# Dispersion of the Kerr Electro-Optic Effect in the Short Infrared Spectrum

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Measurements of the Kerr electro-optic effect have been made on carbon disulphide, nitrobenzene, *o*-nitrotoluene, chlorobenzene, and halowax oil over a spectral region extending from the sodium lines to beyond  $1.6\mu$  ( $2.1\mu$  for CS<sub>2</sub>), or some three times the wave-length range previously investigated by other observers. A spectro-radiometric method was used, involving effectively the measurement of the minor axis of the ellipse into which the plane polarized radiation is converted by the electrostatic stress in the Kerr cell. The potentials across the cell of 3300 to 31,000 volts were furnished by a kenotron and condenser

THE dispersion of the Kerr electro-optic effect (birefringence produced by high electrostatic field) has been extensively investigated for the visible spectrum.<sup>1</sup> In the ultraviolet, Szivessy and Dierkesmann<sup>2</sup> have applied photographic means to the study of a number of liquids in this connection. Apparently no previous investigators, however, have experimented with this effect in the infrared. In this paper<sup>3</sup> we shall describe the method and results of a study of the electro-optic dispersion of five liquids in the wave-length range from that of the sodium lines to about  $2\mu$ , together with a comparison of the results with theory.

### DISPERSION FORMULAS

If  $n_p$  and  $n_s$  are the refractive indices for the components of the light vibrating parallel and perpendicular, respectively, to the lines of force, the phase difference D after passing through l cm of the substance in an electric field of E e.s.u. is

$$D = 2\pi l(n_p - n_s)/\lambda = 2\pi K l E^2 \text{ radians}, \quad (1)$$

equipment. The Havelock formula for electro-optic dispersion  $K = C(n^2-1)^2/n\lambda$  and two others have been tested in connection with the results. In most cases the agreement with the Havelock formula is somewhat better than with the others and for CS<sub>2</sub> this law fits the observed dispersion almost within the limits of experimental error throughout the spectral range investigated. Beyond  $1\mu$  the dispersion of all the liquids is much the same and the agreement with all these formulas reasonably good. In fact, for this region the Kerr effect is very nearly proportional to the inverse wave-length.

where  $\lambda$  is the wave-length of the light. *K* is called the Kerr constant.

Three dispersion formulas will be tested in connection with the present work; they are (a) the well-known Havelock law<sup>4</sup>

$$K = C_1 (n^2 - 1)^2 / n\lambda,$$
 (2)

(b) a development on the basis of the Born<sup>5</sup> classical theory,

$$K = C_2(n^2 + 2)(n^2 - 1)/n\lambda$$
 (3)

and (c) one recently developed by Serber<sup>6</sup> on a quantum basis which, on approximation, simplifies to

$$K = C_3 \frac{(n^2 + 2)(n^2 - 1)}{n\lambda} \left\{ 1 + C_4 \frac{1 + \nu^2 / \nu_1^2}{1 - \nu^2 / \nu_1^2} \right\}, \quad (4)$$

where  $\nu_1$  is the main ultraviolet absorption frequency, really the centroid frequency. The latter two formulas apply primarily to the case of gases, where the mutual influence of the molecules is small, but they should also hold

<sup>6</sup> M. Born, Ann. d. Physik **55**, 177 (1918). See also H. A. Stuart, Zeits. f. Physik **55**, 358 (1929); Ergebnisse d. Exacten Naturwiss. **10**, 159, Julius Springer (1931); C. V. Raman and K. S. Krishnan, Phil. Mag. **3**, 713 (1927); Proc. Roy. Soc. **A117**, 1, 589 (1928).

<sup>&</sup>lt;sup>1</sup>For general references see J. W. Beams, Rev. Mod. Phys. **4**, 133–172 (1932); G. Szivessy, Handb. d. Physik **21**, 724–884, Julius Springer (1929).

<sup>&</sup>lt;sup>2</sup>G. Szivessy and A. Dierkesmann, Ann. d. Physik 3, 507 (1929).

