The Electric Spectrum of Liquid Water from Five to Twenty Centimeters*

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A magnetron generator was used in the production of continuous electromagnetic radiation with wave-lengths ranging from five to twenty centimeters. The refractive index and absorption index of liquid water were determined for nineteen wave-lengths distributed over this region, by using two completely different methods of investigation. The conventional free wave method was studied and an expression for the energy transmitted through an absorption cell derived. This equation was experimentally verified but it is concluded that one must be very careful to exclude undesirable diffraction effects if satisfactory results are to be secured. It is also shown that several methods of calculation frequently applied are incorrect. A wire wave method suggested by the experiments of Seeberger is presented and discussed. This method is analyzed in detail and a simplified procedure is given in which the determinations of absorption index and refractive index are separated. The two methods were compared at a wave-length of 10.20 cm and an agreement between results to within one percent was secured. The wire wave method has a great advantage because of the high reproducibility of its results while the free wave method is laborious to use and its results are difficult to duplicate. The absorption index was observed to increase steadily from 0.048 at 20.44 cm to 0.153 at 4.80 cm. The average refractive index was 8.80 with only one point differing from the mean by more than 0.6 percent. Although there was no clear evidence of dispersion, reasons are given for expecting a slight variation of refractive index. The expected variation however lies within the limits of experimental error. A very complete comparison is given between the data presented in this paper and the abundant but discordant results previously published.

INTRODUCTION

THE absorption and dispersion of electromagnetic waves by different substances, particularly in the liquid state, has been a subject of study since the classical experiments of Hertz in 1888 and a prodigious number of data has been accumulated. Unfortunately much of this work was done with highly damped sources of radiation and provides us with but little qualitative and practically no quantitative information. Subsequent work with continuous radiation has clarified many of the early experiments and now the long wave spectra of many polar liquids are fairly well established. However, great confusion is still encountered in the very short wave spectrum, which is usually the most interesting because here occurs the region of dispersion in which the refractive index decreases from a high value (square root of the static dielectric constant) to the much smaller value observed in the infrared.

Probably the most extensive investigation in the electric spectrum to be carried out before the advent of modern continuous wave generators was the study of liquid water. Observers with damped waves traced the spectrum of water for wave-lengths ranging from 10^6 down to 0.4 cm and found a very complex structure.[1, 2] For wave-lengths greater than 300 cm absorption was found to be very slight and no dispersion was observed, the refractive index being, within the limits of experimental error, equal to the square root of the static dielectric constant. However below 300 cm many bands of dispersion were apparently located, although different observers did not agree upon the location. At the very short wave-lengths an increase of absorption and a sharp decrease of refractive index was indicated but here also flagrant discrepancies exist between different investigators.

With the aid of continuous wave sources and better controlled experiments, these investigations have been repeated in part. For wave-lengths greater than 300 cm continuous wave measurements have confirmed the data of earlier observers. Thus for $\lambda = 391.8$–2547 cm Drake, Pierce and Dow[3] found the refractive index, n,

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[1] Romanoff, "Die Dispersion und Absorption elektrischer Wellen," Geiger u. Scheel, *Handbuch der Physik*, Vol. 15 (1927), p. 491.

[2] Ziegler, Physik. Zeits. **35**, 476 (1934).

[3] Drake, Pierce and Dow, Phys. Rev. **35**, 613 (1930).

at 22°C to be 8.925 while Wyman[4] by a wholly different method found $n_{22}=8.924$ for $\lambda=368.2$–8112 cm. These are in good agreement with $n_{22}=8.899$ for wave-lengths greater than 300 cm as given in the *International Critical Tables*[5] and based largely upon damped wave data. This agreement is not surprising because one would expect the influence of damping to be most marked in a region of dispersion. In the region below 300 cm the complex structure observed by the early experimenters has not been confirmed. Only part of this region has been systematically investigated but no bands of dispersion have ever been found by continuous wave experiments. The more recent results down to 28 cm are summarized in Table I. While there is need for more experiments below 200 cm it is highly probable that there is no dispersion in liquid water for λ greater than 28 cm. There are no continuous wave absorption measurements in this range but the absorption is known to be very slight.

In the region of still shorter wave-lengths the experimental difficulties increase and the disagreement between different observers is great. In addition to the many observations with damped waves, Seeberger[6] and Goldsmith[7] have published results for continuous waves. However these two observers do not agree so that we still have no satisfactory information about the electric spectrum of water below 28 cm. Acceptable results in this region have been greatly delayed by the absence of suitable sources of radiation and by experimental difficulties. The calculations of Malsch[8] have emphasized the necessity of using continuous wave sources. However it is now possible to produce continuous waves in this region by means of the magnetron generator, so the difficulty of securing a proper source is largely removed. While it is questionable whether the radiation from the magnetron is strictly monochromatic,[9] it is unlikely, under proper adjustment, that the band of frequencies would be wide enough to introduce any variation outside the limits of experimental error. The absence of very rapid changes of refractive index in the electric spectrum of polar liquids minimizes the possible effect of such a frequency band.

[4] Wyman, Phys. Rev. **35**, 623 (1930).
[5] *International Critical Tables*, Vol. 6 (1929), p. 78.
[6] Seeberger, Ann. d. Physik **16**, 77 (1933).
[7] Goldsmith, Phys. Rev. **51**, 245 (1937).
[8] Malsch, Ann. d. Physik **19**, 707 (1934).
[9] Cleeton, Physics **6**, 207 (1935).

TABLE I.[1] *Index of refraction of water as determined by various observers.*

Wave-lengths	Number of Different Wave-lengths	n_{22}	Observer
267.8–271.14 cm	14	8.89	Deubner[2]
266.1–268.8	2	8.93	Holborn[3]
220–300	141	8.90	Novosilzew[4]
91.24–93.92	3	8.89	Devoto[5]
68.76	1	8.92	Scheremetzinskja[6]
49.13–63.56	20	8.89	Girard and Abadie[7]
36.75–321.44	11	8.88	Heim[8]
28.4–56.7	34	8.85	v. Ardenne, Groos and Otterbein[9]

[1] In his summary of work in this field Ziegler erroneously reported a value of refractive index at 150 cm by Akerlof. Akerlof worked at 150 meters with a comparison method in which he took water as his standard liquid assuming its refractive index from Wyman's work.
[2] Deubner, Ann. d. Physik **84**, 429 (1927).
[3] Holborn, Zeits. f. Physik **6**, 328 (1921).
[4] Novosilzew, Ann. d. Physik **2**, 515 (1929).
[5] Devoto, Gazz. Chim. Italiana **60**, 208 (1930).
[6] Scheremetzinskja, Russ. fiziko-khim. obsh. Zhurnal **59**, 499 (1927.)
[7] Girard and Abadie, Comptes rendus **191**, 1300 (1930).
[8] Heim, Jahrb. d. drahtl. Telegr. **30**, 176 (1927).
[9] v. Ardenne, Groos and Otterbein, Physik. Zeits. **37**, 533 (1936).

