

# Experimental Study of the Absorption in Distilled Water, Artificial Sea Water, and Heavy Water in the Visible Region of the Spectrum\*

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The absorption of light in distilled water, artificial sea water, and heavy water was measured in the visible region. A Nielsen spectrometer with glass optics was used with a tungsten source and photomultiplier detector. Path lengths were 60.0 and 132.0 cm. The absorption in distilled and artificial sea water differs little; maxima below 745  $m\mu$  were too weak to be observed. The absorption in heavy water is very small, increasing from a broad minimum at 700–600  $m\mu$  until at 390  $m\mu$  it is a factor of 10 larger than the minimum value.

## INTRODUCTION

THE transmission of light through water has been the subject of many investigations, as is borne out in the literature.<sup>1,2</sup> Several studies made of the absorption of light in liquid water in the visible region of the spectrum show some variation in the results reported.<sup>3</sup> In the near infrared region, Curcio and Petty<sup>4</sup> reported five prominent absorption bands between 0.7 and 2.5  $\mu$ .

The object of the present experiment is to investigate the absorption spectrum of distilled water in the visible region from 790–580  $m\mu$ , with the possibility of uncovering similar bands which represent the higher harmonics of the fundamental vibrational frequency. At the same time, the experiment gives an opportunity for looking at the spectrum with greater resolution than previously reported. Finally, the experiment affords a means of comparing the absorption of distilled water, artificial sea water, and heavy water in parts of the visible spectrum.

## EXPERIMENTAL DETAILS

### Apparatus

The dispersing element used was a single-beam single-pass prism spectrometer. It was essentially the same high-resolution spectrometer designed by Nielsen *et al.*<sup>5</sup> For measurements in the infrared. It was adapted for use in the visible region by substituting a dense flint glass 60° prism with a 12.5-cm base in the Wadsworth–

Littrow mounting. Suitable masks and baffles were used to screen off unused optical surfaces which might reflect stray light. Further adaptations were made in the scanning mechanism of the spectrometer so that in the region observed it was possible to scan at speeds not faster than 3  $m\mu$  per min.

Lines from mercury, neon, and argon spectra were used to calibrate the wavelength scale of the spectrometer. The wavelength scale was then related to the readings on a Veeder counter on the wavelength drive by means of a dispersion curve. The settings of the wavelength drive were observed to be reproducible within  $\pm 0.2 m\mu$  in the red end of the spectrum, the reproducibility improving with decreasing wavelength. Spectrometer bandwidths varied from 0.5  $m\mu$  in the far red to 0.1  $m\mu$  in the violet.

A tungsten strip-filament lamp was used as a source. This 18-A 6-V dc lamp was powered by three heavy-duty storage batteries to eliminate line fluctuations. A blower was kept on the lamp housing during the experiment to achieve temperature stability. To insure a constant intensity during the experiment, a current-monitoring device was used. By means of a suitable shunt and a galvanometer circuit, it was possible to detect changes of 0.1% in the lamp current. By using a variable resistor in series with the lamp, the current could be maintained within this limit. It was found that with this control, the recorder signal of the lamp intensity was stable to within 1%.

The light from the source was focused on a 1-mm pinhole in an opaque screen. The emitted light was then rendered parallel by a system of achromatic lenses. The circular beam was stopped down to a diameter of 22 mm to ensure that the beam would not touch the walls of the absorption cell. The light was chopped at 450 cps before entering the slit of the spectrometer. A reference signal from the chopper, generated by a magnetic pickup, was fed into a phase-comparing amplifier.

After passing through the spectrometer, the radiation was detected by an RCA 1-P21 photomultiplier tube placed at the exit slit of the spectrometer. The signal was then fed into a Baird-Atomic 450-cycle phase-comparator amplifier, rectified, and sent through a Leeds and Northrup strip-chart recorder. Prior to tak-

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<sup>1</sup> N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940), 341 ff.

<sup>2</sup> E. F. Dupre and L. H. Dawson, *Transmission of Light in Water: An Annotated Bibliography* (U. S. Naval Research Laboratory, Washington, D. C., 1961).

<sup>3</sup> E. O. Hulburt, *J. Opt. Soc. Am.* **35**, 698 (1945).

<sup>4</sup> J. A. Curcio and C. C. Petty, *J. Opt. Soc. Am.* **41**, 302 (1951).