<sup>&</sup>lt;sup>3</sup> The following brief accounts have been published: L. R. Ingersoll, Phys. Rev. **37**, 1184 (1931); L. R. Ingersoll and W. R. Winch, Phys. Rev. **42**, 909 (1932).

<sup>&</sup>lt;sup>4</sup> T. H. Havelock, Proc. Roy. Soc. **A80**, 28 (1907), **A84**, 492 (1911); Phys. Rev. **28**, 136 (1909).

<sup>&</sup>lt;sup>6</sup> R. Serber, Phys. Rev. 43, 1011 (1933).

approximately for liquids, although in the case of (b) only for nonpolar molecules.

### EXPERIMENTAL METHOD

The method and apparatus are partly the outgrowth of investigations carried out some years ago by one<sup>7</sup> of us on the Faraday and Kerr magneto-optic effects in the infrared. Fig. 1



FIG. 1. Diagram illustrating the principles involved in the measurements.

illustrates the method. As indicated in (a), light vibrating at 45° with the plane of the Kerr cell comes from the polarizer whose azimuth is indicated at  $N_1$ . It is obvious that none of this radiation will pass the analyzer of azimuth  $N_2$ , at right angles to this, until a potential is applied across the cell as in (b). This produces a difference of velocity of the two component beams, which results in the Kerr phase difference D (or  $\delta$  as we have called it, measured in degrees) and the consequent elliptical vibration. If A represents the amplitude of the original vibration and Bthe semi-minor axis of the ellipse, then, as is clear from the figure, the relation is

$$\sin^2(\delta/2) = B^2/A^2.$$
 (5)

While it would be possible to measure the ratio of  $B^2$  to  $A^2$  directly, it is simpler to get at it by means of a rotation  $\alpha$  of the original plane of polarization as shown in (c). This results in a beam of intensity  $C^2$  being transmitted by the analyzer and this is easily compared with the intensity  $B^2$  which results from the excitation of the Kerr cell, being of the same order of magnitude. The equation, as indicated in Fig. 1, is

$$\sin^2(\delta/2) = \sin^2\alpha B^2/C^2.$$
 (6)

#### Apparatus

Fig. 2 shows the general arrangement of the apparatus. Light from the special strip-filament



FIG. 2. General arrangement of the apparatus. S, strip filament tungsten lamp;  $N_1$ ,  $N_2$ , double image (or nicol) prisms, crossed; K, Kerr cell; and B, bolometer or thermopile.

lamp was focussed by a silvered concave mirror and, after passing through the polarizer, was converged in a narrow conical beam between the plates of the Kerr cell. It then went on to the analyzer which was crossed so that no light passed until the Kerr cell was excited, in which case the transmitted radiation was focussed on the slit of the spectrometer and, after dispersion into a spectrum, fell on the receiver. It may be remarked that both polarizer and analyzer were really double-image prisms instead of nicols, but they were used in exactly the same way, for the second image, being turned aside at a small angle, was readily cut off. The polarizer was mounted in a large conical bearing so that it could be rotated between stops by the angle  $\alpha$ , mentioned above, which in the present work was 21° 20'.

In the first work with this apparatus the radiation receiver was a bolometer used with a Thomson galvanometer. It was later replaced, however, by a sensitive bismuth-tellurium thermopile. This had a receiving surface (using a double couple—uncompensated) of 0.5 mm $\times$ 10

<sup>&</sup>lt;sup>7</sup>L. R. Ingersoll, Phil. Mag. **11**, 41 (1906); Phys. Rev. **23**, 490 (1906); Phil. Mag. **18**, 74 (1909); Phys. Rev. **9**, 257 (1917); J.O.S.A. and R.S.I. **6**, 663 (1922).

mm and was used in high vacuum maintained by a charcoal trap in liquid air. When connected with a Zc (Kipp and Zonen) galvanometer it gave a tenfold gain in sensitivity over the bolometric outfit, even when used with narrower slit and longer focus mirrors in the spectrometer. Since a variety of conditions—in most cases the absorption of the liquid under test was the limiting factor—confined the measurements to the short infrared, a glass prism could be used in the spectrometer. This was a large 45° prism of heavy glass, the dispersion of which was calibrated with the aid of a grating.