The method of investigation most commonly used in the ultra-short wave region is the free wave method in which a beam of radiation, directed by mirrors, is passed through a cell and the reflected or transmitted beam is studied. Since the wave-length in many such experiments is comparable to the dimensions of the apparatus, one must expect serious difficulty due to diffraction. A second general method of directing these waves is the wire wave method in which the waves are guided by a Lecher system so that the energy is largely concentrated between the wires and diffraction is minimized. While there are many variations of the method their use has been confined to the longer wave-lengths.

It is the purpose of the present paper to present a wire wave method which can be used below 10 cm and to report a study of both methods in the ultra-short wave region where they were applied to the investigation of liquid water in the wave-length range 5–20 cm.

Free Wave or Optical Method

1. Production of radiation

Conventional split anode magnetron tubes were used in the generator built by Cleeton and Williams.[10] To concentrate the radiation into a

[10] Cleeton and Williams, Phys. Rev. **45**, 234 (1934).

beam, a parabolic brass mirror (diameter 90 cm) was set up in a vertical position with the magnetron tube at its principal focus. The parallel beam of radiation was directed to an echelette grating, the angle of incidence being about $6\frac{1}{2}°$. The paper of Cleeton and Williams gives the details of construction of this grating by means of which wave-lengths up to 12 cm can be measured directly. From the grating the beam of radiation was reflected to a second parabolic mirror at the focus of which was located the detector.

2. Detection

A detector composed of an iron pyrite crystal and a tungsten wire was found to be very satisfactory and was used for all final observations. A thermal detector of the Klemencic type with an Advance-Chromel C cross and a tungsten heater wire was used in some of the preliminary work but was abandoned because of ambiguity in the experimental determination of the law of response.

The absorption index of a material is defined as

$$\kappa = (\lambda/4\pi n x) \log (I_0/I_x)$$

where the intensity of radiation of wave-length λ decreases from I_0 to I_x when the thickness of the material in the beam is increased by an amount x. The refractive index of the material is designated by n. The rectified current through the detector is a measure of the energy incident upon it but the precise relation between rectified current and energy must be known before I_0/I_x, and hence κ, can be calculated. Experiments at lower frequencies[6, 11, 12] indicate that the pyrite crystal detector responds linearly to energy but it seemed desirable to verify this at higher frequency inasmuch as the exponent in the law of response enters directly into the calculated absorption index as a multiplicative factor. Thus if the rectified current varies with the β power of intensity and one has assumed linearity, the calculated value of absorption index will be $\beta\kappa$ instead of the true value κ. The law of response can be determined experimentally by controlling the energy incident upon the detector through the use of Hertzian grids. One of these grids consists of a set of suitably spaced parallel wires. That such a grid acts as an analyzer for electromagnetic waves is shown by the experimental work of Hertz[13] and the analysis of Gans[14] and Ignatowsky.[15] When a beam of radiation strikes such a grid it is resolved into two component fields; the one having its electric vector parallel to the wires is largely reflected or absorbed, and the other having its electric vector perpendicular to the wires is largely transmitted. Blake and Fountain [16] found the wire spacing must be of the order of a fortieth of a wave-length for no transmission to occur when the wires are parallel to the electric vector.

The grids used in this experiment were made by fastening copper wires (diameter 0.25 mm) onto wooden frames about 110 cm square. Uniform spacing was secured by winding the wires over threaded rods, two rods being permanently attached to each frame. Since this work was done with approximately 10 cm radiation a wire spacing of 2.5 mm was used. Each frame was mounted so it could be rotated about an axis perpendicular to the plane of the frame. One frame was provided with a graduated circle for reading inclinations. One of these grids was placed about one meter from the detector mirror so as to receive the beam of radiation at normal incidence. When a second grid was used it was placed directly in front of, or behind, the first one and parallel to it. A cylindrical shield of sheet metal one meter long and 90 cm in diameter was attached to the detector mirror and reached to the nearer grid so there was no possibility of diffracted waves passing around the grids and reaching the detector.

When only one grid was used it was found that the radiation from the magnetron generator is plane polarized with the electric vector in the plane of the Lecher wires and perpendicular to them. When the grid wires were set up perpendicular to this electric vector the presence of the grid did not appreciably reduce the intensity; but when the grid wires were parallel to the

[11] Bergmann, Ann. d. Physik **67**, 13 (1922).
[12] Zakrzewski, Bull. Int. Acad. Polon. Sciences Lettres Serie A, 489 (1927).
[13] Hertz, *Electric Waves* (MacMillan, 1893), p. 177.
[14] Gans, Ann. d. Physik **61**, 447 (1920).
[15] Ignatowsky, Ann. d. Physik **44**, 369 (1914).
[16] Blake and Fountain, Phys. Rev. **23**, 276 (1906).

electric vector no measurable energy was transmitted.

When a single grid is used the electric and magnetic field amplitudes transmitted by the grid will vary with cos θ where θ is the angle of inclination of the grid wires measured from the position of optimum response. The energy reaching the detector will vary with $\cos^2\theta$ and the fields will rotate with the grid, the electric field vector remaining perpendicular to the grid wires. By plotting rectified current, as measured by the galvanometer deflection, as a function of the inclination of the grid wires one can determine β, where it is assumed that the rectified current varies with the β power of the incident energy. With one grid this function is $\cos^{2\beta}\theta$ and the calculated value of β is 1.01. Since the fields at the detector rotate, the question of a preferred direction at the detector and the possibility of a second resolution of fields arises. When the detector itself was rotated there was no evidence of a preferred direction, but this test is rather crude since there is considerable danger of shifting the detector slightly away from the focus of the mirror. This question is eliminated by the use of two grids. The one next to the detector is left fixed while the one in front of it is rotated. There is now a resolution of field amplitudes at each grid so the energy transmitted by the grids will vary with $\cos^4\theta$ but the fields at the detector will be constant in direction. Fig. 1 shows a plot of galvanometer deflection as a function of inclination of the rotating grid. For two grids this function is $\cos^{4\beta}\theta$ where

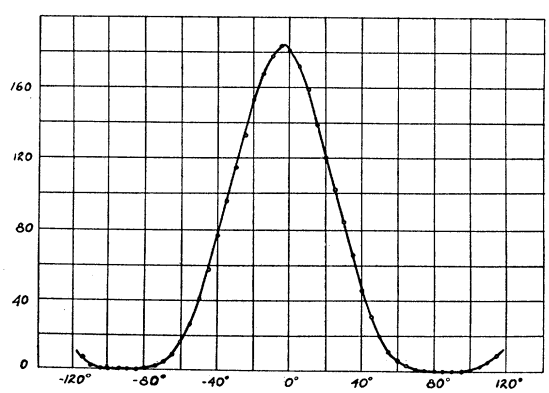

FIG. 1. Calibration curve for an iron pyrite crystal detector. The ordinate is galvanometer deflection in cm; the abscissa the inclination of grid wires measured from an arbitrary position.