<sup>5</sup> J. R. Nielsen, F. W. Crawford, and D. C. Smith, *J. Opt. Soc. Am.* **37**, 246 (1947).

ing the data, it had been ascertained under what conditions the response of the system was linear.

To hold the liquid samples, two cylindrical cells were constructed of nonflexible clear cast Acrylic plastic, one 60.0 cm and the other 132.0 cm in length. The ends of these tubes were milled and caps were made to hold 2-mm-thick circular Pyrex windows. Neoprene O rings were used as seals. The caps were fitted with set screws placed 120° apart on the circumference of the windows to allow adjustments to be made for the parallel settings of the windows.

### Preparation of the Samples

The distilled water used in the experiment was triply distilled over quartz. To maintain the best possible optical purity and to remove as many dust particles as possible, it was decided to filter the water just before taking the data. Pyrex fritted-glass filter cylinders of ultra-fine porosity were used; the average pore size of these filters was 0.9–1.4  $\mu$ . As an indication of the optical purity, the transmission of the sample in the 60.0-cm tube at the wavelength 470 m $\mu$  was noted. After filtration, it was found that a transmission of 88.5%  $\pm$  1.0% could be maintained; this figure includes the reflection losses at the air-glass and glass-water surfaces. After standing for 24 h, the same sample was found to have a transmission of 80% or less at the same wavelength.

The artificial sea water was made by combining chemicals with triply distilled water. The composition was such as to approximate sea water and the sample contained about 0.60 equivalents of positive and negative ions per liter.<sup>6</sup> The following chemicals were used: NaCl, MgSO<sub>4</sub>, MgCl<sub>2</sub>, NaHCO<sub>3</sub>, CaCl<sub>2</sub>, KCl, and KBr. The water was filtered immediately after being made up. Its specific gravity was measured and found to be 1.025  $\pm$  0.002.

The heavy water was composed of 99.7% deuterium oxide. Its density at 20° was 1.1057  $\pm$  0.0001 g/cc. This density showed no measurable change after filtration.

### Procedure

In taking the data for the various samples, a uniform procedure was followed. Before placing the cell in the optical path, a signal trace of the source spectrum was recorded. Care was taken to mount the cell the same way each time in the optical path. In order to ensure uniformity in this and to avoid any displacement of the image due to the insertion of the cell, a system consisting of an optical lever and a projecting lens was used to check the image position. With the cell out of the mount, an image of the pinhole magnified approximately 25 times was projected on a screen and its position marked; the cell was then mounted and position of the image again checked. At no time was the image displaced by

more than 4% of its diameter; in all cases it was adjusted, if necessary, by means of the set screws on the cell windows. This ensured reproducibility in mounting the cell.

Signal traces of the transmission of both empty cells were recorded to measure the air-glass reflection losses of the windows.

For all three types of water, at least three sets of data were taken. Prior to the observations, each sample was filtered in such a way that the filtrate flowed down the side of the flask, thus avoiding the formation of bubbles. The sample was then carefully siphoned into the absorption cell. All samples were tested within 3 h after filtration. For any longer delay, the water was not considered safe from some deterioration.

The source spectrum was recorded before the cell was mounted; this was repeated after the data was taken with the cell mounted. It was found that the source spectrum was reproducible to within 1%. Throughout the tests, the current-monitoring galvanometer was checked at frequent intervals, and the variable resistor adjusted accordingly. The room temperature was checked and did not vary by more than 3°C over all the tests. The temperature of the sample was read before and after each observation; the mean temperature over all the observations was 23.0  $\pm$  1.5°C. In taking the data, the spectrum was broken up into several regions. The 60.0-cm cell was used for all three types of water in the region 790–695 m $\mu$ . The 132.0-cm cell was used for the distilled water and the artificial sea water from 720–580 m $\mu$ , and for the heavy water from 750–390 m $\mu$ . To minimize the effect of stray light, optical filters were inserted in the optical path. For the distilled water and the artificial sea water, Corning red filters 2030, 2404, and 2424 were used in the regions 790–695, 720–635, and 635–580 m $\mu$ , respectively; a Corning blue filter, 5543, was used in the region 450–400 m $\mu$ . For the heavy water, red filters 2030 and 2404 were used in the regions 790–695 and 720–640 m $\mu$ ; no filter was used from 640–478 m $\mu$ ; a blue filter, 5543, was used in the region 480–390 m $\mu$ .

