plastic cell used for measurement of the Kerr coefficient of water. The plate spacing is adjustable between about 0.25 and 1 cm.

7

large as 0.1 K was detected after a stabilization time of about 1.5 hrs. A very limited amount of work was performed using the plast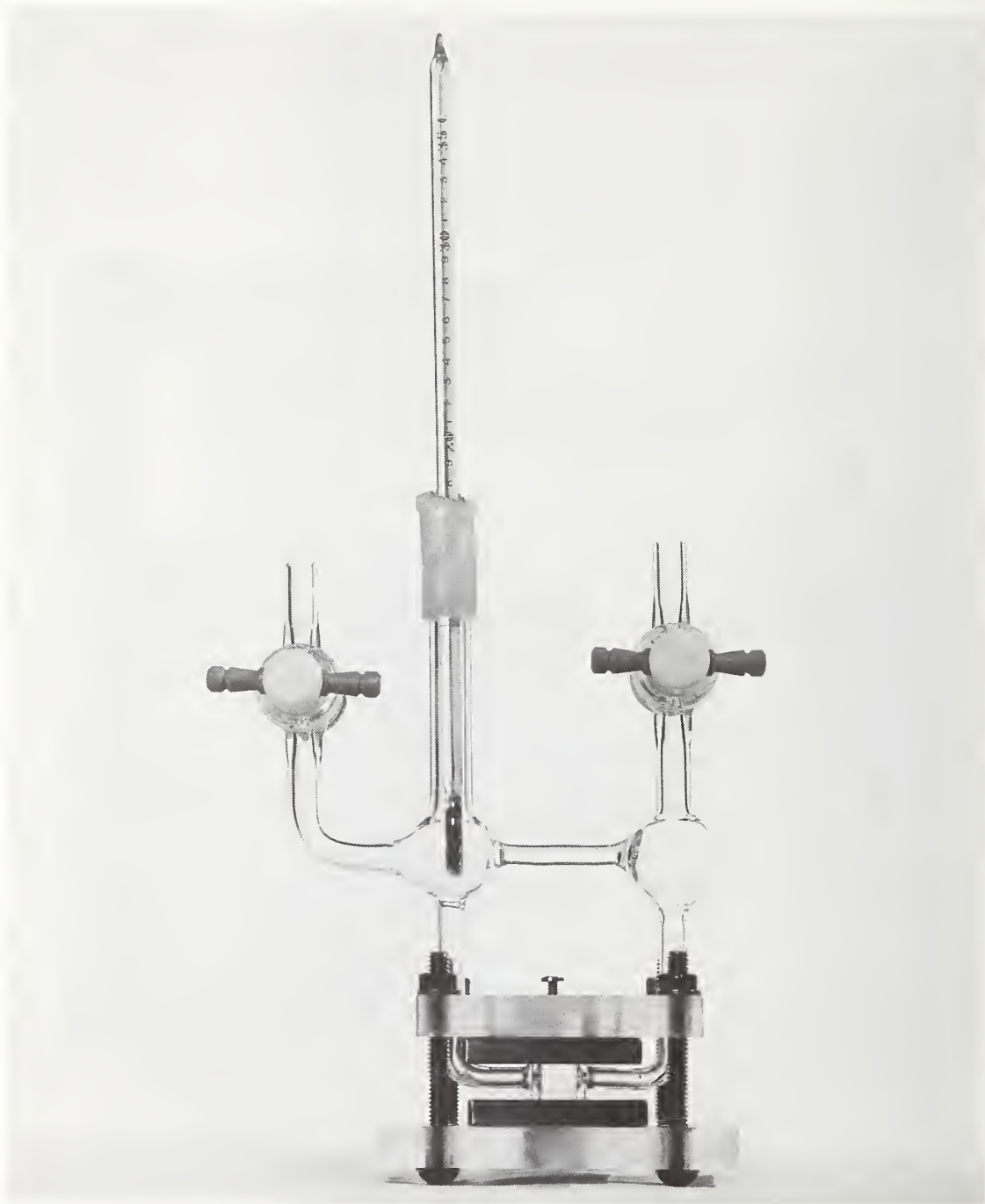ic cell at various temperatures. In this case the temperature of the liquid was controlled by passing heated or cooled transformer oil through a loop of copper tubing on the back side of the grounded electrode.

III. Experimental Approach

A) Identification of Sources of Error

The Kerr coefficient of a substance, B, can be defined by the relationship

$$n_{11} - n_{\perp} = \lambda BE^2 \tag{1}$$

where $n_{11(\perp)}$ is the index of refraction for light polarized parallel (perpendicular) to the direction of the applied field E and λ is the wavelength of the monochromatic light traversing the Kerr cell. Eq. (1) can be solved for the phase shift, φ, between the components of the light beam polarized parallel to and perpendicular to the direction of the applied field:

$$\varphi = 2\pi \int_0^L BE^2 \, d\ell \tag{2}$$

In Eq. (2), L is the length of the optical path through the applied field. Making the usual assumptions[1], Eq. 2 can be rewritten

$$\varphi = 2\pi BV^2 \ell' d^{-2} \,, \tag{3}$$

where ℓ' is an effective length which includes the effects of fringing fields at the edges of the plates, V is the applied voltage and d is the plate spacing. From (3),

$$B = \varphi d^2 / 2\pi \, \ell' V^2 \,. \tag{4}$$

Eq. 4 can be used to provide an estimate of the measurement uncertainty. Assuming all uncertainties are small,

$$\frac{\Delta B}{B} = \pm \frac{\Delta \varphi}{\varphi} \pm \frac{\Delta \ell'}{\ell'} \pm 2 \frac{\Delta d}{d} \pm 2 \frac{\Delta V}{V} \,. \tag{5}$$

The measurement uncertainty of the pulsed high voltage is ±1% of the peak value, so

$$2 \frac{\Delta V}{V} = 0.02 \,.$$

The plate spacing can be controlled and measured only to within 0.01 cm, so

$$2 \frac{\triangle d}{d} \simeq 0.03$$

With the cells used, the total contribution of the uncertainty of length measurements is less than 1% even if the effects of fringing fields are included[2,3], so

$$\frac{\triangle \ell'}{\ell'} \simeq 0.01 \quad .$$

The uncertainty $\frac{\triangle \varphi}{\varphi}$ is somewhat more difficult to express because the phase shift is not directly measured. The experiment is arranged in such a way that light polarized at an angle of $45°$ to the direction of the applied field passes through the Kerr cell and then impinges upon an analyzer oriented perpendicular to the direction of the polarization. Under these conditions, the transmittance through the optical system is described by the relationship[4,5]

$$I/I_m = \sin^2 [\varphi/2] \tag{6}$$

where I is the instantaneous value of the transmitted light and I_m denotes the maximum amount of transmitted light. Eq. 6 can be solved to yield

$$\frac{\triangle \varphi}{\varphi} = \frac{\cos^{-1}\{(-1)^n (1-2[I/I_m \pm \triangle I/I_m])\} - \cos^{-1}[(-1)^n(1-2 I/I_m)]}{n\pi + \cos^{-1} [(-1)^n (1-2 I/I_m)]} \tag{7}$$

In Eq. 7, n is an integer defined by the relationship:

$$\frac{\varphi}{\pi} = n + \alpha \quad ,$$

where α is the appropriate positive number between 0 and 1. The method of determining the value of n from the Kerr system response was discussed in previous publications[2,9]. In order to clarify the relationship between the uncertainty in the relative transmittance and the uncertainty in the phase shift, approximate values calculated from Eq. 7 are presented in Table 1. In the preparation of this table it was assumed that $\triangle(I/I_m) = 0.1$. The values for $\triangle\varphi/\varphi$ are not symmetrical about φ for a symmetrical choice of $\triangle(I/I_m)$, i.e., ± 0.1. For this reason the values listed in Table 1 are approximate and only intended to indicate the trend of measurement uncertainty with increasing phase shift.

