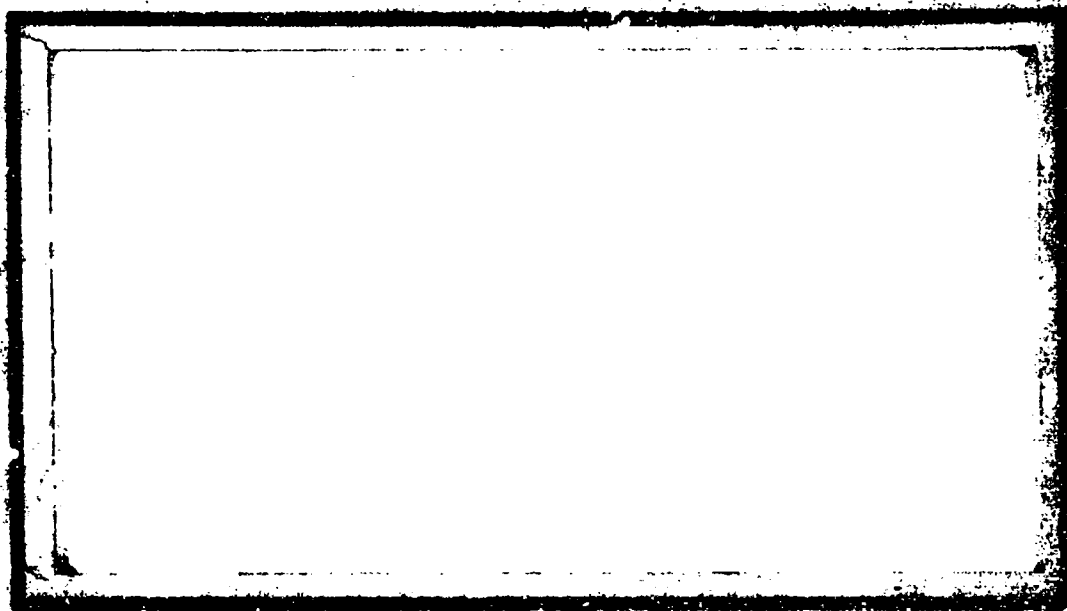


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The Optical Constants of Water
and Sea Water in the Infrared •

Scientific Report No. 1 ✓

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Submitted by Dudley Williams

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Dudley Williams

Department of Physics
Kansas State University
Manhattan, Kansas 66506

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FOREWORD

Under the present contract and its predecessor, we have been engaged in a study of water and hydrated materials by means of "intensity spectroscopy" in the infrared. In work of this type emphasis is placed on the quantitative measurements of band intensities in the infrared as contrasted with "frequency spectroscopy", which places primary emphasis on the determination of line and band frequencies and contours.

The present report consists of the reprints of two journal articles, the first dealing with the optical constants of water and the second dealing with the corresponding constants for synthetic sea water. The results are based on careful absorption and reflection measurements in the infrared.

As an appendix to the report we are including a complete list of the publications resulting from our work. Reprints of most of the journal articles are available for distribution; copies will be supplied to those interested on the basis of individual requests.

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Optical Constants of Water in the Infrared:

HARRY D. DOWNING AND DUDLEY WILLIAMS

Department of Physics, Kansas State University, Manhattan, Kansas 66506

The results of our earlier studies of reflection and absorption in various spectral regions are reviewed and then used to provide values of the complex index of refraction $\tilde{N} = n + ik$ of water at 27°C in the spectral range 5000–10 cm^{-1} , corresponding to wavelengths in the range 2 μm to 1 mm. Values of n , k , and the Lambert absorption coefficient α , which are presented graphically and in tabular form, should prove useful in studies of the scattering of infrared radiation by water droplets in the atmosphere and in studies of radiative heat balance at water surfaces.