### CALCULATIONS AND RESULTS

The absorption coefficient,  $\alpha$ , is defined by the equation

$$I = I_0 e^{-\alpha x}, \quad (1)$$

where  $I_0$  and  $I$  are the intensities of the radiation, at a given wavelength, before and after passing through a path of length  $x$  through the sample. Since in this experiment no reference cell was used, corrections had to be made for the reflection losses at the air-glass and glass-water surfaces.

For this purpose we may write two similar forms of Eq. (1),

$$I = I_0 e^{-\alpha_1 x} \quad (2)$$

<sup>6</sup> *Smithsonian Physical Tables* (Smithsonian Institution, Washington, D. C., 1954), 9th revised ed., p. 776.

TABLE I. Absorption coefficient  $\alpha$  for distilled water, artificial sea water, and heavy water in the region 790–580  $m\mu$  ( $\times 10^4 \text{ cm}^{-1}$ ).

Wavelength ( $m\mu$ )	Distilled water	Artificial sea water	Heavy water	Wavelength ( $m\mu$ )	Distilled water	Artificial sea water	Heavy water
790	205.2	209.7	7.4	715	111.4	110.7	4.9
8	207.0	210.6	7.2	4	106.2	105.2	4.9
6	210.2	213.7	7.0	3	102.6	102.2	5.1
4	209.7	216.4	7.5	2	97.9	98.1	5.3
2	217.7	224.3	7.2	1	93.8	94.9	5.2
780	234.6	237.6	6.7	710	90.4	90.8	5.1
8	237.5	241.4	6.4	9	87.1	86.4	5.3
6	240.3	243.8	6.9	8	83.6	83.9	5.1
4	246.8	246.8	6.4	7	80.4	80.2	4.9
2	248.5	250.7	6.6	6	77.9	77.0	4.9
770	251.9	254.0	6.5	705	75.0	74.5	4.7
8	252.5	256.7	6.3	4	72.7	73.3	4.7
6	261.5	261.0	6.8	3	70.4	70.7	4.7
4	263.3	270.1	6.8	2	68.3	68.8	4.6
2	265.3	271.7	6.8	1	66.5	66.4	4.5
760	268.5	272.7	6.9	700	64.8	64.7	4.5
9	268.8	273.7	6.4	9	63.2	63.3	4.3
8	269.2	273.3	6.8	8	61.5	61.8	4.3
7	268.5	273.1	6.7	7	59.6	60.4	4.5
6	268.8	272.4	6.9	6	58.1	58.5	4.4
755	269.6	271.4	6.3	695	56.9	57.0	4.3
4	270.9	270.5	6.4	4	55.5	55.2	4.1
3	267.9	271.8	6.6	3	54.3	54.2	3.7
2	268.3	270.5	6.7	2	52.9	53.5	3.8
1	268.7	271.0	6.9	1	51.8	51.2	3.4
750	268.3	269.8	6.9	690	51.1	50.1	3.3
9	270.3	271.2	6.7	9	50.2	49.4	3.5
8	270.5	273.3	6.9	8	49.1	48.6	3.5
7	270.0	274.0	6.9	7	48.0	47.9	3.5
6	272.3	276.3	6.6	6	47.7	47.9	3.5
745	271.2	275.3	6.4	685	46.7	47.4	3.5
4	271.3	275.7	6.5	4	45.8	47.3	3.3
3	271.1	275.1	6.2	3	45.5	46.8	3.3
2	270.4	274.2	6.7	2	45.2	46.6	3.3
1	271.8	271.8	6.3	1	45.0	46.0	3.3
740	269.8	272.9	6.7	680	44.7	45.0	3.2
9	269.7	269.2	6.7	9	44.5	44.9	3.4
8	268.6	269.3	6.4	8	44.4	44.3	3.5
7	265.7	266.4	5.9	7	44.0	44.0	3.4
6	264.3	264.7	5.9	6	43.9	43.7	3.3
735	260.8	260.0	5.9	675	43.8	43.2	3.3
4	255.3	255.5	5.5	4	42.8	43.1	3.3
3	249.2	248.3	5.6	3	43.1	43.1	3.4
2	244.7	245.3	6.1	2	42.9	43.0	3.3
1	239.5	239.8	5.8	1	42.5	43.1	3.6
730	230.9	230.8	5.9	670	42.5	42.2	3.5
9	221.1	219.1	6.0	9	42.5	42.2	3.4
8	210.1	210.4	5.7	8	42.2	42.3	3.5
7	197.3	194.6	6.0	7	42.0	42.1	3.4
6	186.3	186.5	6.1	6	41.9	42.4	3.7
725	175.6	175.9	6.0	665	41.9	41.9	3.4
4	167.6	166.4	5.5	4	41.7	41.6	3.1
3	159.0	159.7	5.4	3	41.5	41.4	3.3
2	151.2	150.2	5.4	2	41.1	41.1	3.4
1	144.7	144.6	5.4	1	41.0	40.6	3.3
720	137.5	137.2	5.4	660	40.7	40.5	2.9
9	132.5	133.4	5.4	9	40.3	40.3	3.0
8	127.4	127.0	5.3	8	39.5	40.6	3.0
7	122.1	121.7	5.5	7	39.2	40.7	2.7
6	116.8	117.3	5.4	6	39.3	39.9	3.2