Table 1. The approximate measurement uncertainty, $\frac{\triangle \varphi}{\varphi}$, is tabulated as a function of the magnitude of the total phase shift. The phase shift is presented in terms of $n + (I/I_m)$ because this is the quantity obtained from the measurement.

Phase Shift $[n + (I/I_m)]$	$\triangle\varphi/\varphi$ (%)
0.3	18
0.6	11
0.9	19
1.2	4.8
1.5	4.3
1.8	6.3
2.1	6.7
2.4	2.7
2.7	2.7
3.0	13
3.3	1.9
3.6	1.9
3.9	4.6
4.2	1.9
4.5	1.4
4.8	1.7
5.1	2.5
5.4	1.2
5.7	1.3
6.0	12
6.3	1.1
6.6	1.0
6.9	2.1

For measurements in nitrobenzene $n \gg 6$, so the error due to $\triangle\varphi/\varphi$ was negligible compared to other errors in the system. Most of the water data were taken with $[n + (I/I_m)] = 2.2 - 2.8$. The estimated uncertainty is then $\pm2\%$ as 0.1 would be an upper limit to the uncertainty in I/I_m in these experiments. This analysis leads to an uncertainty of $\pm6\%$ for nitrobenzene and $\pm8\%$ for water.

In Eq. 5, the sources of error were identified and their relative magnitudes have been estimated. To minimize the error a number of cells were specially constructed and a variety of measurement techniques were developed. Consistency between these approaches lends credibility to

the results. The three measurement techniques used can conveniently be labeled "End-Field Free" Cell Technique, Two Cell Technique and Single Cell Technique.

B) "End-field free" Cell Technique.

The "end-field free" cell, Fig. 3, used to make Kerr coefficient measurements is designed specifically so that the applied electric field is uniform over the liquid-filled segment of the light path, i.e., so that the edge field distortions are exterior to the portion of the light path through the liquid. The cell was constructed with two parallel plate electrodes overlapping a four-sided, rectangular, glass chamber used to confine the nitrobenzene. The surfaces of the glass chamber and electrodes were ground optically flat so as to allow glass-to-metal sealing and the glass chamber was designed to provide a liquid volume of 1 cm x 1 cm x 4 cm.

For a light path centrally located in the glass chamber and parallel to the length of the electrodes the total phase retardation φ is given by

$$\varphi = \frac{2\pi B \ell V^2}{d^2} + \varphi_{mech} \qquad (7)$$

where ℓ is the interior length of the glass chamber (the length of the nitrobenzene portion of the light path) and φ_{mech} is the phase retardation resulting from mechanical strain present in the glass windows at the ends of the chamber. During construction of more conventional Kerr cells[5] the cell is annealed to reduce φ_{mech} to a negligible quantity. In this case, however, the glass is subjected to mechanical stress so $\varphi_{mech} \neq 0$. The approach taken was then to assume that φ_{mech} was independent of the applied voltage. The strain-optic coefficients of the glass that was used are not well enough known to predict the magnitude of the voltage dependent phase shift. An order of magnitude estimate can be obtained, however, using published typical values[6]. With the geometry of the cell used, it would require a force in excess of 100 N to cause a phase shift of $10^{-2} \pi$. With the field strength used during this investigation, the net attractive force should not exceed 15 N.

So under the assumption that φ_{mech} is a constant, the electro-optic coefficient can be determined from two separate experiments which measure the phase retardations φ_1 and φ_2 at two different applied voltages V_1 and V_2, respectively. Using this information, both B and φ_{mech} can be calculated from Eq. 7:

$$B = \frac{(\varphi_1 - \varphi_2)d^2}{2\pi\ell (V_1^2 - V_2^2)} \qquad (8)$$

11

and

$$\varphi_{mech} = \frac{V_1^2 \varphi_2 - V_2^2 \varphi_1}{V_1^2 - V_2^2} \tag{9}$$

The total uncertainty in B depends on the uncertainties in measuring the phase retardation, applied voltages and the geometry parameter d^2/ℓ .

C) Two Cell Technique

This technique utilizes the two Kerr cells of conventional design shown in Fig. 2. For a centrally located light path between the electrodes in each cell the applied electric field will vary along the length of the light path due to the fringing fields at the ends of the electrodes. Each cell is constructed to be identical with the other except for the length of the electrodes where the respective lengths for cell A and cell B are 24 cm and 12 cm.

From Eq. 3, the phase retardation for each cell can be written

$$\varphi_A = 2\pi B \left(\frac{V}{d_A}\right)^2 \ell'_A \quad , \tag{10}$$

$$\varphi_B = 2\pi B \left(\frac{V}{d_B}\right)^2 \ell'_B \quad . \tag{11}$$

The cells are constructed so that $d_A = d_B$ and it is assumed that

$$\ell'_A = \ell_A + \triangle \ell \tag{12}$$

$$\ell'_B = \ell_B + \triangle \ell \tag{13}$$

where $\triangle \ell$ is the correction that must be added to the geometric length of the plates to obtain the effective length. The basis for the assumption that $\triangle \ell$ is independent of the plate length is the theoretical work of Lemoine[7], Chaumont[8], and most recently by Thacher[3]. In Thacher's

12

work he derived expressions for

$$< \ell E^2 > = \int_0^L E^2 \, d\ell \ . \tag{14}$$

This is related to our ℓ' through the equation

$$\ell' = < \ell E^2 > d^2/V^2 \ . \tag{15}$$

For Rogowski profile electrodes and a central light path, he derives

$$\ell' = \ell + d/\pi \ , \tag{16}$$

which is of the form of Eqs. 12 and 13. For electrodes which do not conform to Rogowski profile and for non-central paths the correction term is more complex, but is still independent of path length.

Using Eqs. 12 and 13 and assuming $d_A = d_B = d$, Eqs. 10 and 11 can be solved to yield

$$B = \frac{d^2}{2\pi V^2} \ \frac{\varphi_A - \varphi_B}{\ell_A - \ell_B} \ . \tag{17}$$

D) Single Cell Technique

To clarify the motivation for this approach, Eq. 3 can be rewritten

$$\varphi = \pi V^2 / V_m^2 \ ,$$

where

$$V_m = \frac{d}{\sqrt{2B\ell'}} \ . \tag{18}$$

A physical significance of V_m is that it is the lowest voltage necessary to produce a transmittance maximum through the system. If two different liquids are used in the same cell, the following

13

relationship is valid

$$\left(\frac{V_{m1}}{V_{m2}}\right)^2 = \frac{B_2}{B_1} \; , \tag{19}$$

where the subscripts 1 and 2 refer to the two liquids.