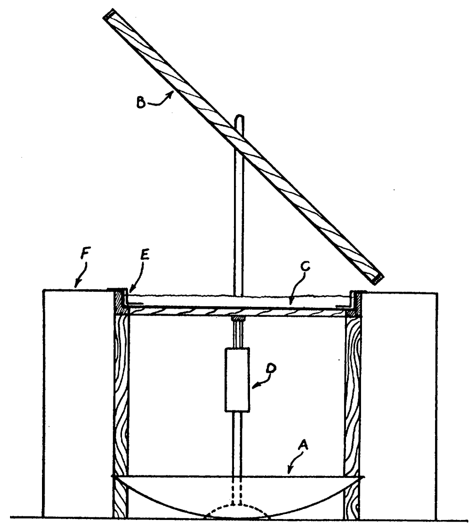

FIG. 2. Diagram of a section through the free wave absorption cell and receiving unit.

β is calculated to be 0.99. If the fields which are not transmitted by the fixed grid should be largely reflected instead of absorbed, there is the possibility of additional energy reaching the detector after multiple reflection between the grids. No evidence of such additional energy was found. From these calibrations it appears that to within about one percent, at most, the crystal detector responds linearly to energy.

3. Absorption cell

A vertical section through the absorption cell is shown in Fig. 2. A horizontal beam of radiation was reflected from the grating to the inclined mirror B. This mirror (90×120 cm) was built of 5 mm sheet aluminum attached to a wooden frame. After passing through the cell C, the radiation was focused by the parabolic mirror A upon the detector D. The detector, which was shielded on five sides by a metal box, was connected through a shielding cable to a high sensitivity Leeds and Northrup galvanometer.

The cell ($76.2\times 91.4\times 4.5$ cm) was constructed of plate glass supported by a wooden frame, the glass joints being sealed with a special aquarium cement and paraffin. A guard strip E of sheet tin, built to reach completely around the cell, had the effect of placing the cell aperture within the liquid where the wave-length was much reduced. It was hoped that this might minimize diffraction at the aperture. The guard strip reached out over the heavy sheet metal shield F which completely enclosed the receiving unit except for the cell aperture. When the shield and guard strips were in place it was impossible for any radiation to reach the detector without passing through the cell. A large sheet of metal shielded the cell from any direct rays from the tube. The cell supports were set back from the aperture so that no obstruction was presented to the beam except a narrow soft wood bar which supported the detector.

4. Preliminary experiments

The obvious method of determining the absorption index of a liquid is to vary the thickness of the liquid layer in the beam and observe the transmission. An annoyance immediately arises, however, in the case of liquids of high refractive index because of the high reflectivity of liquid surfaces. The direct beam through the cell is augmented, unless the absorption is very great, by other beams arising from multiple reflection between the liquid surfaces; and the net result is such a curve as is shown in Fig. 3.

It is frequently assumed that one can determine the absorption index from such a curve by drawing a sort of average curve through the middle of the interference maxima and minima. This amounts to assuming that the energy transmitted by the cell can be written as the sum of a simple exponential and one or more periodic terms. On this assumption one calculates values of κ which cannot be verified by other methods. Analysis of the free wave method shows this assumption to be too simple. Moreover there seems to be no satisfactory way of eliminating these troublesome secondary beams. Since they are absorbed more rapidly than the direct beam one can begin observations with enough liquid in the cell to quite completely absorb all but the direct beam. To do so however is to greatly reduce the energy available for observations and to probably endanger the cell bottom since about 20 liters of water is required for 10 cm radiation.

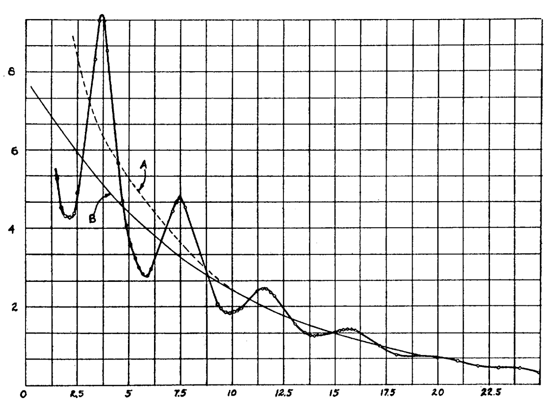

FIG. 3. Interference curve with the free wave method for water at 24°C and for $\lambda = 10.20$ cm. The ordinate is galvanometer deflection in meters (ordinates above three result from reduction to no shunt values); the abscissa is liters of water in the cell (6.95 liters produce a layer of liquid one cm thick).

There is also the possibility of isolating the direct beam by refraction. If one edge of the cell is elevated a bit the liquid layer is converted into a prism surmounted by a uniformly thick layer of liquid which still receives the radiation at normal incidence. Since the direct and multiply reflected beams have different angles of incidence at the lower liquid surface they are separated by refraction. An angular separation of 20° between the direct and twice reflected beam is easily obtained. By tilting the detector mirror these two distinct beams can be picked up. Moreover when the mirror is set to receive the direct beam there is no possibility of the twice reflected beam entering the detector for one can show by rotating the mirror that a beam 10° off the axis has practically no effect. However, when the mirror is set on the direct beam and the thickness of the liquid layer is varied interference peaks are still found. Their spacing is related to twice the layer thickness, so they are evidently due to double reflection within the liquid. The origin of this interfering beam is apparently oblique radiation produced by diffraction at the inclined mirror and the cell aperture. Evidently one must be very careful to avoid undesirable diffraction effects when doing free wave experiments at these wave-lengths.

5. Analysis of the free wave method

Consider a horizontal layer of liquid of uniform but variable thickness x bounded above by air and below by glass. A plane wave strikes the upper surface at normal incidence. Let the electric component of this wave be $E_0 e^{i\omega t}$ where E_0 is the amplitude and ω is the angular frequency. The transmission factor at the air-liquid surface may be written $Te^{-i\tau}$ where T represents the ratio of transmitted amplitude to incident amplitude and τ gives the retardation in phase upon transmission. Similarly $T'e^{-i\tau'}$ will be the transmission factor at the liquid-glass surface. $Re^{-i\rho}$ and $R'e^{-i\rho'}$ are the internal reflection factors at the upper and lower surfaces, respectively.

The amplitude of the electric vector after direct transmission through the liquid layer will evidently be:

$$E_1=E_0TT'\exp\left[-\alpha x+i(\omega t-\tau-\tau'-2\pi x/\lambda')\right]$$

where λ' is the wave-length in the liquid and α is an abbreviation for $2\pi n\kappa/\lambda$. A wave which is twice reflected internally before entering the glass will have an amplitude: $E_2=E_0TT'RR'\times\exp\left[-3\alpha x+i(\omega t-\tau-\tau'-\rho-\rho'-6\pi x/\lambda')\right]$. In the case of four internal reflections the electric amplitude becomes: $E_3=E_0TT'R^2R'^2\exp\left[-5\alpha x+i(\omega t-\tau-\tau'-2\rho-2\rho'-10\pi x/\lambda')\right]$. No more than four internal reflections need be considered for a liquid which absorbs as strongly as does water, although one can continue and treat an infinite number of internal reflections. Neglecting all internal reflections beyond the fourth we can represent by $E'=E_1+E_2+E_3$ the net amplitude transmitted through the liquid layer into the glass.