TABLE I (continued)

Wavelength ( $m\mu$ )	Distilled water	Artificial sea water	Heavy water	Wavelength ( $m\mu$ )	Distilled water	Artificial sea water	Heavy water
655	38.7	38.9	3.1	615	30.0	30.1	
4	37.6	38.4	3.0	4	29.8	29.9	3.6
3	36.5	37.3	3.0	3	29.4	30.2	
2	35.9	37.0	2.7	2	29.6	30.0	4.3
1	36.0	35.7	3.1	1	29.8	30.1	
650	35.1	35.7	3.4	610	29.3	29.9	4.0
9	34.7	35.2	3.2	9	29.4	29.7	
8	34.3	34.2	3.2	8	29.6	29.7	3.7
7	34.4	34.1	3.2	7	29.4	29.7	
6	34.3	33.5	3.2	6	29.5	29.6	4.0
645	33.9	33.6	3.2				
4	33.9	32.9	3.3	605	29.3	28.9	
3	33.7	32.8	3.0	4	29.0	29.0	4.1
2	33.7	32.9	3.3	3	28.9	29.0	
1	33.6	32.6	3.1	2	28.4	28.7	4.3
640	33.4	32.6	3.2	1	28.0	28.1	
9	33.3	32.5					
8	32.6	32.3	3.3	600	27.2	26.5	4.2
7	33.1	32.3		9	26.1	24.6	
6	32.6	32.9	3.3	8	24.6	24.0	4.1
635	32.5	32.0		7	23.5	23.2	
4	32.3	32.1	3.4	6	22.2	21.7	4.1
3	32.6	32.0					
2	32.1	31.9	3.4	595	21.4	20.8	
1	32.1	31.8		4	20.1	19.8	3.8
630	32.0	31.2	3.3	3	19.0	18.8	
9	31.3	31.7		2	18.5	18.1	4.7
8	31.2	31.2	3.8	1	17.6	17.5	
7	31.0	31.7					
6	31.2	31.7	3.8	590	17.2	16.7	4.4
625	30.5	31.7		9	16.0	16.3	
4	30.9	31.4	3.8	8	15.2	16.3	4.6
3	31.0	31.5		7	14.3	15.7	
2	30.7	31.5	4.1	6	13.0	15.6	4.6
1	30.7	31.1					
620	30.9	31.7	4.0	585	11.9	14.6	
9	30.6	31.0		4	12.2	15.1	4.9
8	30.4	30.7	4.0	3	12.0	14.1	
7	30.0	30.8		2	11.1	14.7	4.8
6	30.3	29.9	3.8	1	10.2	13.1	
				580	10.9	13.3	4.9

and

$$I = RI_0 e^{-\alpha x} \quad (3)$$

In Eq. (2),  $I_0$  is the intensity of the radiation at a given wavelength with no cell in the path;  $I$  is the intensity with the cell in the path, and  $\alpha_t$  is a total attenuation coefficient due to the absorption of the water plus the losses due to the interface reflections. In Eq. (3),  $I_0$  and  $I$  are again the intensities with the cell out of and in position.  $R$  is a transmission factor containing the surface reflection losses; its value was found to be 0.916. To obtain this value, the transmission of light through the empty cells was measured over the spectral region; the value of this transmission representing the loss due to four air-glass surfaces was  $0.850 \pm 0.005$  for both cells. From this observed value, the air-glass reflection coefficient was calculated to be 0.0398 and the index of refraction of the glass to be 1.4985. Using 1.3328 as the index of refraction for water, the glass-water reflection coefficient was calculated to be 0.0034. Using these data, one ar-

rives at a value of 0.916 for the transmission factor  $R$  for two air-glass and two glass-water surfaces.  $\alpha$  now is the absorption coefficient due to the water alone.