This approach is convenient in that years of development have demonstrated that V_m for a given cell can be determined with an uncertainty no larger than ±1%.[9] If the Kerr constant of one substance is known, then the measurement of the cell constants of the same cell containing first the known liquid then the unknown liquid provides a measure of the Kerr constant without the associated problems of geometrical measurement. This approach was used to determine the ratio of the Kerr coefficient of water to the Kerr coefficient of nitrobenzene. The final, and historically most common, method to determine B using a single cell is to measure the geometry of the cell, the applied voltage and the phase shift and use Eq. 3,

$$\varphi = 2\pi B \ell' V^2/d^2 \; ,$$

to calculate B. This approach was used but in a slightly modified form to conform with established practice in the authors' laboratory. Using Eqs. 3, 6, and 18, one obtains

$$I/I_m = \sin^2\left[(\pi/2)\,(V/V_m)^2\right] \; .$$

Then I/I_m and V are measured and V_m is calculated. Rewriting Eq. 18,

$$B = \frac{1}{2\ell'}\left(\frac{d}{V_m}\right)^2 \; , \tag{20}$$

is obtained. So from V_m, which contains the measurement of φ and V, and the cell geometry, B is calculated.

IV Results

    A) Magnitude of the Kerr Coefficient of Water and Nitrobenzene

    A flow chart showing the measurement strategy and the inter-relationships between the various experimental techniques is shown in

Fig. 5. This section describes the results obtained in each of the diagramed measurements.

Using the "end-field-free" cell, the Kerr electro-optic coefficient, B, was measured at a number of different wavelengths. Values B of nitrobenzene were determined from a series of at least ten experiments at each specified wavelength. Within each set of measurements no determination of B differed from the average by more than 3%. The measurement technique consisted of recording the phase shift and the applied voltage at two different voltage levels. Using these values in combination with the cell geometry allows Eqs. 8 and 9 to be solved for the Kerr coefficient B and for φ_{mech}. The results are summarized in Table 2.

Table 2. The electro-optic Kerr coefficient of nitrobenzene as measured using the "End-Field Free" Technique at 296 K.

Wavelength (nm)	$B(m/V^2)$	φ_{mech}
632.8	3.17×10^{-12}	-0.46
514.5	4.22×10^{-12}	-0.56
496.5	4.43×10^{-12}	-0.68
488.0	4.59×10^{-12}	-0.58
476.5	4.70×10^{-12}	-0.27

The results in Table 2 need two points of additional clarification. First, data were taken at nominal voltage levels of 60, 80, and 100 kV. Three sets of voltage pairs were then used at each wavelength to compute B according to Eq. 8. No determination differed from the average by more than 1.5% and no evidence of a voltage dependence of B could be identified. This observation is significant, not because the Kerr coefficient of nitrobenzene is expected to have a measurable voltage coefficient at these field strengths, but because Eq. 8 was derived assuming φ_{mech} was voltage independent to within the precision of this experiment. It therefore seems reasonable that φ_{mech} is primarily due to residual strain left in the glass during fabrication of the cell. The variation in φ_{mech} would then be due small variations in the optical path through the cell. An additional source of evidence supporting this interpretation is that expanded beam observations did show existence of strain birefringence and that the magnitude of this birefringence is indeed a function of position.
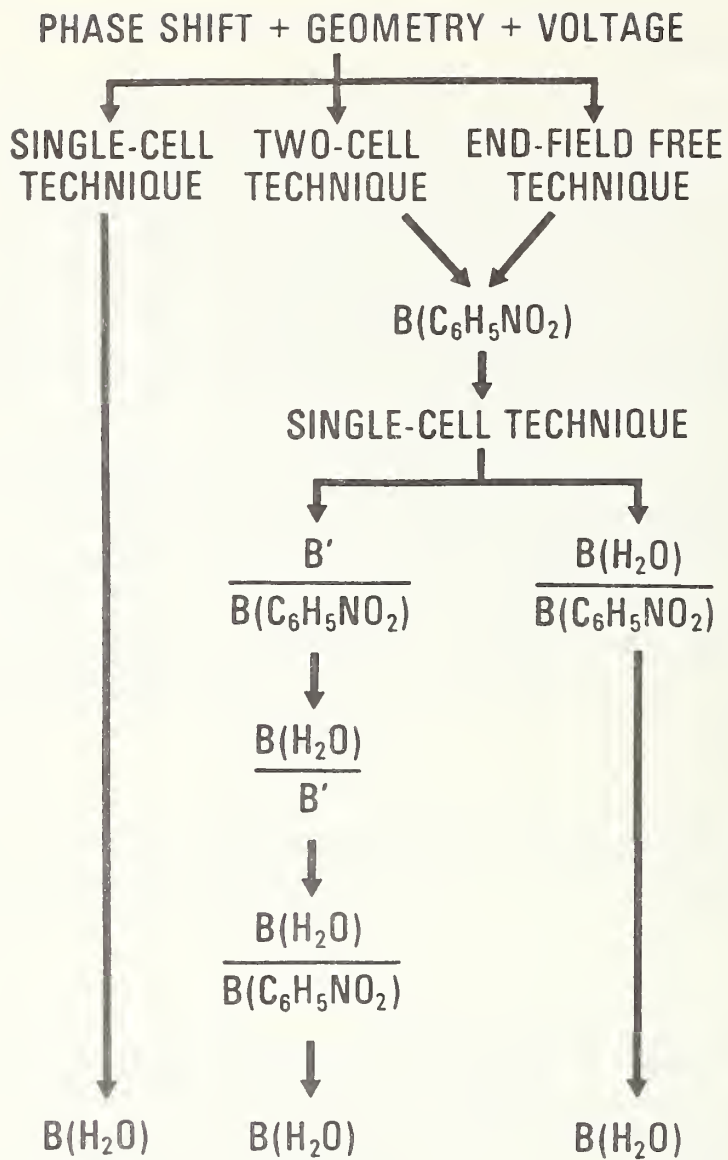
Fig. 5. Flow chart for the various measurements made of the Kerr coefficients of water and nitrobenzene. B' denotes the Kerr coefficient of Halowax Oil. This fluid was used to transfer measurements between two different cells.

16

Because the errors associated with cell geometry could lead to a systematic error in the results, it was decided to repeat the measurements using the two-cell technique. Using this technique, applying the same voltage pulse to both cells, and calculating B according to Eq. 17 led to a value $B = 3.24 \times 10^{-12}$ mV^{-2} at 296 K and a wavelength of 632.8 nm. The two methods therefore agree to about 2% which is well within the predicted measurement uncertainty.

The cells that were used in the two cell technique were then used to determine the ratio of the Kerr constant of water to the Kerr constant of nitrobenzene. The measurement involved determining the cell constant of the cell with longer electrodes when it was filled with nitrobenzene and when it was filled with water. Using Eq. 19, it was determined that

$$B(H_2O)/B(C_6H_5NO_2) = 1.058 \times 10^{-2}, \text{ at } 295.6 \text{ K.}$$

As a further check, it was decided to perform measurements of the Kerr coefficient of water using a plastic cell with electrodes having approximately a Rogowski profile. This would yield two different determinations of the Kerr constant. One would be simply from measurements of the phase shift and geometry and the other would utilize the single cell technique. Unfortunately nitrobenzene could not be used in the plastic cell because nitrobenzene, a good solvent, would destroy the cell's structural integrity. A less direct procedure was then used. First, a glass cell was filled with nitrobenzene and its cell constant was measured. The cell was then filled with Halowax Oil, a commercial blend of chlorinated naphalenes, and its cell constant determined. From these observations, the following ratio was obtained at 295.6 K,

$$B'/B(C_6H_5NO_2) = 4.209 \times 10^{-2},$$

where B' represents the Kerr coefficient of the Halowax Oil. Now Halowax Oil and water could be used in the plastic cell to determine the ratio of their cell constants. The procedure used in this case was first to fill the cell with water (water used was the house distilled water), seal the cell, and determine its cell constant. Through a small hole in the top of the cell, the water was then pumped out, the cell was dried and filled with Halowax Oil. This procedure was adapted to insure that the plate spacing remained unchanged during the refilling process.