The high voltage was furnished by two kenotrons and condenser connected with a 140,000 volt transformer, which, in turn, was controlled by an autotransformer allowing the application of any fraction of the 220 volt primary e.m.f. in 1 percent steps. Because of the minuteness of the current the output voltage ripple was only a fraction of a percent in most cases. To measure the voltage on the Kerr cell a Wulf electrometer (Leybold) was connected across its terminals. This had a range up to 50,000 volts and was an essential part of the equipment since inevitable small voltage fluctuations were of frequent occurrence.

Four different Kerr cells were used, varying in length from 5 to 39 cm, the shorter cells being used for liquids of high Kerr constant such as nitrobenzene and the longest for carbon disulphide. They consisted in all cases of glass tubes of 6 cm or more in diameter with ends of tested plate glass cemented on, usually with water glass. The Kerr plates were of heavy brass, nearly as long as the cell, from 4 to 5 cm wide and from 4 to 13 mm apart. Drilled glass plates screwed on top and bottom kept them accurately spaced.

The making of measurements was relatively simple. With the spectrometer set at the desired wave-length the high voltage was alternately thrown on and off the Kerr cell at regular intervals of about a minute and the corresponding galvanometer deflection measured. The Wulf electrometer was also read each time the cell was excited. Then, with the voltage off, the galvanometer deflection was read as the polarizer was turned through the angle  $\alpha$ . The Kerr effect, measured by  $\delta$ , could then be calculated at once from Eq. (6). To avoid correction for errors in galvanometer proportionality it was very desirable to have the deflections for B and C as nearly equal as possible. This was accomplished by cutting down one or the other intensity by a suitable and known factor, and, after some experimentation, the best way found to do this was to place in the beam a rotating sector of accurately measured opening.

The application of the Havelock or other electro-optic dispersion equation demands a knowledge of the index of refraction n and since this is known in the infrared for only a few liquids it had to be measured specially in the present case. This was done by the method of total reflection, using two glass plates cemented together to form a very thin air cell. It rotated in a cell filled with the liquid and was mounted in a divided circle which allowed the angle to be read to 1'. The check of these measurements at the sodium wave-length with the ordinary tabulated values was very good.

#### Sources of Error

## 1. Impurities

The best available material was used and this was further purified, if necessary, by the usual chemical and physical means. The last step in purification was usually to shake up the liquid with  $P_2O_5$ , let stand for a day or two, and then distill. In most cases, however, the current drawn by the cell on the initial application of the voltage was many times that (of the order of a milliampere, sometimes much less) to which it finally settled down after perhaps an hour. This was attributed to the presence of a minute amount of water and water-soluble impurities which were electrolyzed out and held on one of the plates. Reversing the current at once released these impurities, so throughout the work the voltage was always applied in the same direction. This self-purification was an important step in the process of the measurements and no readings were taken until the current had settled down to its minimum value.

#### 2. Lack of field uniformity, edge and end effects

The use of a slightly conical beam (necessary to secure sufficient energy) meant that parts of the beam would approach nearer the plates than others and into a region of inevitable field nonuniformity because of the rather wide (up to 13 mm) distance necessary between the plates. This would be a vital source of error if absolute values were demanded in the measurements, but in view of the fact that only relative values are necessary for dispersion measurements it became of somewhat secondary importance. It was necessary nevertheless to see that the position of the beam in the cell did not shift in the slightest degree during any one run, i.e., series of measurements throughout the spectral range.

### 3. Temperature variation

A thermometer in the cell was read at occasional intervals and the cell cooled by fan, if necessary, to keep temperature variations within 1°C. The mean temperature in most cases was 24°C.

## 4. Voltage variations

As already explained, the Wulf electrometer was read every time the voltage was applied to the cell. Making use of the fact that the Kerr effect is proportional to the square of the field, a correction was accordingly applied to each measurement to bring it effectively to a definite mean voltage.