* 1/5 $\phi\phi\phi$ - 10 cm

alpha p. 554

Although the infrared spectrum of water had been the subject of numerous investigations, Irvine and Pollack [1968] made a critical survey of published results that revealed many inconsistencies and a general paucity of quantitative data on which to base values of the real and imaginary parts of the complex index of refraction $\tilde{N} = n + ik$. In view of the importance of n and k in calculations of the transmission, scattering, and absorption of electromagnetic radiation by water droplets in the earth's atmosphere, our laboratory group has devoted considerable attention to the quantitative determination of the optical properties of water in the infrared. We have based our earlier listings of the optical constants n and k on quantitative measurements of various types in various spectral regions. The purpose of the present paper is to give a critical review of our earlier studies with the purpose of providing a set of 'best values' for use in atmospheric studies.

In our initial study, covering the 5000- to 400- cm^{-1} region, Querry *et al.* [1969] attempted to measure the reflectance of polarized radiation at two large angles of incidence and to determine n and k by solution of the generalized Fresnel equations. In the range 5000–330 cm^{-1} , Rusk *et al.* [1971] employed reflectance measurements at near-normal incidence and at an angle of 53° near Brewster's angle. Although there was fair agreement in the values of n and k obtained in these two studies, serious uncertainties were introduced as a result of the imperfect polarizers employed at nonnormal incidence in the first study and the failure to achieve Brewster's angle in the vicinity of absorption bands in the second study.

In view of these uncertainties, Hale *et al.* [1972] applied a Kramers-Kronig (KK) phase shift analysis to obtain values of the optical constants from Rusk's measurements of reflectance at near-normal incidence. The values of n based on the KK analysis represented an improvement on the earlier values; the KK analysis gave good values of k in the vicinity of strong absorption maximums but was unreliable in spectral regions where k is small. In general, reflectance measurements can give reliable values for n and also for large k ; they thus complement careful absorption measurements, which can provide reliable values for small k but somewhat questionable values for large k .

Our next study by Robertson and Williams [1971] was the quantitative measurement of the Lambert absorption coefficient α defined by $I = I_0 \exp[-\alpha x]$; in this work we used a wedge-shaped absorption cell designed by Robertson, and we covered the spectral range 4300–300 cm^{-1} . The values of $k = \lambda\alpha/4\pi$ based on absorption measurements were more precise than those based on reflectance in spectral regions of

small k and agreed, within the stated limits of uncertainty, in the centers of absorption bands where k is large; in the spectral range $\nu < 600 \text{ cm}^{-1}$ the uncertainties in k became larger because of limitations imposed by the spectrometers employed. The values of k were measured in this low-frequency region by Robertson *et al.* [1973], who used a far infrared grating instrument to determine α in the spectral range between 800 and 50 cm^{-1} ; these authors also obtained values of n by means of a KK analysis of measured values of α .

In the spectroscopy of the remote infrared, interferometers used with Fourier transform techniques have marked advantages over conventional grating instruments. Using interferometric methods, John Chamberlain and his associates at the National Physical Laboratory (NPL) have obtained values of n and k in the range 100–20 cm^{-1} ; in the course of this work, Davies *et al.* [1970] employed absorption techniques, and Zafar *et al.* [1973] employed reflection techniques. Existing water data in the microwave and radiofrequency regions have been summarized by Ray [1972].

PRESENT STUDY

In preparing the present summary of our work on water we have based our values of the optical constants primarily on (1) Robertson's absorption measurements and (2) Rusk's measurements of spectral reflectance at near-normal incidence. In extensions of these primary data to the near-infrared and visible we have made use of the recent work of Palmer and Williams [1974]; in the extreme infrared we have used the NPL results in the 100- to 20- cm^{-1} region and results taken from Ray's survey in the frequency range below 20 cm^{-1} . In spectral regions where accurate values of absorption coefficients and reflectances have been determined independently we have obtained values of n and k from Fresnel's equation; in other regions we have employed KK methods.