Using this technique, the following ratio was obtained at 295.6 K,

$$B(H_2O)/B' = 0.2499.$$

So,

$$B(H_2O)/B(C_6H_5NO_2) = 1.052 \times 10^{-2}$$

at 295.6 K.

It should be noted that the two single cell techniques yield results that differ by less than 0.6%. From the temperature data presented in Table 3, the Kerr constant of nitrobenzene at 295.6 K is 3.26×10^{-12} m/V^2. The two corresponding values of $B(H_2O)$ are

$$B(H_2O) = 3.45 \times 10^{-14} \ \text{m/V}^2$$

and

$$B(H_2O) = 3.43 \times 10^{-14} \ \text{m/V}^2 \ .$$

From the cell constant and the geometry of the plastic cell an additional value of the Kerr coefficient of water can be derived.

Recall from Eq. 16 that

$$\ell' = \ell + \frac{d}{\pi} \ .$$

Inserting this into Eq. 20, yields

$$B = \frac{1}{2(\ell + d/\pi)} \ (\frac{d}{V_m})^2$$

In this case $\ell = 0.2998$ m, $d = 6.32 \times 10^{-3}$ m and $V_m = 44{,}010$ V. So,

$$B = 3.42 \times 10^{-14} \ \text{m/V}^2$$

The close agreement among these three values is thought to be serendipity, because, as was discussed in connection with Eq. 5, the estimated uncertainty in these measurements is ±8%.

An additional source of error was identified during the course of these investigations. Under microsecond duration pulses the water was occasionally in sufficiently turbulent motion as to modulate I_m, the

18

maximum transmitted irradiance. This is in marked contrast to experience by the authors with nitrobenzene and α-dichloronaphalene in which no turbulence is detected under high voltage pulses of this duration.

In order to put this anomalous behavior into perspective, Schlieren studies[10] have determined that if nitrobenzene is subjected to a step voltage pulse, it takes a few milliseconds for turbulence to become established. In addition theoretical studies[11] of unipolar injection predict an approximately equal time interval for the initial injected charge to traverse the gap from the injecting electrode to the collecting electrode. The agreement between these two studies is to be expected if the motion of charge through the fluid is the cause of turbulence.

One can assume in water, as in other polar fluids, that the primary source of carriers at these field strengths is unipolar injection. This would, however, require that the mobility of the carriers be three orders of magnitude larger than the mobility in other polar fluids. This possibility cannot be ruled out without more detailed knowledge of the nature of the charge carriers in the two cases.

Another possibility is that the source of carriers is not injection but volume dissociation in the water. Previous work[12] has indicated that about one in 10^9 of the water molecules will be dissociated into ionic carriers. It is therefore possible that the turbulence, rather than propagating from one electrode to the other, is formed at approximately the same time throughout the liquid.

A more detailed investigation of the conduction mechanisms in water is beyond the scope of this work, but is an area for further investigation. For completeness, it should be noted that the water used in this study had a typical resistivity of 10^6 Ω ·cm.

Previous results[5] have indicated that accurate Kerr measurements can be made even in the presence of turbulent motion. This was true because in that case the ratio of the amount of scattered light to the amount of transmitted light was undetectably small with the apparatus used. A second effect occurs, however, when the scale of turbulent motion is of order the size of the light beam. In this situation the fluid motion causes density gradients in the fluid. The density gradients lead to a change in the index of refraction which serve to deflect the light beam. As a consequence, the light beam "wanders" across the photo-sensitive surface of the detector. Because of spatial variations in quantum efficiency of the detectors used and/or because of the fact that a portion of the light beam may miss the photosensitive surface altogether, the photocurrent is amplitude modulated. This leads to an envelope on the Kerr response and was first detected in this study as an apparent voltage dependence of the cell constant. In this study the effects of fluid motion were minimized in three ways. First the distance between

the photodetector and the Kerr cell was kept as short as possible. The
other two approaches exploited the fact that this larger scale turbulence
was apparently modified by the geometry of the cell. In the glass cell
there was no detectable amplitude modulation during the first 6 μs of the
applied voltage pulse. Kerr constant measurements were then taken only
during this relatively quiescent period. In the plastic cell the time
interval between the rise of the voltage pulse and the onset of amplitude
modulation could be varied by varying the water level in the cell. By
a judicious choice of water level no amplitude modulation occurred during
the entire 10 μs voltage pulse.

A final word of caution is in order concerning the electric field
dependence of the Kerr coefficient of water. There is some evidence[13]
that the dielectric constant of water is 0.7% lower when measured at a
field strength of 250 kV/cm than when measured in weak fields. The
uncertainty in the present work precluded the observation of any
corresponding saturation effect, but the possibility of saturation
cannot be ignored if the present work serves as the basis of measurement
of voltage at significantly higher field strengths.

B) Temperature Dependence of the Kerr Coefficients

Experimental evidence[14] and theoretical investigations[15], which
assume that the structure of the liquid molecules and their interactions
are independent of temperature and applied fields, predict the following
temperature dependence for the electro-optic Kerr coefficient

$$B(T) = \alpha_0 + (\alpha_1/T) + (\alpha_2/T^2) , \qquad (21)$$

where the α's are constants.

This expression has been sufficient to describe the behavior of the
Kerr coefficient of nitrobenzene. Recent observations of the Kerr effect
in water[16,17], however, indicate an inflection point for the temperature
dependence of B at 308 K. Those authors suggest that in water

$$B(T) = \delta_0 + \delta_1/T + \delta_2/T^2 + \delta_3/T^3 , \qquad (22)$$

may be a more accurate functional form for the Kerr coefficient. The
values of the electro-optic coefficient measured at selected temperatures
are fitted by the method of least squares using Eq. 21 for nitrobenzene
and Eq. 22 for water. The α's and δ's are determined by this fitting
procedure. The functional form of the temperature dependence for both
fits are normalized by taking the ratio of B(T) to the value predicted
by the fit at 298 K.

20

For the first observation of the temperature dependence in nitrobenzene, the two cell technique was used over a temperature range from 296 K to 305 K. The measurement procedure was to heat the cells to approximately 310 K and then allow them to cool to room temperature. Measurements of the electro-optic coefficient were made after every 1 K drop in temperature as the cooling rate was approximately linear with a slope of about 2 K/h. The fit to these measured values of B, when extrapolated beyond the temperature range of the measurements, indicated a minimum in the Kerr electro-optic coefficient at 350 K.