# 5. "Creep"

This was one of the most serious difficulties. In certain liquids, notably chlorobenzene, the Kerr effect, as measured, began to decrease slightly after the field had been on for a minute or more; in other cases a small increase would take place. No explanation could be found for this and it is planned to make it the object of a special study in the future. Its effect was minimized in the present case by taking readings at definite regular intervals.

### 6. Spectral impurity

This may be of two sorts: (1) a very small amount of general impurity due to radiation scattering in the prism-mirror system and (2) the inevitable coverage by the receiver (and slit image) of an appreciable spectral range. The first sort was taken account of by making a series of Kerr measurements in the neighborhood of the sodium wave-length with a piece of heatabsorbing glass before the slit. This cut out practically all the infrared impurity and led to a correction of the order of 0.5 percent which was applied to the results for the sodium and adjoining wave-lengths. A similar test made with a cell containing iodine in  $CS_2$ , which absorbed the visible, indicated that no such corrections were necessary in the infrared.

The second sort of error was minimized by making the receiver and slit as narrow as possible. That this error was not large enough to be taken seriously into account was indicated by a comparison of results with the bolometer and those made later with the thermopile under conditions of somewhat larger effective dispersion. These indicated that the only uncertainty is in the neighborhood of the sodium wave-length. This is as applied to the results as a whole. There is one case, however, in which this error is so serious as to render measurements almost meaningless and that is in the immediate neighborhood of an absorption band. After much time spent in fruitless investigation of this point with the use of double dispersion, we were compelled to limit our study for the present to spectral regions free of marked absorption, although we hope at some time in the future to be able to develop a means of studying in this connection the interesting phenomena which may group around an absorption line or band.

### RESULTS

The following liquids were tested:

### Carbon disulphide

This was purified by treatment with mercury and filtration, then phosphorus pentoxide and distillation and used in Kerr cell with plates 37.5 cm long and 1.3 cm apart at 31,200 volts.

## Nitrobenzene

Purification was by fractional freezing, followed by  $P_2O_5$  treatment and distillation. The cell was 8.0 cm long with plates 0.6 cm apart. Voltages were 3310, 5250, and 8710.

### o-Nitrotoluene (Eastman)

This was dehydrated and distilled. The cell was 4.5 cm long, 0.4 cm plate separation. Voltages were 4795 and 10,020.

## Chlorobenzene (Eastman)

This was dehydrated and distilled. The cell was 10.0 cm long, 0.6 cm separation. Voltages were 22,840 and 28,550.

## Halowax Oil No. 1007, from the Halowax Corporation of New York

This is a chloronapthalin whose properties make it a good liquid to test in the present connection. It was used untreated. The cell was 8.0 cm long, 0.6 cm separation. Voltages were 13,590, 19,420, and 25,970.

The results are given in the table and the curves of Fig. 3. The values of  $\delta$  plotted in the curves are the actual angles in degrees as measured. While it would be possible to compute

the absolute values of the Kerr constant by using the voltages and cell dimensions as given, the error involved would be large because of the edge and end effects as already mentioned. These, however, in no way affect the dispersion results which are considered to have a probable error of not more than 1 percent for the spectral range  $0.7\mu$  to  $1.4\mu$  ( $2.0\mu$  for CS<sub>2</sub>). The approximate values of the Kerr constant for the sodium wave-length are, referred to CS<sub>2</sub> as 1: nitrobenzene, 99; o-nitrotoluene, 37; chlorobenzene, 3; halowax, 4.

While measurements were made for two or three different voltages on all liquids save  $CS_2$ all the separate results are not given, for it was found, as might be expected, that the dispersion

TABLE I. Relative Kerr constants.