Simultaneous solution of Eqs. (2) and (3) leads to a relation for the correction term  $k$  where

$$k = \alpha_t - \alpha = -(\ln R/x) = 0.0883/x. \quad (4)$$

For the 60.0-cm cell,  $k$  equals  $14.7 \times 10^{-4} \text{ cm}^{-1}$ ; for the 132.0-cm cell,  $k$  equals  $6.7 \times 10^{-4} \text{ cm}^{-1}$ .

Table I contains the absorption coefficient  $\alpha$  for all three types of water in the region 790–580  $m\mu$ . For the distilled water and the artificial sea water, it is reported at 20- $m\mu$  intervals from 790–760  $m\mu$ , and at 1- $m\mu$  intervals from 760–580  $m\mu$ . For the heavy water, the coefficient is given for 2- $m\mu$  intervals from 790–760  $m\mu$ , at 1- $m\mu$  intervals from 760–640  $m\mu$ , and at 2- $m\mu$  intervals from 640–580  $m\mu$ . Table II contains the absorption coefficient for heavy water at 2- $m\mu$  intervals from 580–390  $m\mu$ , and for distilled water at 2- $m\mu$  intervals from 450–400  $m\mu$ .

TABLE II. Absorption coefficient  $\alpha$  for heavy water (580–390  $m\mu$ ) and for distilled water (450–400  $m\mu$ ) ( $\times 10^4 \text{ cm}^{-1}$ ).

Wavelength ( $m\mu$ )	Heavy water	Distilled water	Wavelength ( $m\mu$ )	Heavy water	Distilled water
580	4.9	...	480	13.1	...
8	4.8		8	13.4	
6	5.2		6	13.3	
4	5.3		4	13.3	
2	5.2		2	13.5	
570	5.4	...	470	14.1	...
8	5.4		8	14.4	
6	5.3		6	14.5	
4	5.4		4	15.0	
2	5.5		2	14.9	
560	5.3	...	460	15.6	...
8	5.5		8	15.6	
6	5.6		6	15.7	
4	5.8		4	16.5	
2	5.8		2	17.7	
550	5.8	...	450	18.2	3.3
8	5.9		8	18.7	3.0
6	6.1		6	19.1	3.4
4	6.4		4	19.7	3.4
2	6.3		2	20.3	3.5
540	6.3	...	440	20.8	3.2
8	6.4		8	21.3	3.2
6	6.9		6	21.7	3.6
4	7.0		4	22.3	3.4
2	7.2		2	23.3	3.9
530	7.4	...	430	23.4	4.0
8	7.4		8	23.4	4.1
6	7.9		6	24.3	4.5
4	7.9		4	24.7	4.2
2	8.3		2	26.2	3.6
520	8.6	...	420	26.3	3.8
8	8.7		8	26.8	4.5
6	8.7		6	27.4	4.5
4	8.9		4	27.8	4.7
2	8.8		2	28.4	5.3
510	8.9	...	410	28.5	4.7
8	9.2		8	28.9	4.7
6	8.9		6	29.7	5.3
4	9.6		4	31.5	6.2
2	9.6		2	31.7	5.8
500	10.1	...	400	31.8	5.8
8	10.2		8	31.9	
6	10.2		6	32.5	
4	10.4		4	33.3	
2	10.9		2	33.7	
490	11.6	...	390	33.3	
8	11.7				
6	12.2				
4	12.2				
2	12.6				

## DISCUSSION OF RESULTS

The absorption coefficients shown in Tables I and II represent the mean value of at least three observations in all cases except for the distilled water from 450–400  $m\mu$ ; for many wavelengths the number of observations was greater.

Representative standard deviations from the mean absorption coefficient for a given wavelength were calculated for 30- $m\mu$  intervals throughout the spectral region. Table III shows the absolute standard deviation

$\sigma$  and the relative deviation in percentage for all three types of water in the region 790–580  $m\mu$ . Table IV contains similar deviations for the heavy water in the region 570–390  $m\mu$ .

From Tables III and IV, it is clear that the absolute deviation is fairly independent of the absolute value of the coefficient—for example, at 760  $m\mu$ ,  $\sigma$  is the same for the distilled water and the heavy water, despite the great difference (a factor of 40) in the absolute value of the coefficient itself. On the other hand,  $\sigma$  decreases as one goes from the red toward the green; this is due to

the greater lamp intensity in this region and to the need for less amplification resulting in an improved signal-to-noise ratio.