To verify that the minimum was only a result of the extrapolation and as an additional check on the original data, the experiment was repeated several months later using the single cell technique. In this case measurements were made at selected temperatures between 280 K and 315 K. Over a common temperature range the measurements agreed to within ±1%. In addition, over the common temperature range between these measurements and those of Gabler and Sokab[14], there was agreement of order ±2%. These results are plotted in Fig. 6. It should also be noted that with this extension of the measurements to a higher temperature, the minimum value of Eq. 21 is shifted to a higher temperature. This implies that Eq. 21 is an accurate description of the temperature dependence of nitrobenzene over the range the model is intended to be applied.

If the normalized temperature dependence is fitted to an equation of the form

$$B/B(298 \text{ K}) = A_0 + (A_1/T) + (A_2/T^2),$$

the following are the values for the constants

$A_0 = 8.085$

$A_1 = -5.450 \times 10^3 \text{ K}$

$A_2 = 9.954 \times 10^5 \text{ K}^2$

These constants are intended to serve only as guide for the interpolation between the data points given. Experimental values for B at selected temperatures, and at a wavelength of 632.8 nm are presented in Table 3. At least 5 determinations of B were made at each temperature; each value of B differed by no more than 0.6% from its average value.
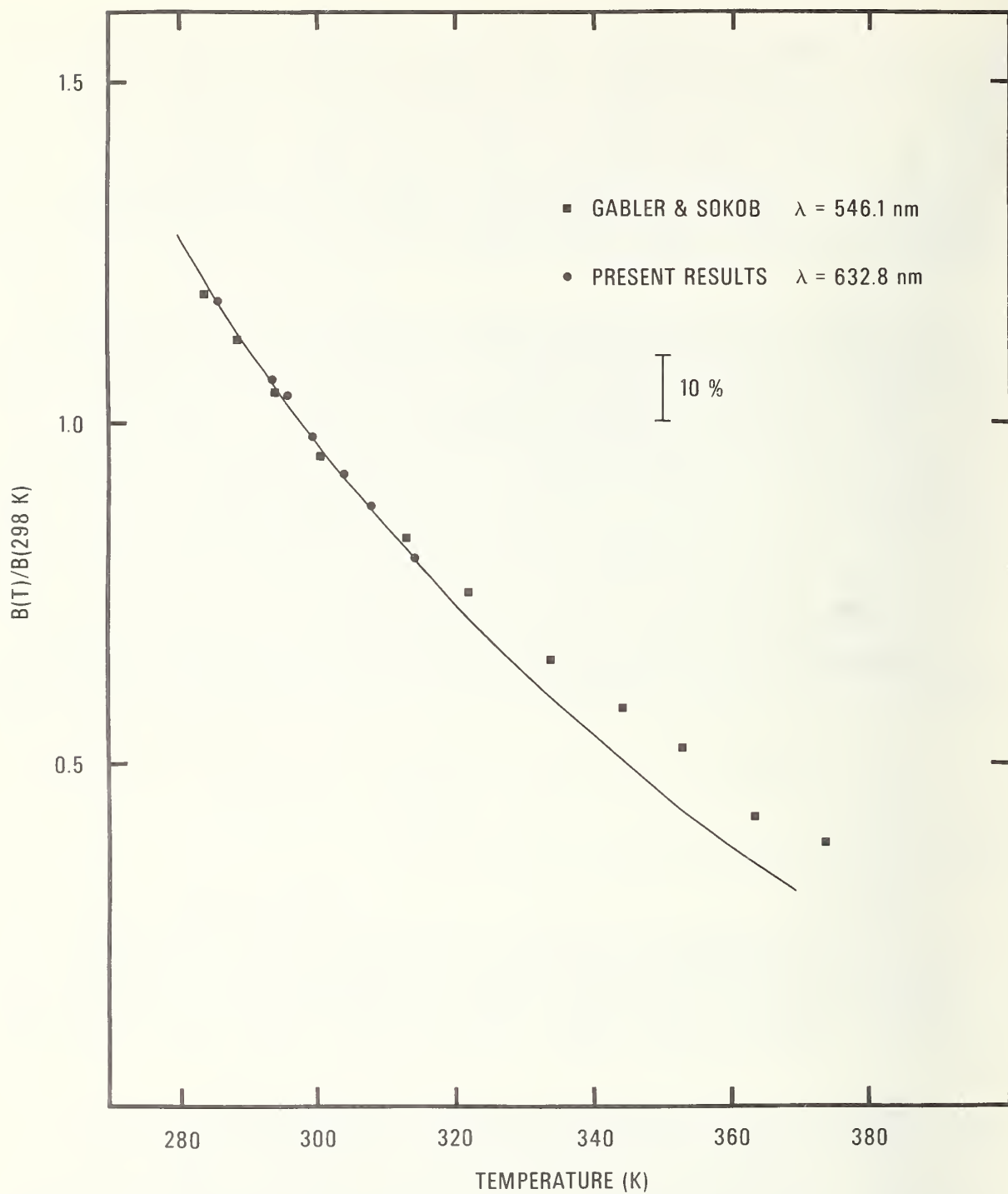
Fig. 6 Comparison of present and previously published data for the
temperature dependence of the Kerr coefficient of nitrobenzene.
Solid line represents least-squares fit to present data.

Table 3.   The Kerr coefficient of nitrobenzene at selected temperatures.

$B(m/V^2)$	$T(K)$
3.89×10^{-12}	286
3.47×10^{-12}	294
3.39×10^{-12}	295
3.22×10^{-12}	299
3.04×10^{-12}	304
2.86×10^{-12}	308
2.61×10^{-12}	314

Using the single cell technique (glass cell) the Kerr electro-optic coefficient of water was also determined for selected temperatures between 280 K and 315 K at a wavelength of 632.8 nm.   The mean values of B determined from a series of at least 5 experiments are compared in Table 4 at each specified temperature.   The values of B determined in each series of experiments did not vary by more than 1.3% of the mean value.

Table 4.   The Kerr coefficient of water at selected temperatures.

$B(m/V^2)$	$T(K)$
3.56×10^{-14}	280
3.70×10^{-14}	286
3.64×10^{-14}	288
3.45×10^{-14}	296
3.21×10^{-14}	305
3.05×10^{-14}	313
3.03×10^{-14}	314
2.95×10^{-14}	322

Again if the normalized temperature dependence is fitted to an equation of the form

$$B/B(298 \text{ K}) = D_0 + (D_1/T) + (D_2/T^2) + (D_3/T^3),$$

the values for the coefficients are

$$D_0 = 255.46$$

$$D_1 = -2.322 \times 10^5 \text{ K}$$

$$D_2 = 7.038 \times 10^7 \text{ K}^2$$

$$D_3 = -7.087 \times 10^9 \text{ K}^3$$

as was the case for the fit to the nitrobenzene data, these coefficients are intended only to aid interpolating between experimental values.

In Fig. 7, these data are compared with the recent experimental data of Chen[16]. An analysis of the difference between these results is presented following the discussion of the wavelength dependence of the Kerr coefficient of water.

The temperature dependence data were taken using the glass cell because for glass and metal the coefficient of linear expansion is of order 10^{-5}/K. The change in cell dimensions with temperature should, therefore, be negligible. To verify the accuracy of the values found for the temperature dependence, however, measurements were made in the plastic cell at 288, 295.5 and 304 K. These observations were within ±5% of the values obtained in the glass cell.