The glass-air surface reflects but little because of the low refractive index of glass while the glass-liquid surface will reflect strongly because of the high refractive index of the liquid. Hence no appreciable part of the wave which once enters the glass will ever get back into the liquid and then reenter the glass. In passing from within the glass to the detector, changes of phase and amplitude will occur; but all terms of E will be equally affected and there will be no dependence upon x. If A represents the fraction of amplitude transmitted and θ the retardation in phase in passing from within the glass to the detector, the electric field at the detector may be written $E=E'Ae^{-i\theta}$. The average energy reaching the detector may be written aEE^* where a is a constant and E^* is the complex conjugate of E. Computing we have:

$$\begin{aligned}\text{Energy}=B(&e^{-2\alpha x}+2RR'e^{-4\alpha x}\cos\phi\\&+R^2R'^2e^{-6\alpha x}+2R^2R'^2e^{-6\alpha x}\cos 2\phi\\&+2R^3R'^3e^{-8\alpha x}\cos\phi+R^4R'^4e^{-10\alpha x}),\qquad(1)\end{aligned}$$

where $B=aA^2E_0^2T^2T'^2$ is a constant and $\phi=2\pi(2x/\lambda')+\rho+\rho'$. Additional terms of higher order in $RR'e^{-2\alpha x}$ would occur had we not neglected internal reflections beyond the fourth. If $RR'e^{-2\alpha x}$ is very small this equation indicates the usual exponential decrease of transmission with increasing thickness. When this condition is not met it may be that Eq. (1) can be approximated by its first two terms. This will be the case for liquids with a low refractive index, high absorption index or for any liquid after a certain thickness is reached. Under these circumstances, and only then, is the calculation of absorption index from an average curve drawn through the experimental curve permissible. For water at 10 cm a layer of water about 15 mm thick is necessary to meet these requirements. For thinner layers additional terms must be taken into account. At a wave-length of 10 cm, RR' is approximately 0.5 and $e^{-2\alpha x}$ varies in value from about 0.8 to 0.3 over the first half of the experimental curve, so we can safely omit the last two terms of Eq. (1) for water at 10 cm or less.

We have then finally:

$$\begin{aligned}\text{Energy}=B\{&e^{-2\alpha x}+2RR'e^{-4\alpha x}\\&\times\cos\left[2\pi(2x/\lambda')+\rho+\rho'\right]+R^2R'^2e^{-6\alpha x}\\&+2R^2R'^2e^{-6\alpha x}\cos 2\left[2\pi(2x/\lambda')+\rho+\rho'\right]\}\qquad(2)\end{aligned}$$

where $\alpha=2\pi n\kappa/\lambda$.

It is possible to determine κ and also n from an experimental curve without completely isolating any of these four terms. We note that the last term has a maximum value whenever the second term has either a maximum or minimum value so that its effect is to shift all of the maxima and minima of Eq. (2) up by an amount which depends upon x. If, by trial and error, we draw a curve through the interference maxima and minima in such a fashion that the successive maximum deviations of this curve from the experimental curve decrease exponentially we effectively isolate the extremes of the second term. Such a curve, illustrated by curve A, Fig. 3, would constitute an average curve in the sense in which that term is used in this work. The maximum deviations of the experimental curve from the average curve are the extreme values of the second term in Eq. (2). Since the spacing of these maximum deviations is $\lambda'/4$ we can calculate the refractive index from their spacing. Also the ratio of successive extreme values is $e^{-2\pi\kappa}$ from which κ can be calculated. At the points where this second energy term is an extreme, curve A represents the sum of the other three energy terms. Having calculated n and κ we can also plot the first term of Eq. (2) which is represented by curve B in Fig. 3. The ordinate difference $A-B$ is due to the second and third terms of Eq. (2) and therefore should decrease with $e^{-6\alpha}$.

6. Discussion

The conclusions drawn from this analysis are experimentally verified. Fig. 3 was obtained for a wave-length of 10.20 cm and at a temperature 24.0°C. From the analysis of the second term in Eq. (2) we have $n=8.85$ and $\kappa=0.078$. If we calculate κ from the ordinate difference $A-B$ we find 0.075. These results may be compared with $n=8.80$ and $\kappa=0.077$ obtained by wire wave methods. It is obvious that if we assume the average curve A to be a simple exponential and calculate κ from it we will get a value which is too large. This fact was observed many times in the course of this work. Unfortunately it is not possible to check on this point from other work in this region because too many other uncertainties enter. Thus if diffraction around the cell is not prevented, this will operate to make the absorption index calculated from the average curve too small, so that a partial compensation may occur.

We may note that the refractive index must be determined from the periodic term and not from the total curve. The spacing of the maxima and minima of the periodic term gives the true wave-length in the liquid because the spacing of the extremals of the function $e^{-\alpha x}\cos\beta x$ is the same as the spacing for the cosine function alone. Multiplication by the exponential shifts the maxima and minima but by a constant amount. When the function $e^{-\alpha x}\cos\beta x$ is added to another exponential, however, the maxima are shifted toward smaller values of x and the minima are shifted toward larger values of x by an amount which depends upon x. If one determines the wave-length in the liquid from the total curve by measuring from the first minimum to the first maximum he obtains values which are too small. The calculated refractive index then becomes too large. This accounts for the unusually large values of refractive index found by Zakrzewski[12] and by Miesowicz.[17] It also explains the curious observation of Miesowicz that at about 7 cm the refractive index of water increased with decreasing wave-length, inasmuch as the error pointed out will increase with increasing absorption, i.e., with decreasing wave-length.

Wire Wave Method

1. Apparatus

The design of the horizontal Lecher system and the absorption cell (Fig. 4) was suggested by the work of Seeberger.[6] The cell C ($18.5\times18.5\times15.0$ cm) was built of soft wood 13 mm thick and lined with rubberized cloth. The Lecher wires L were copper (dia. 1.9 mm) and were spaced one centimeter apart. They were sealed into the front cell wall but the length outside the cell could be varied from 73 to 83 cm by means of the trombone arrangement T which consisted of a 15 cm section of brass tubing (3.3 mm outside dia.) into which the movable end section of the Lecher system fitted. This end section was inductively coupled to the magnetron tube. The Lecher system was supported at the trombone by a pin of soft wood. The open end of the Lecher system came within the cell. The reflecting bridge B ($8\times13\times0.3$ cm) was made of brass. The wires passed through the bridge by means of two small holes which fitted the wires closely. By means of the micrometer screw M, the displacement of the bridge could be controlled to within about 0.005 mm.