		Observed Korr	Computed Kerr constants						Observed	Computed Kerr constants			
λ	n	constants	Havelock	Born	Serber	$1/\lambda$	λ	n	constants	Havelock	Born	Serber	$1/\lambda$
Carbon disulphide							o-Nitroto	luene					
0.589	1.6275	1.872	1.885	1.810	1.899	1.697	0.589	1.5472	1.857	1.857	1.793	1.739	1.697
0.60	1.6253	1.836	1.835	1.768	1.850	1.667	.60	1.5442	1.807	1.798	1.745	1.695	1.667
0.70	1.6138	1.515	1.510	1.476	1.514	1.428	.70	1.5357	1.491	1.494	1.466	1.444	1.428
0.80	1.6060	1.287	1.289	1.272	1.288	1.250	.80	1.5305	1.277	1.272	1.267	1.257	1.250
0.90	1.6006	1.124	1.123	1.122	1.122	1.111	.90	1.5269	1.120	1.122	1.117	1.114	1.111
1.00	1.5969	1.000	1.000	1.000	1.000	1.000	1.00	1.5244	1.000	1.000	1.000	1.000	1.000
1.10	1.5942	0.896	0.899	0.903	0.899	0.909	1.10	1.5223	0.905	0.901	0.905	0.907	0.909
1.20	1.5922	0.816	0.818	0.825	0.817	0.833	1.20	1.5208	0.823	0.822	0.827	0.827	0.833
1.30	1.5905	0.749	0.751	0.757	0.750	0.769	1.30	1.5198	0.761	0.751	0.761	0.766	0.769
1.40	1.5891	0.695	0.694	0.700	0.694	0.714	1.40	1.5191	0.708	0.699	0.705	0.710	0.714
1.50	1.5880	0.647	0.645	0.653	0.646	0.667	1.50	1.5186	0.664	0.653	0.657	0.663	0.667
1.60	1.5870	0.601	0.602	0.608	0.603	0.625	1.60	1.5181	0.618	0.610	0.616	0.621	0.625
1.70	1.5861	0.566	0.565	0.576	0.565	0.588	Chloroba						
1.80	1.5852	0.538	0.531	0.543	0.534	0.555	Childrober	izene	4.007	4.020	4 7 7 0	4 (04	4 (05
1.90	1.5845	0.510	0.503	0.511	0.503	0.526	0.589	1.5240	1.806	1.839	1.770	1.084	1.697
2.00	1.5840	0.485	0.479	0.480	0.477	0.500	.60	1.5230	1.750	1.799	1.735	1.055	1.007
2.10	1.5835	0.462	0.454	0.462	0.454	0.476	.70	1.5101	1.448	1.496	1.460	1.424	1.428
							.80	1.5111	1.250	1.283	1.262	1.245	1.250
Nitrobenzene							.90	1.5085	1.110	1.129	1.115	1.109	1.111
						1.00	1.5009	1.000	1.000	1.000	1.000	1.000	
$0.589\mu$	1.5525	1.825	1.853	1.789	1.945	1.697	1.10	1.5055	0.907	0.912	0.907	0.910	0.909
.60	1.5506	1.770	1.806	1.742	1.891	1.667	1.20	1 5027	(0.032)	0.033	0.020	0.034	0.000
.70	1.5417	1.470	1.497	1.472	1.537	1.428	1.30	1 5022	(0.772)	0.700	0.704	0.716	0.709
.80	1.5355	1.280	1.279	1.267	1.298	1.250	1.40	1 5020	(0.123)	0.710	0.708	0.710	0.714
.90	1.5318	1.125	1.120	1.117	1.128	1.111	1.50	1.5029	(0.000)	0.002	0.000	0.009	0.007
1.00	1.5296	1.000	1.000	1.000	1.000	1.000	1.00	1.5025	(0.044)	0.020	0.019	0.027	0.025
1.10	1.5282	0.900	0.901	0.900	0.900	0.909	Halowax						
1.20	1.52/1	0.818	0.825	0.828	0.818	0.833	0.589	1 6374	1 807	1 885	1 797		1 607
1.30	1.5201	0.751	0.759	0.703	0.750	0.709	60	1 6354	1 771	1.837	1 757		1 667
1.40	1.5255	0.097	0.702	0.707	0.093	0.714	70	1.6251	1 480	1 522	1 475		1 4 2 8
1.50	1.5240	0.003	0.034	0.039	0.044	0.007	.80	1.6183	1.278	1.302	1.252		1.250
1.00	1.5240	0.020	0.012	0.029	0.001	0.025	.90	1.6132	1.124	1.136	1.119		1.111
							1.00	1.6098	1.000	1.000	1.000		1.000
							1.10	1.6073	0.902	0.902	0.903		0.909
							1.20	1.6054	0.827	0.821	0.826		0.833
							1.30	1.6042	0.763	0.755	0.761		0.769
							1.40	1.6031	0.712	0.698	0.704		0.714
							1.50	1.6023	0.658	0.649	0.656		0.667
							1.60	1.6015	0.617	0.607	0.614		0.625
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FIG. 3a. Kerr effect dispersion curves for *o*-nitrotoluene, halowax, and carbon disulphide; *b*, Kerr effect dispersion curves for nitrobenzene and chlorobenzene.