C) Wavelength Dependence of the Kerr Coefficients

The Kerr coefficient as a function of wavelength at a constant temperature is given in Table 2. From the definition of the Kerr coefficient, Eq. 1, it can be seen that in the absence of dispersion, i.e., if the index of refraction is independent of wavelength, the product λB should be a constant. From the data in Table 1 the average value of $B\lambda$ is 2.171×10^{-18} $(m/V)^2$. No individual value differs by more than 8% from this average value. For purposes of comparison, the measurement of the wavelength dependence of the Kerr coefficient of nitrobenzene by a number of workers is presented in Fig. 8. Note that there is satisfactory agreement among all authors over the common range of measurement.

The present determinations of the Kerr coefficient of water as a function of wavelength and previous work by Orttung and Meyers[18] are
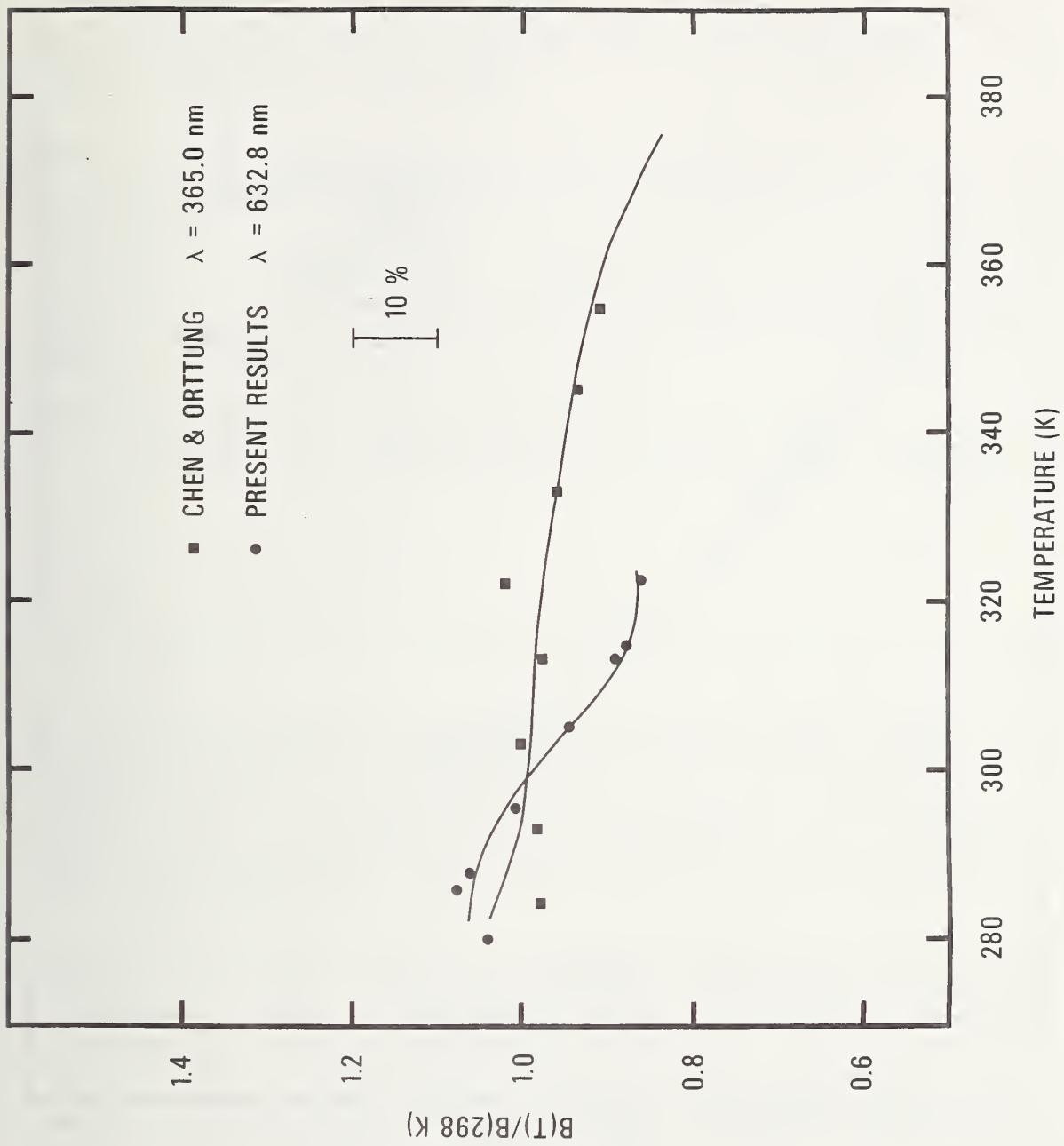
24

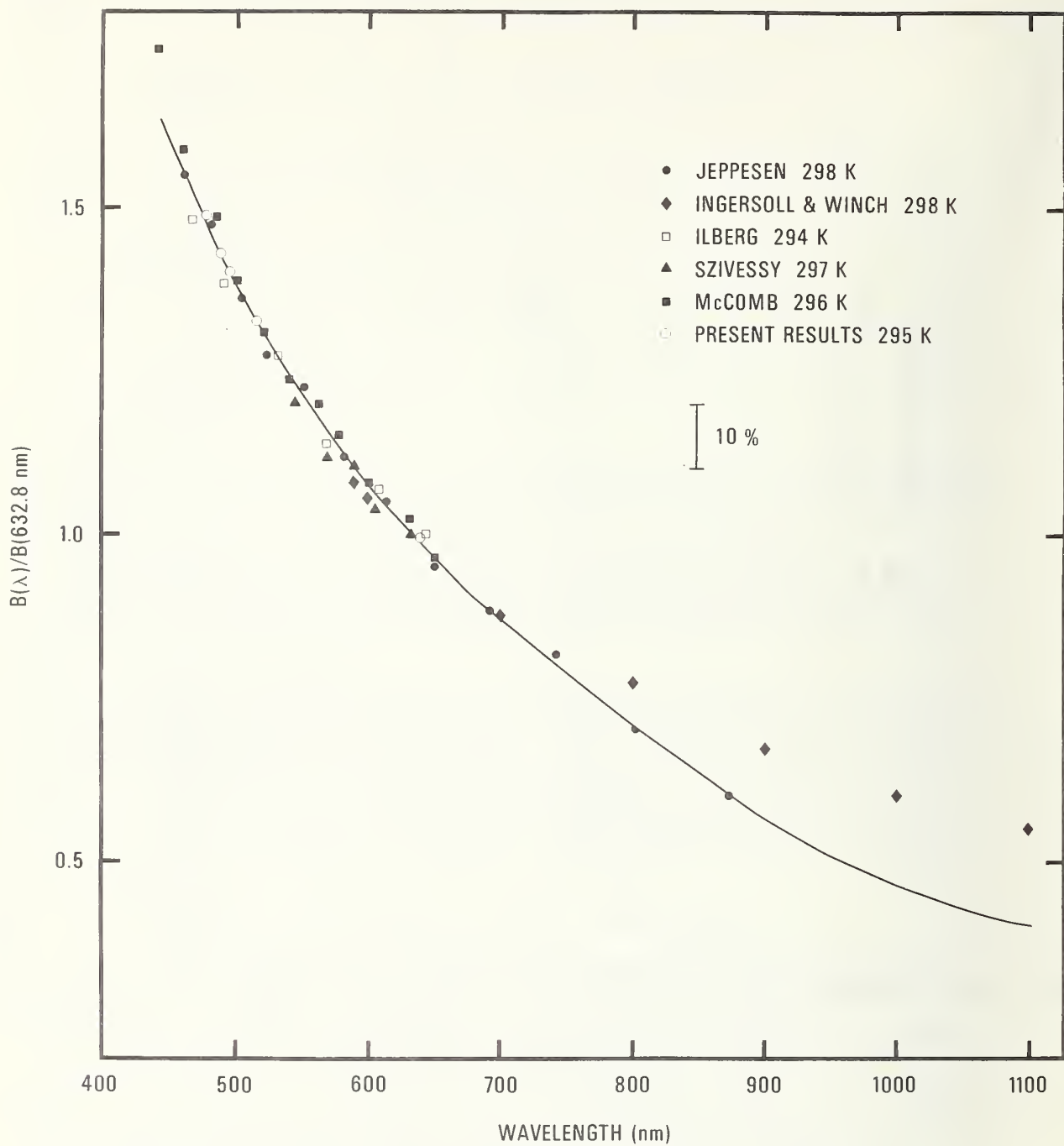Fig. 7 Comparison of present and previously published data for the temperature dependence of the Kerr coefficient of water.