The detector D was held in a wooden mounting which permitted adjustment in any direction. The detector was a fixed iron pyrite-tungsten crystal detector and was connected in series with a microammeter. The pick-up wires of the detector were spaced at about 8 mm and their tips were brought up to about one or two millimeters from the Lecher wires. At this distance there was no evidence that their presence influenced the oscillation of the wire system. The

[17] Miesowicz, Bull. Int. Acad. Polon. Sciences Lettres Serie A, 95 (1934).

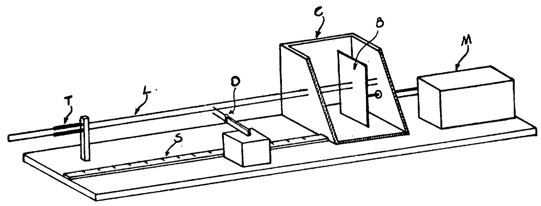

FIG. 4. Diagram of the wire wave apparatus.

meter stick S served as a guide for the detector mounting and provided an easy means of measuring the distance between electric field loops or nodes and hence the wave-length. The measured wave-length corresponds to the wave-length of a free wave, however, only if the waves propagate along the wires with the velocity of light. It is well known[18] that on account of the resistance of the wires the velocity of propagation along a wire system is less than the velocity of light by an amount which depends upon the frequency, resistance, and geometry of the system. The dependence upon frequency is inverse and at these frequencies the correction is negligibly small for copper wires. An alternate method of measuring wave-lengths less than 12 cm was to withdraw the wire wave apparatus from the oscillator and set up a parabolic mirror. The free wave apparatus was then complete and the grating could be used.

To adjust the system one first places the reflecting bridge well back in the liquid so that the portion of a wave transmitted into the cell will be very largely absorbed by the liquid before getting out into the external circuit again. Then by adjusting the Lecher system to the most favorable length one can get a system of standing waves between the liquid surface and the tube end of the wire system. The detector is now adjusted to a position of maximum response, i.e., to an electric loop. By varying the coupling with the tube the energy of oscillation of the system is controlled. As the reflecting bridge is moved toward the front cell wall increasing amounts of energy will be transmitted back into the external circuit. The combination of these waves and the standing wave system of the external circuit will yield an interference pattern from which the optical constants of the liquid in the cell can be determined.

[18] Hund, Scientific Papers of the National Bureau of Standards, No. 491 (1924).

2. Analysis of the wire wave interference curve

For a similar wire wave system Seeberger has given an equation for the energy reaching the detector which involves only one term dependent upon the thickness of the liquid layer. But, because of the complexity of the free wave interference pattern, one suspects that Seeberger's equation is no more than a first approximation and that, therefore, a more complete analysis is desirable.

Let l be the distance of the detector from the cell wall and L its distance from the tube end of the Lecher system. Denote by x the distance of the reflecting plate from the front cell wall. The length of the external Lecher system $L+l$, the position of the detector as given by l, and the thickness x of the liquid layer are all variable. Consider first the case of x so large that a wave entering the cell will be almost completely absorbed by the liquid layer and no appreciable part of it will reenter the external Lecher system. For water at a wave-length of ten centimeters, $x=10$ cm is sufficient to meet this requirement. A plane wave set up by the oscillator and propagating toward the cell from the tube end of the external circuit may have its electric component at the detector represented by $E_0e^{i\omega t}$. The energy of the wave is largely concentrated in the space between the two wires and in this small region the assumption of a plane wave is a justified approximation.

After one complete passage around the external circuit the electric amplitude of this wave may be written: $E_0R_1R_2 \exp\{-2\beta(L+l)+i[\omega t-\rho_1-\rho_2-4\pi(L+l)/\lambda]\}$ where β is the attenuation constant for the external wire system, λ is the wave-length in air, and $R_1e^{-i\rho_1}$ and $R_2e^{-i\rho_2}$ are the reflection factors at the tube end of the circuit and at the cell wall respectively. The R gives the fraction of amplitude reflected and the ρ gives the retardation in phase upon reflection. The preliminary adjustment of the length $L+l$ of the external Lecher system for a maximum response of the detector is such that this twice reflected wave will be in phase with the wave being set up by the oscillator, i.e., $2\pi[2(L+l)/\lambda]+\rho_1+\rho_2$ is an integral multiple of

2π. Under this adjustment all waves moving toward the cell after any number of reflections will be in phase and can be represented by a single wave. Similarly the sum of all waves moving away from the cell can be represented by a single wave. The preliminary adjustment of the detector location for a maximum response places it at one of the positions where the electric components of these two net waves are in phase, i.e., at an electric antinode of the standing wave system. The total electric amplitude at the detector may then be written as $\mathcal{E}=Ee^{i\omega t}=(E_1+E_2)e^{i\omega t}$ where E_1 is connected with the wave moving toward the cell and E_2 with the wave moving away from the cell. Since E_1 is always greater than E_2 there will be no true electric nodes but antinodes will appear. The difference E_1-E_2 is very small compared with E_1+E_2, however, for liquids of high refractive index. This is verified for water by shifting the detector along the Lecher wires. The average energy at the detector is given by $a\mathcal{E}\mathcal{E}^*$ where a is a constant depending upon units and $\mathcal{E}^*$ is the complex conjugate of $\mathcal{E}$. This becomes aE^2 which is constant as long as the output of the oscillator remains unchanged.

As a next step we consider the layer thickness to be reduced to such an extent that a wave entering the cell may be only partially absorbed and will reenter the external circuit with considerable amplitude. We will however require the thickness to be great enough to quite completely absorb a wave which passes through the liquid layer a second time. In terms of the previous notation the wave represented by $E_1e^{i\omega t}$ at the detector will move to the cell and be partially transmitted. After passing through the liquid layer and again reaching the detector the electric component may be written:

$$E_1T_1T_2R_3 \exp\left[-2\beta l-2\alpha x+i(\omega t-\tau_1-\tau_2-\rho_3-4\pi l/\lambda-4\pi x/\lambda')\right],$$

where λ' is the wave-length in the liquid, $R_3e^{-i\rho_3}$ is the reflection factor at the reflecting bridge within the cell, $T_1e^{-i\tau_1}$ and $T_2e^{-i\tau_2}$ are the transmission factors upon entering the cell and upon leaving respectively and α is the attenuation constant for the wire system within the cell. The attenuation within the cell due to absorption by the liquid is so much greater than losses due to radiation and ohmic heat that we may neglect these latter two and set $\alpha=2\pi n\kappa/\lambda$. Because of the length adjustment of the external circuit all waves which have gone through the liquid layer once will be in phase with all other waves going in the same direction, i.e., a second system of quasi-standing waves will be set up. Moreover this second system of standing waves will have its antinodes coincident with the antinodes of the system composed of waves which have not entered the cell at all. This is also a consequence of the length adjustment of the external circuit. Of course the two standing wave systems will be in phase with each other only for definite values of layer thickness. Since all the waves of this second system will have the same phase at the detector as did the wave written out explicitly above, the total electric amplitude at the detector due to the two systems of waves may be written: $\mathcal{E}_1=E\exp[i\omega t]+B\exp[-2\alpha x+i(\omega t-\tau_1-\tau_2-\rho_3-4\pi l/\lambda-4\pi x/\lambda')]$ where B is a constant. Calculating the average energy we find:

$$\text{Energy}=aE^2+aB^2e^{-4\alpha x}+2aEBe^{-2\alpha x}\cos\left[(4\pi x/\lambda'+\delta)\right], \quad (3)$$

where $\delta=\tau_1+\tau_2+\rho_3+4\pi l/\lambda$. The second term will be relatively small if α is large, if x is large, or if B is very small. We will then have an oscillating term added to a constant. If we plot energy as a function of x we have the third term oscillating about a horizontal line. If the second term enters, as it may at small x, we have an oscillation about an average curve which rises exponentially as x decreases. The presence of this second term is obvious in all experimental curves for water (see Fig. 5). This exponential rise was also observed by Seeberger but he did not explain its origin.

Because of the relatively high absorption this energy equation must be essentially correct and any additional terms due to additional passages through the cell must be very small terms except at a small layer thickness. However, to see something of the influence of these correction terms, we shall consider the effect of those waves which go through the cell a second time. The second passage of a wave through the cell may occur as a result of an internal reflection at the front cell wall or by a reentry into the cell after having passed through once. The amplitude of these waves will be small and not particularly interesting but their phases will be very significant. For simplicity we shall not write out these amplitudes in terms of the amplitudes of the waves treated above but we shall write out the phase retardations of these waves, referring the phase when the wave first reaches the detector after its double passage, to the phase of the original wave $E_0e^{i\omega t}$. The angular retardation of a wave which reenters the cell and passes through the liquid layer twice will be $2\pi(4l+2L)/\lambda+8\pi x/\lambda'+2\tau_1+2\tau_2+2\rho_3+\rho_1$, while the retardation for a wave which is reflected internally at the front cell wall will be $4\pi l/\lambda+8\pi x/\lambda'+\tau_1+\tau_2+2\rho_3+\rho_4$ where ρ_4 is the phase retardation upon internal reflection at the front cell wall. Because of the condition on L and l any complete transits around the outside circuit do not introduce any phase displacements and so are omitted here. Also because of this condition $2\pi(2L+2l)/\lambda+\rho_1$ may be replaced by $-\rho_2$. These two waves will be in phase provided $\tau_1+\tau_2-\rho_2$ and ρ_4 are equal. These angles can be calculated from the optical constants of the liquid and the electromagnetic theory.

It follows from the boundary conditions that upon entering a medium, characterized by n and κ, from free space the reflected electric field is retarded in phase by $\pi+\gamma$ and the transmitted field is advanced in phase by α. While upon entering free space from the denser medium the reflected electric field is retarded in phase by γ and the transmitted field is retarded by β where

$$\tan\alpha=\frac{n\kappa}{n+1},\quad \tan\beta=\frac{\kappa}{n\kappa^2+n+1}$$

and
$$\tan\gamma=\frac{2n\kappa}{n^2+n^2\kappa^2-1}.$$

For water at 10 cm $\gamma=1.5°$, $\alpha=4°$, and $\beta=0.5°$ so that the two waves above lack only about 7° of being completely out of phase. This is considering a liquid-free space boundary but this is a satisfactory approximation because of the very low reflecting and absorbing power of the cell wall. For most polar liquids these two waves will be essentially out of phase and will eliminate each other if the two amplitudes are approximately equal. In the case of water the amplitude of the wave reflected internally is much the greater and a contribution from these waves is to be expected. Since $4\pi l/\lambda+\rho_1$ is an integral multiple of 2π as a result of the adjustment of the detector, we may write the resultant electric field as $\pm C\exp[-4\alpha x+i(\omega t-2\delta-8\pi x/\lambda')]$ where C is a constant and δ has the meaning given above. The alternate sign occurs because either of the component waves may predominate, the negative sign indicating predominance of the wave reflected internally. Combining this with the previous expression for total electric amplitude at the detector we have:

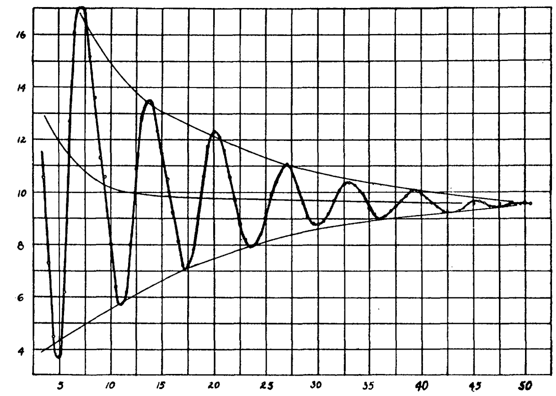

FIG. 5. Interference curve with the wire wave method for water at 22°C and for $\lambda=10.87$ cm. The ordinate is rectified current in microamperes; the abscissa bridge displacement in mm.

$$\begin{aligned}\mathcal{E}_2=&E\exp[i\omega t]\\&+B\exp[-2\alpha x+i(\omega t-\delta-4\pi x/\lambda')]\\&\pm C\exp[-4\alpha x+i(\omega t-2\delta-8\pi x/\lambda')]\end{aligned}$$

and

$$\begin{aligned}\text{Energy}=a[&E^2+B^2e^{-4\alpha x}\\&+2EBe^{-2\alpha x}\cos(4\pi x/\lambda'+\delta)+C^2e^{-8\alpha x}\\&\pm 2BCe^{-6\alpha x}\cos(4\pi x/\lambda'+\delta)\\&\pm 2ECe^{-4\alpha x}\cos 2(4\pi x/\lambda'+\delta)]\end{aligned}\quad(4)$$

where $\alpha=2\pi n\kappa/\lambda$.

The last three terms are new but because of the smallness of C and the rapid absorption, the fourth and fifth could have an effect only with very thin liquid layers. The last term may be appreciable because of the large value of E and less rapid absorption. But due to the double angle the periodic term will be a maximum when the main periodic term (third term) is either a maximum or a minimum. Hence its effect will be to shift the extremes of the main periodic term up or down depending upon the sign of C. In either case it is still easy to isolate the main periodic term by simply drawing an average curve about which the periodic term oscillates symmetrically. From this periodic term, $2aEBe^{-4\pi n\kappa x/\lambda}\cos(4\pi x/\lambda'+\delta)$, the optical constants of the liquid can be determined.

3. Experimental procedure

In practice it is more convenient to separate the determination of n and κ because it is very tedious to make the hundred or more observations necessary to plot a curve such as Fig. 5 and the time required is so great that there is some chance for change in the output of the oscillator. This separation can be satisfactorily made only in that region where the average curve is essentially horizontal so that the spacing of the extremals of the periodic term become the same as for the total function represented by Eq. (4). The usual experimental curve shows a considerable region where this method is applicable. The spacing of the maxima and minima is very easily and quickly determined by means of the micrometer screw. By taking ten to twenty observations consistent averages for λ' can be obtained.