The relative deviation, indicated by the percentage, can be seen to increase with decreasing absorption. The large relative deviation in the heavy water is due to the generally small absorption it exhibits throughout the entire visible region.

TABLE III. Absolute and relative deviations from the mean value of the absorption coefficient for the three types of water from 790–580  $m\mu$ .

Wave-length ( $m\mu$ )	Distilled water		Artificial sea water		Heavy water	
	$\sigma$	%	$\sigma$	%	$\sigma$	%
790	0.8 <sup>a</sup>	0.4	2.5 <sup>a</sup>	1.2	0.7 <sup>a</sup>	9.5
760	0.5	0.2	1.1	0.4	0.5	7.2
730	1.1	0.5	1.4	0.6	0.3	5.1
700	0.4	0.6	0.4	0.6	0.6	12.8
670	0.2	0.5	0.3	0.7	0.2	5.7
640	0.2	0.6	0.2	0.6	0.2	6.3
610	0.2	0.7	0.2	0.7	0.4	10.0
580	0.3	2.8	0.3	2.2	0.3	6.1

<sup>a</sup> All values in these columns are times  $10^4 \text{ cm}^{-1}$ .

From these tables, it is not clear whether the deviations are due to the difference in the water samples or to errors in measurement. No extensive systematic investigation of this was made. Fortunately, there was one case when a single sample of heavy water was measured three times at 730  $m\mu$ . This showed a standard deviation of  $0.2 \times 10^{-4} \text{ cm}^{-1}$  (it is recognized that three samples are not really enough to calculate a standard deviation), while five different samples showed a standard deviation of  $0.3 \times 10^{-4} \text{ cm}^{-1}$ . If the differences between samples and the errors of measurement are treated as independent in this case, the deviation due to the differences between samples is

$$[(0.3)^2 - (0.2)^2]^{\frac{1}{2}} = 0.22 (\times 10^{-4} \text{ cm}^{-1}),$$

so that the two effects contribute about equally to the measured standard deviation. If this is true in general, the standard deviation due to the differences in the samples is  $\sigma/\sqrt{2}$ .

The absorption coefficients for the distilled water and the artificial sea water differ little from each other in the observed region. Both show a strong absorption in the region 790–730  $m\mu$ , that of the artificial sea water being slightly greater in the neighborhood of the maximum. The maximum is found to be at  $745 \pm 3 \text{ } m\mu$  in both the distilled and artificial sea water, with some evidence of a smaller maximum in the latter at 760  $m\mu$ . This maximum, which is observed in both types of water, is undoubtedly the same as that reported by Curcio and Petty.<sup>4</sup> The value we report for the maximum absorption coefficient is about 4% higher than

that reported by them. McLennan *et al.*<sup>7</sup> in their investigation reported a diffuse absorption band from 635–599  $m\mu$ . We were able to find no maximum in this region. We did observe an almost step-like decrease in the absorption from about 680–590  $m\mu$  very similar to that shown by McLennan.<sup>7</sup> This is also in general agreement with the findings of Hulburt.<sup>3</sup>

In the area where our investigation of distilled water coincided with that of Hulburt,<sup>3</sup> our results were generally 8%–10% higher. The reason for this discrepancy is not known.

TABLE IV. Absolute and relative deviations from the mean value of the absorption coefficient for heavy water from 570–390  $m\mu$ .

Wavelength ( $m\mu$ )	$\sigma$ ( $\times 10^4 \text{ cm}^{-1}$ )	%
570	0.2	3.7
540	0.3	4.8
510	0.3	3.4
480	0.2	1.5
450	0.1	0.6
420	0.2	0.7
390	0.4	1.1

The spectrum of the heavy water shows a very small absorption throughout the visible region. No maximum was observed. There is a gradual decrease evident in the absorption from 790–700  $m\mu$ , reaching a broad minimum in the region 700–600  $m\mu$ . The absorption then gradually increases with decreasing wavelength until, in the neighborhood of 390  $m\mu$ , it has increased by a factor of ten over the minimum value. In absorption measurements of  $\text{D}_2\text{O}$ ,  $\text{H}_2\text{O}$ , and  $\text{HDO}$  between 190 and 185  $m\mu$ , Barret and Mansell<sup>8</sup> found that the absorption increased with decreasing wavelength, but that at 185  $m\mu$  the absorption of the distilled water is larger than that of heavy water by a factor greater than 10.