25

Fig. 8 Wavelength dependence of the Kerr coefficient of nitrobenzene as determined by Jeppsen[19], Ingersoll and Winch[20], Ilberg[21], Szivessy[22], McComb[23], and the present authors.

26

compared in Table 5. In the present work no measurement differed from the average by more than 1.2%. In the work of Orttung and Meyers the standard deviation of all measurements at each given wavelength was less than ±4% of the average value.

Table 5. Wavelength Dependence of the Kerr Coefficient of Water

	B (m/V^2)	Wavelength (nm)	Temperature (K)
Present	3.45×10^{-14}	632.8	295.6
Results	4.17×10^{-14}	514.5	
Orttung	4.14×10^{-14}	436	
and	3.22×10^{-14}	546	298.2
Meyers[18]	3.03×10^{-14}	578	

For the present work the average value of $B\lambda$ is 2.16×10^{-20} $(m/V)^2$ and the two determinations were within ±1% of that. From the work of Orttung and Meyers[18] a value of $B\lambda$ equal to 1.77×10^{-20} $(m/V)^2$ is obtained. Their three readings agree to within ±2%. The difference between the two determinations of $B\lambda$ is indicative of the fact that the present data yield a value for B which is about 20% larger than that obtained by Orttung and Meyers.

A disagreement of that magnitude is, however, consistent with the cumulative uncertainty of the two experiments. The estimated uncertainty of the present results is approximately ±8% as was discussed previously. Orttung and Meyers make no estimate of the uncertainty of their measurements, but they do state that the precision of their measurements is of order 3-5%. It is assumed that this is due to $\triangle\varphi/\varphi$ in Eq. 5, because this would be typical of the uncertainty in when measurements are made below the first transmittance maximum. It is difficult to estimate their uncertainty with only their publication as guidance but their dimensional measurement uncertainty was somewhat less than that in the previous work, so in their case

$$2 \frac{\triangle d}{d} = 0.01\text{-}0.02 \ ,$$

$$\frac{\triangle \ell}{\ell} = 0.01 \ .$$

27

From their description of their voltage measurement system, the measurement uncertainty is probably of order 0.03-0.05. If these estimates of their uncertainty are valid, the two experiments agree in the sense that their error bars "overlap".

A seemingly more serious problem is the substantial disagreement between the temperature dependence data presented here and that determined by Chen[16]. As an analogy to this situation, the wavelength dependence of the Kerr coefficient of nitrobenzene was plotted in Fig. 8. The results of six different investigators are presented and they all agree to within a few percent. The unnormalized values of the Kerr coefficient however differ by as much as 40%.

In this case neither the magnitude nor the shape of the temperature dependence agree. A significant source of error in the measurement of the temperature variation of the Kerr coefficient is a thermal change in cell characteristics[18]. This is the reason the results presented here were verified using a completely different cell and a completely different method of temperature control.

A final point to be considered is the role of turbulence as a source of error. When turbulence was present on a sufficiently large scale to deflect the beam, there was significant error; typically a reduction of the apparent value for B by 10-30%. Neither of the previous works mentions the existence of turbulent motion in their fluid. In order to use the Kerr effect in water for accurate voltage measurement, the prediction and control of turbulent behavior in the liquid must be accomplished.

V.   Summary and Conclusions

The Kerr coefficients of both water and nitrobenzene were measured and the variation of these quantities with temperature and wavelength was investigated. At a temperatureof 296 K and at a wavelength of 632.8 nm the following values for the Kerr coefficients were obtained

$$B(C_6H_5NO_2) = 3.24 \times 10^{-12} \text{ m/V}^2, \text{ and}$$

$$B(H_2O) = 3.43 \times 10^{-14} \text{ m/V}^2.$$

The estimated uncertainty in the measurement in nitrobenzene is ±6% while in water the estimated uncertainty is ±8%.

The agreement between this determination of the Kerr coefficient of nitrobenzene and previous measurements is judged to be satisfactory. The determination of the temperature and wavelength variations agreed,

within experimental uncertainty with all other measurements. The magnitude of the Kerr coefficient as measured for this report lies within the range of previously published data. The spread of published values, approximately ±30% of an average value, discourages more precise comparison.

The smaller Kerr constant of water causes a smaller phase shift per unit field strength. The percentage uncertainty is then larger for water because the percentage uncertainty in the phase shift is larger. Not only were the results with water less precise than those with nitrobenzene, but there was also an additional source of experimental difficulty. In water there was substantial fluid motion during 10 μs duration pulses. In contrast, nitrobenzene does not demonstrate any fluid motion until the voltage has been applied for a few milliseconds. Two qualitative explanations for this behavior were postulated. First, if the production of charge carriers in water is due to unipolar injection, as is probably the case in nitrobenzene, one can infer that the effective mobility of the carriers in water is about three orders of magnitude larger than it is in nitrobenzene. As no detailed knowledge of the nature of the carriers exists in either case, this must be accepted as a possible explanation. A second explanation might be that bulk dissociation rather than unipolar injection is the primary source of carriers. If one accepts the model that turbulence is caused by the motion of charges through the fluid, it then follows that turbulence will form more rapidly in a fluid if the carriers are formed by bulk dissociation. This is because experimental studies have shown that turbulence propagates from one electrode to the other in the case of unipolar injection. Theoretical work has shown that the propagation rate is approximately equal to the transit time of the injected charge carriers. If the carriers are, on the other hand, uniformly distributed through the interelectrode region it seems likely that the turbulence would be formed at approximately the same time throughout the gap. To the authors' knowledge, there have been no experimental investigations of this phenomenon, and a more detailed study was beyond the scope of this work. Turbulence in water does remain an area that merits further study, because in Kerr effect measurements it is a source of error of unknown magnitude at best and at worst makes Kerr results uninterpretable.

A final observation is that although the results in nitrobenzene demonstrate the expected agreement with previously published data, this is not true in water. The difference in magnitude of the Kerr coefficient between this and previously published work can probably be attributed to the cumulative error in the two experiments. The difference in the temperature dependence is more striking and no convincing explanation for the difference is apparent.