To determine κ we note that the displacement from one extremal to the next one is $\lambda'/4$ and hence the ratio of amplitudes of the periodic term at adjacent extremals is $e^{-\pi\kappa}$. Therefore we do not need the value of n nor the value of x in centimeters but we simply record the series of maximum and minimum microammeter readings. By plotting these with an equal but arbitrary spacing on the abscissa axis we can draw two curves, one connecting the maxima and the other the minima of Eq. (4). These two curves will mark the limit of the main periodic term and their ordinate difference will decrease with $e^{-\pi\kappa}$ from one extremal to the next. From a series of five to ten such runs one easily obtains fifty or more values of κ from which consistent averages can be obtained. Fig. 5 shows two of these auxiliary curves as calculated from the data shown in the figure.

4. Comparison of methods

Because of the wide discrepancies existing between the published results of different observers in this region of the spectrum, a satisfactory investigation must cover a region of the spectrum systematically and be checked as thoroughly as is practical. It is particularly desirable to secure a check between essentially different methods of measurement. On this account considerable work was done at about 10 cm with both the free wave and the wire wave method in an attempt to establish the validity of these methods. The results given under the discussion of the free wave method show the data obtained by these two methods to agree to within about one percent, which is within the limits of experimental error for the free wave method. This certainly indicates the possibility of securing trustworthy data at these frequencies.

The wire wave method has one great advantage over the free wave method in regard to the reproducibility of data. The results of the wire wave method can be reproduced very closely under the most favorable conditions. For example, at 11.12 cm three measurements distributed over an interval of three hours gave $\lambda'=1.259$, 1.260 and 1.257 cm, respectively. When the experiment is repeated after several days the agreement is naturally not as good, but careful work secures agreement between individual observations to within about one percent. On the other hand it is very difficult to obtain consistent free wave data. This is probably partly due to the necessity of taking a complete curve and then isolating the periodic term by trial and error methods, but it is also difficult to secure good experimental curves. The time required for taking a complete experimental curve, the clumsy method of varying the layer thickness (pouring liquid into the cell), and diffraction effects probably all contribute to this difficulty.

Since the essential experimental points for the wire wave method are $\lambda'/4$ cm apart and at least six points are required for a calculation of absorption index, this method will finally be limited by the absorption. In the free wave method the interference effect will disappear at high absorption so that the refractive index cannot be obtained but it will still be possible to investigate the absorption. Thus at 4.80 cm the refractive index of water could not be determined but the absorption could still be measured by the free wave method.

Experimental Results and Discussion

A summary of the data obtained for water is presented in Table II and the wave-length dependence of κ is shown in Fig. 6. The wire wave method was successfully applied to the determination of both λ' and κ from 20.44 to 6.48 cm. Beyond the range of this method the free wave apparatus was used but not enough of the interference curve could be obtained to secure a measure of λ'. Consequently the interference was eliminated by the use of thick liquid layers and $n\kappa$ was calculated from the exponential graph of transmitted energy. For comparison with the remainder of the absorption curve it was assumed that $n=8.80$, and κ was calculated. For some of the wave-lengths only the one item of data was obtained because of experimental difficulties which cut short the work. Difficulties are occasionally experienced in securing satisfactory adjustments and the danger of burning out tube filaments is always present.

Although that part of the absorption index which is due to conductivity of the water can be calculated from Maxwell theory and is known to be completely insignificant in comparison with the dipole absorption in this region, the conductivity of the distilled water used was measured. It was of the order of 10^{-6} ohm^{-1} cm^{-1} when the water came from the still but increased about tenfold during exposure to the air and the cell during the course of an experiment. This increase had no appreciable effect but fresh water was regularly used as a safeguard against the influence of impurities.

TABLE II. *Summary of data on index of refraction and index of absorption.*

λ (cm)	λ' (cm)	κ	n
4.80 (free wave)	—	0.153*	—
5.34 " "	—	.141*	—
6.48	0.732	.123	8.85
8.05	0.917	.097	8.78
8.16 (free wave)	—	.097*	—
8.80	1.004	.093	8.77
9.55	1.095	.086	8.72
9.85	1.119	—	8.80
10.10	—	.082	—
10.20	1.160	—	8.79
10.87	—	.075	—
11.12	1.259	.074	8.83
11.80	1.333	.071	8.85
13.41	—	.068	—
14.48	1.642	.062	8.82
15.29	1.746	.062	8.76
16.83	1.902	—	8.85
18.41	—	.052	—
20.44	2.327	.048	8.78

* Calculated from the measured value of $n\kappa$, assuming $n=8.80$.

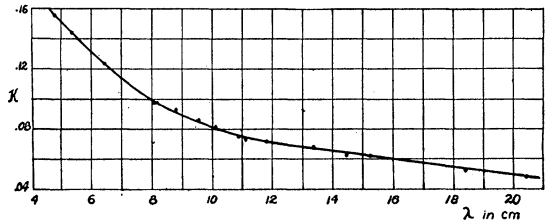

FIG. 6. Absorption index of water at 22°C as a function of wave-length. Legend: open circle, wire wave method; closed circle, free wave method.

Since the temperature coefficients of the indices of refraction and absorption are unknown at these wave-lengths it is necessary to work at a single temperature, 22.0°C having been chosen as the most convenient one.

The monotonic increase of absorption with decreasing wave-length shown by Fig. 6 is to be expected on the basis of the Debye theory if one is here approaching the dispersion region in which the refractive index decreases sharply. While no systematic investigation of absorption has been previously attmpted, the data that do exist are scattered about the present curve as shown in Fig. 7. The only continuous wave results here are recorded by Seeberger who used both wire wave and free wave methods but the results are not consistent and show no definite trend. The observation of Zakrzewski,[19] made with slightly damped radiation and using a free wave method, shows a great displacement from the present curve and leads one to suspect an error of the type discussed under Section 6 of the "Free Wave Method." The data of Eckert[20]

[19] Zakrzewski uses a peculiar notation in which κ has the meaning usually attached to $n\kappa$ so that his result $\kappa=0.62$ means $n\kappa=0.62$ in the usual notation. Because of this fact errors have crept into the literature in connection with Zakrzewski's data.

[20] Eckert, Ber. d. D. Phys. Ges. **15**, 307 (1913).

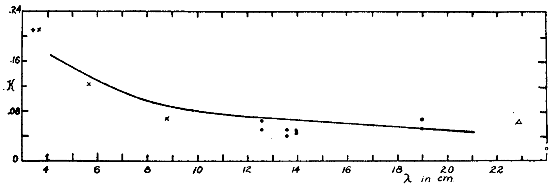

FIG. 7. Comparison of observed absorption index with previous data. Legend: open circle, Seeberger (wire waves); closed circle, Seeberger (free waves); △, Zakrzewski; +, Mobius; ×, Eckert.

and Mobius[21] were obtained by free wave methods but with very highly damped radiation so that these points give us no reliable quantitative information. However they do indicate the general trend of the absorption. At still shorter wave-lengths (2.7–0.42 cm) we have the results of Tear[22] but these were secured with highly damped waves and are of little present significance. While all of these earlier results are unsatisfactory they confirm the present data in a general way.