is not dependent on the voltage. A possible exception to this is *o*-nitrotoluene, which is to be investigated further in this connection. Two voltages are plotted in Fig. 3b to indicate the general accuracy and agreement of the results. The results for the different voltages gave a general agreement with the law of proportionality of the Kerr effect to the square of the field but, for the same general reasons as already mentioned, the suitability and accuracy of the method in this connection was not particularly good.

The observed values in Table I are a composite of the results for all the different voltages for each material. The Havelock and Born computed values need no explanation since each involves only a single constant, which is fixed by the fact that all values are referred to that at  $1\mu$  as unity. In using the Serber formula the main ultraviolet absorption wave-length for each substance was used, varying from 2000 to 2600A. The second constants were determined by fitting the observed curves at two points between 0.8 and  $1.4\mu$ .

The values listed for the refractive index are those determined (temp.  $22^{\circ}C$ ) in the present work, save those for CS<sub>2</sub> which are from the L. and B. tables.

# DISCUSSION OF RESULTS: CONCLUSIONS

Perhaps the most striking thing about the results is the fact that the simple Havelock formula, with its rather meager theoretical background, fits the facts on the whole better than either of the others. However, the Born formula really applies only to nonpolar materials so, in all strictness, its use here should be limited to  $CS_2$ . Regarding the Serber formula, it may also be explained that there is no certainty that the ultraviolet frequencies as chosen are really

the centroid frequencies which should be used. To find these by a process of fitting the observed curve, however, would require the determination of one more constant.

It will be noted from the tables that the Havelock formula gives slightly *larger* values than the observed for shorter wave-lengths and slightly *smaller* for the longer wave-lengths, i.e., a somewhat steeper dispersion curve. This was also found to be the case by Szivessy and Dierkesmann<sup>2</sup> for three of the five liquids they tested in the visible and ultraviolet. Only one liquid, *viz.*, chlorobenzene, was common to these two investigations. For this liquid Havelock's law fits somewhat better in the ultraviolet than in the infrared.

As a matter of fact, beyond  $1\mu$  the simple law of the inverse wave-length fits the observed values about as well as any of the more complicated formulas, particularly for the polar liquids. A little study of this point shows that a formula of the type

$$K = C[(n^2+2)^2/n\lambda] \{1+a/\lambda^2+b/\lambda^4+\cdots\},$$

which by some simplification can be read out of Serber's work<sup>6</sup> would fit the results best of all.

The general conclusion to be drawn from our results is that for wave-lengths beyond  $1\mu$  the electro-optic dispersion is much the same for the five liquids investigated, is in reasonably good agreement with any of the three dispersion formulas tested and, indeed, departs only slightly from the simple inverse wave-length law. For the shorter wave-lengths agreement with theory is not as good, although in some cases the Havelock formula fits very well. For carbon disulphide the deviations of our results from Havelock's law is almost within the limits of experimental error for the whole spectral region investigated.