## CONCLUSION

Our investigation shows that for distilled water and artificial sea water the absorption maxima representing the higher harmonics of the fundamental vibrational frequency in the visible region observed—with the exception of the maximum at 745  $m\mu$ —are too weak to be observed. Our high-resolution examination of the observed regions leads us to conclude that there is no “optical window” in this portion of the spectrum. A comparison of the absorption spectra of the distilled water and the artificial sea water indicates that the variations in the observed spectra of ordinary sea water

<sup>7</sup> J. C. McLennan, R. Ruedy, and A. C. Burton, Proc. Roy. Soc. (London) A120, 296 (1928).

<sup>8</sup> J. Barret and A. L. Mansell, Nature 187, 138 (1960).

are due to something other than the water itself. The spectrum of the heavy water, while showing no maximum in the visible region, suggests that this maximum might be found in the infrared as might be expected from the isotopic effect of the deuterium.

Further investigations of the absorption spectra of all

three types of water in the ultraviolet would be of significant interest.

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## Application of Characteristic Vector Analysis to Photographic and Optical Response Data\*

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Characteristic vector analysis of multivariate response data has been successfully applied to a variety of optical and photographic response functions. The method provides a simple characterization of complex response functions. The philosophy of the method is discussed.

### INTRODUCTION

THE experimenter in the photographic and optical sciences is often concerned with the analysis or characterization of multivariate response data. Examples are optical densities of photographic images resulting from a series of exposures, spectrophotometric data at many wavelengths, or modulation transfer data at many spatial frequencies. Multivariate data of this type are most commonly presented graphically to aid in comparing the results of several experiments. The comparisons become unwieldy, however, when many curves are being intercompared. For quantitative analysis of the data, it becomes desirable to derive parametric data which represent the graphical data.

An analysis which reduces the dimensionality of a set of responses to an intrinsic minimum is characteristic vector analysis (sometimes referred to as "principal component analysis" or "eigenvector analysis"). The technique is a method of examining a number of sets of multivariate response data and determining linear transformations of the data to a smaller number of parameters which contain essentially all the information in the original data. The technique has been used frequently in statistical analyses of test data in a number of dissimilar fields.<sup>1-4</sup> Increasing use of the technique is

being made in the optical and photographic sciences.<sup>5-7</sup> It is the purpose of this paper to review the philosophy of characteristic vector analysis to promote increased understanding and utilization of the method.

### GENERAL BASIS OF THE METHOD

A hypothetical response curve is shown in Fig. 1. The response being measured will be called  $z$ . The curve represents measurements made at a series of values of  $x$  and plotted. In Fig. 2, the dashed curve is the curve of Fig. 1. The other curves represent a family of response curves artificially constructed for purposes of demonstration. The response curves of Fig. 2 represent the additions of linear combinations of the ordinates from the two curves of Fig. 3 to the curve of Fig. 1. For instance, Curve A is constructed by adding to the curve

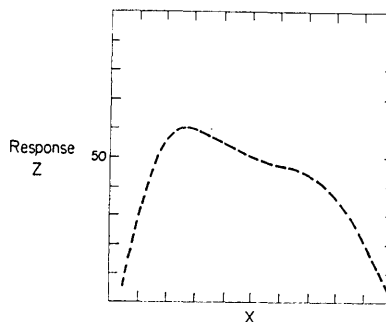


FIG. 1. A hypothetical response curve.

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<sup>1</sup> H. Hotelling, *J. Educational Psychol.* **24**, 417-441, 498-520 (1933).

<sup>2</sup> W. C. Krumbein and J. W. Tukey, *J. Sedimentary Petrol.* **26**, 322-337 (1956).

<sup>3</sup> R. Harper, *Appl. Statistics* **5**, 32-48 (1956).

<sup>4</sup> H. Gulliksen, *Am. Scientist* **47**, 178-201 (1959).

<sup>5</sup> R. H. Morris and J. H. Morrissey, *J. Opt. Soc. Am.* **44**, 530-534 (1954).

<sup>6</sup> J. L. Simonds, *Phot. Sci. Eng.* **2**, 205-209 (1958).

<sup>7</sup> J. L. Simonds, *Phot. Sci. Eng.* **5**, 270-277 (1961).