The average value of refractive index for the twelve wave-lengths shown in Table II is 8.80 with only one point departing more than 0.6 percent from the mean. While this result indicates no dispersion over the region 6.48–20.44 cm there are several lines of evidence which support the conclusion that probably a very slight dispersion occurs: (*a*) The average refractive index as reported over the interval 6.48–20.44 cm is 1.4 percent smaller than the square root of the static dielectric constant, 1.1 percent smaller than n as observed by Novosilzew for 141 wave-lengths between 220 and 300 cm, and 0.6 percent smaller than the value given by v. Ardenne, Groos and Otterbein for 34 wave-lengths between 28 and 57 cm. Moreover, in the results of Table II the average n for the six observations below 11 cm is 0.3 percent smaller than the average n for the six observations above 11 cm. All of these results suggest a small decrease of n over the entire short wave region. (*b*) The data of Merczyng,[23] Mobius, Tear, and some further data of Eckert below 5 cm, while very unsatisfactory and for the most part contradictory, do consistently show a marked decrease of refractive index in the region 1–5 cm which leads one to expect some slight dispersion over the lower part of the present region. (*c*) The observed increase of absorption index with decreasing wave-length implies, on the basis of the Debye dipole theory, an accompanying dispersion. Although these facts indicate the existence of a slight dispersion, the expected variation of refractive index is of the order of one percent and it is very doubtful if present methods could detect so small a variation over an interval of two octaves.

In comparing the present results with the discordant data already existing in this region one naturally considers first the continuous wave data. This comparison is shown in Fig. 8. Seeberger has $n=8.80$, 8.84, 8.57, 9.10 and 8.76 at $\lambda=12.6$, 13.6, 14.0, 19.0 and 24 cm, respectively. While these points do not show a definite trend the average value, 8.81, agrees well with the present results. It seems more reasonable to attribute the variation in the results at 14 and 19 cm to experimental error than to dispersion because of the lack of any other points to support these two departures from the average value. Moreover the sharp break in refractive index over the interval 13.6–14.0 cm is hardly plausible because of the absence of a corresponding break in the absorption index which would be expected if marked dispersion occurred at this point.

The recent investigation of Goldsmith[7] indicates a linear decrease of refractive index from 9.73 at 23.82 cm to 8.36 at 8.53 cm but this investigation is open to the criticism that the method of measuring the wave-length is very unsatisfactory, particularly for the longer waves. These results as they stand are not consistent with those of the present report nor with the data of Seeberger. Moreover they conflict with established long wave data above 28 cm inasmuch as the curve of Goldsmith indicates an increase of n as one goes to longer wave-lengths in spite of the fact that his value at 23.82 cm is already over 10 percent above the value found in the region 28–60 cm by v. Ardenne, Groos and Otterbein, Girard and Abadie, and Heim. Frankenberger[24] has investigated the region from 23 to 73 cm with slightly damped radiation and

[21] Mobius, Ann. d. Physik **62**, 293 (1920).
[22] Tear, Phys. Rev. **21**, 611 (1923).
[23] Merczyng, Ann. d. Physik **34**, 1015 (1911).
[24] Frankenberger, Ann. d. Physik **1**, 948 (1929).

found $n=8.91$ with no evidence of dispersion so it seems unlikely that a marked decrease of refractive index occurs between 23 and 28 cm as would be required to bring Goldsmith's data into harmony with the long wave results.

From the paper of v. Ardenne, Groos and Otterbein there are four observations with continuous waves at the single wave-length 13.45 cm which give $n=8.72$. This result is 1.5 percent smaller than the value reported by these writers at 28–57 cm and hence indicates dispersion but unfortunately only the one point was secured in the region of suspected dispersion so the evidence is not very conclusive.

The refractive index as measured for slightly damped waves by Zakrzewski and by Miesowicz is rather high but this is evidently due to the method of measurement as was pointed out in Section 6 under the "Free Wave Method." If this is correct it brings their data into closer agreement with the present result. Frankenberger's data from 10.6 to 24.9 cm were obtained with slightly damped waves but are tentative. They were not regarded by the author as satisfactory because of the evident influence of bridge diameter upon the results. Further experiments were indicated but no results have been published so far. The average of the data presented is 8.89.

The remaining results due to Wildermuth,[25]

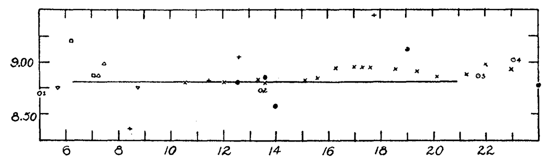

FIG. 8. Comparison of observed refractive index of water with previous data. The ordinate is refractive index at 22°C; the abscissa wave-length in cm. The solid line represents the present data. Legend: ⊕, Seeberger; +, Goldsmith; ×, Frankenberger; □, Miesowicz; ▽, Eckert; △, Becker; ⊙1, Cole; ⊙2, v. Ardenne, Groos and Otterbein; ⊙3, Wildermuth; ⊙4, Zakrzewski.

Eckert, Becker[26] and Cole[27] lie within about one percent of the present data but all of these were obtained with highly damped waves and consequently are of doubtful significance.

While it is apparent that none of these earlier reports (when the criticisms pointed out are considered) contradict the present results, it is also true that none of them are complete or precise enough to verify the small dispersion which is suspected.

In conclusion I wish to acknowledge my indebtedness to Professor D. M. Dennison and Professor N. H. Williams for many helpful discussions of the problem, and to Dr. C. E. Cleeton, who assembled the detectors, for many suggestions on the production and detection of ultra-short waves. I also wish to express my thanks to the University of Michigan for financial aid during the course of this research.

[25] Wildermuth, Ann. d. Physik **8**, 212 (1902).

[26] Becker, Ann. d. Physik **8**, 22 (1902).

[27] Cole, Wied. Ann. **57**, 290 (1896).

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Accommodation Coefficients of the Noble Gases and the Specific Heat of Tungsten

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By the use of the specific heat theory developed by A. H. Compton and a simple one-dimensional model, a semi-classical treatment of the problem of the thermal accommodation coefficients for monatomic gases against solid surfaces has been obtained. Application of this theory to the data of Roberts gives a satisfactory fit if the heats of adsorption of helium and neon on tungsten are taken as 50 cal. per gram atom and 278 cal. per gram atom, respectively. The Compton characteristic temperature for tungsten is found to be 148°K, which leads to the conclusion that the excess specific heat of tungsten above the classical value is partially due to anharmonic terms in the potential energy of the atomic oscillators, as suggested by Born and Brody.