The primary conclusion is that although nitrobenzene can be used for accurate measurement of a wide, and fairly well defined, variety of high voltage pulses, the situation in water is more poorly understood. This report indicates water can be used for the measurement of pulsed high

voltage, but it also identifies two unresolved areas of difficulty. The first is the existence of turbulence under pulses of duration of a few microseconds. The performance of accurate measurements in water requires a more precise definition of the dependence of turbulence on both electric field strength and time. The second is the possibility of a voltage dependence of the Kerr coefficient of water due to saturation of the alignment of the molecules with the applied field. The field strength at which this effect becomes significant must be determined so that the range of applicability of the observations presented in this report can be established.

References

1) R. E. Hebner and E. C. Cassidy, "Measurement of 60 Hz Voltages Using the Kerr Effect" Rev. Sci. Instru., vol. 43, pp. 1839-41, 1972.

2) E. C. Cassidy, W. E. Anderson, S. R. Booker, "Recent Refinements and Developments in Kerr System Electrical Measurement Techniques" IEEE Trans. on Instr. and Meas., vol. IM-21, pp. 504-510, 1972.

3) P. D. Thacher, private communication.

4) D. C. Wunsch and A. Erteza, "Kerr Cell Measuring System for High Voltage Pulses" Rev. Sci. Instru., vol. 35, pp. 816-820, 1964.

5) E. C. Cassidy, R. E. Hebner, R. J. Sojka and M. Zahn, "Kerr-Effect Studies of an Insulating Liquid Under Varied High-Voltage Conditions" IEEE Trans. Elec. Insul., vol. EI-9, pp. 43-56, 1974.

6) N. F. Borrelli and R. A. Miller, "Determination of the Individual Strain-Optic Coefficients of Glass by an Ultrasonic Technique" Appl. Optics, vol. 7, pp. 745-750, 1968.

7) J. Lemoine, "Verification de la Loi de Kerr-Measures Absolutes" Compte Rend., vol. 122, pp. 835-837, 1896.

8) L. Chaumont, "Recherches Experimentales sur le Phenomene Electro-optique de Kerr et sur les Methods Servant a l'Etude de la Luminere Polarisee Elliptiquement" Ann. de Phys., vol. 5, pp. 17-78, 1916.

9) E. C. Cassidy, "Development and Analysis of Techniques for Calibration of Kerr Cell Pulse-Voltage Measuring Systems V" NBS Report 10 493, Oct. 1971 and the references contained therein.

10) E. J. Hopfinger and J. P. Gosse, "Charge Transport by Self-Generated Turbulence in Insulating Liquids Submitted to Unipolar Injection" Phys. Fluids, vol. 14, pp. 1671-1682, 1971.

11) M. Zahn, C. F. Tsang, and S. Pao, "Transient Electric Field and Space Charge Behavior for Unipolar Ion Conduction" J. Appl. Phys., vol. 45, pp. 2432-2440, 1974.

12) D. Eisenberg and W. Kauzmann, The Structure and Properties of Water. Oxford Press, London, 1969.

13) J. B. Hasted, "Liquid Water: Dielectric Properties" Water A Comprehensive Treatise, F. Franks, ed., Plenum Press, New York, vol. 1, p. 262, 1972.

14) F. Gabler and P. Sokob, "Die Temperaturabhangigkeit des Kerreffektes am Nitrobenzol" Zeitschr. F. Techn. Physik, vol. 6, pp. 197-201, 1936.

15) A. D. Buckingham and R. E. Raab, "A Molecular Theory of the Electro-optic Kerr Effect in Liquids" J. Chem. Soc., pp. 2341-51, 1957.

16) Y. Chen, "Temperature Dependence of the Kerr Constants of Water and Heavy Water" University Microfilms, Inc., Ann Arbor, Michigan, #71-3874, 1970.

17) Y. Chen and W. H. Orttung, "Observation of a Minimum in the Kerr Constants of Light and Heavy Water Near $30°$" J. Phys. Chem., vol. 72, pp. 3069-70, 1968.

18) W. H. Orttung and J. A. Meyers, "The Kerr Constant of Water" J. Phys. Chem., vol. 67, pp. 1905-1910, 1963.

19) M. A. Jeppeson, "Measurements of the Kerr Electro-optical Effect" Am. J. Phys., vol. 24, pp. 623-25, 1956.

20) L. R. Ingersoll and W. R. Winch, "Dispersion of the Kerr Electro-optic Effect in the Short Infrared Spectrum" Phys. Rev., vol. 44, pp. 399-405, 1933.

21) W. Ilberg, "Eine Methods zur Bestimmung der Kerr-Konstante Schlecht Isolierender Staffe mit Hilfe Elektrischer Wechselfelder" Physik. Zeitschr., vol. 29, pp. 670-78, 1928.

22) G. Szivessy, "Über die Temperatura bhängigkeit der Dispersion des Elektrooptischen Kerreffektes" Z. Physik, vol. 2, pp. 30-49, 1920.

23) H. E. McComb, "Dispersion of Electric Double Refraction and Ordinary Dispersion in Liquids" Phys. Rev., vol. 29, pp. 525-40, 1909.

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET	1. PUBLICATION OR REPORT NO. NBSIR 74-544	2. Gov't Accession No.	3. Recipient's Accession No.

4. TITLE AND SUBTITLE	5. Publication Date
Kerr Coefficients of Nitrobenzene and Water	August 7, 1974
	6. Performing Organization Code

7. AUTHOR(S) Robert E. Hebner, Jr., Richard J. Sojka, and Esther C. Cassidy	8. Performing Organ. Report No. NBSIR 74-544

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. Project/Task/Work Unit No.
NATIONAL BUREAU OF STANDARDS DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234	11. Contract/Grant No. AFWL 74-067

12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP)	13. Type of Report & Period Covered Final Sept. 17, '73-June 30, '74
Air Force Weapons Laboratory Kirtland Air Force Base, N.M. 87117	14. Sponsoring Agency Code

15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

The Kerr coefficients of both water and nitrobenzene were measured and the variation of these quantities with temperature and wavelength was investigated. At a temperature of 296 K and at a wavelength of 632.8 nm, the following values for the Kerr coefficients were obtained $B(C_6H_5NO_2) = 3.24 \times 10^{-12}$ m/V^2, and $B(H_2O) = 3.43 \times 10^{-14}$ m/V^2.

The estimated uncertainty in the measurement in nitrobenzene is ±6% while in water the estimated uncertainty is ±8%.

The primary conclusion drawn is that although nitrobenzene can be used for accurate measurement of a wide, and fairly well defined, variety of high voltage pulses, the situation in water is more poorly understood. The primary areas of difficulty using water are the existence of turbulence under pulses of duration of a few microseconds and the possibility of a voltage dependence of the Kerr coefficient due to a saturation of the alignment of the molecules with the applied field.

17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Dielectric fluids; electrical properties of fluids; high voltage measurements; Kerr coefficient; Kerr effect; nitrobenzene; pulse measurements; water

18. AVAILABILITY [x] Unlimited	19. SECURITY CLASS (THIS REPORT) UNCLASSIFIED	21. NO. OF PAGES 32
☐ For Official Distribution. Do Not Release to NTIS		
☐ Order From Sup. of Doc., U.S. Government Printing Office Washington, D.C. 20402, SD Cat. No. C13	20. SECURITY CLASS (THIS PAGE) UNCLASSIFIED	22. Price
☐ Order From National Technical Information Service (NTIS) Springfield, Virginia 22151		

American Revolution Bicentennial 1776-1976