The refractive index n can be determined from the KK relation

$$n(\nu) = 1 + (1/2\pi^2)P \int_0^\infty \frac{\alpha(\nu')}{\nu'^2 - \nu^2} d\nu' \quad (1)$$

where α represents the Lambert absorption coefficient, for which we have values in the range between the radiofrequency region and 14,500 cm^{-1} in the visible. In order to obtain values of n in the infrared from (1) it is sufficient to take account of ultraviolet contributions by assuming a single far ultraviolet band which will give the proper value of n at some frequency for which it is accurately known from independent measurements; we chose characteristics for the hypothetical ultraviolet band that would yield a value $n = 1.306$ at 5000 cm^{-1} in agreement with all our own earlier measurements.

On the basis of n evaluated from (1) and of direct experimental values of $k = \lambda\alpha/4\pi$ we calculated the values of the normal incidence reflectance R in the range 800–120 cm^{-1} ; these calculated values of R served to check Rusk's values in the 800- to 350- cm^{-1} range and to provide values of R in the 350- to 120- cm^{-1} range, where no reflectance measurements have been made. In the 120- to 90- cm^{-1} range we joined our calculated values to a reflectance curve for the 90- to 10- cm^{-1} range calculated from the NPL optical constants and those listed by Ray. On the basis of measured and calculated values of reflectance over the whole range from the near ultraviolet to the radiofrequency range, we then employed the KK phase shift theorem

$$\phi(\nu) = (2\nu/\pi)P \int_0^\infty \frac{\ln [R(\nu')^{1/2}]^{1/2}}{\nu'^2 - \nu^2} d\nu' \quad (2)$$

where $[R(\nu)]^{1/2}$ is the modulus of the complex reflectivity $\hat{R} = [R(\nu)]^{1/2} \exp [i\phi(\nu)]$. In terms of ϕ and R the values of n and k at any frequency are given by the relations

$$n = (1 - R)/(1 + R - 2R^{1/2} \cos \phi) \quad (3)$$

$$k = (-2R^{1/2} \sin \phi)/(1 + R - 2R^{1/2} \cos \phi) \quad (4)$$

We have used (2) along with (3) and (4) to provide n and k over the entire frequency range of present interest.

In the computer programs used for the solution of (1) and (2) we have employed methods based on Simpson's rule with a basic increment of 10 cm^{-1} except in the vicinity of the singularity at ν , where analytic solutions involving quadratic approximations of $\alpha(\nu)$ and $\ln [R(\nu)]^{1/2}$ were used. The 10- cm^{-1} mesh is satisfactory over most of the range of present interest but becomes coarse at the lowest frequencies.

OPTICAL CONSTANTS

In Figure 1 we give our final values of the absorption index k as a function of frequency in waves per centimeter and wavelength in micrometers. The values represent the weighted average of k based on direct measurements of α and on KK analyses; greater weight is given to the values based on direct measurement. The error bars shown in the figure represent the maximum differences between measured values and values based on (1), (2), and (4); the error bars thus give a measure of the in-

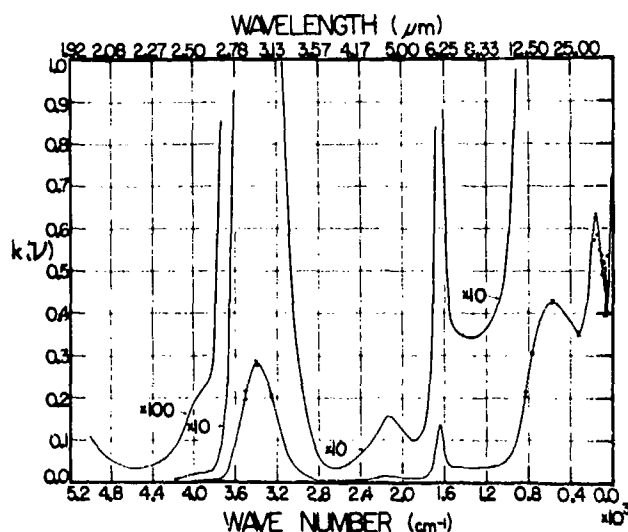


Fig. 1. Absorption index k as a function of wave number and wavelength.

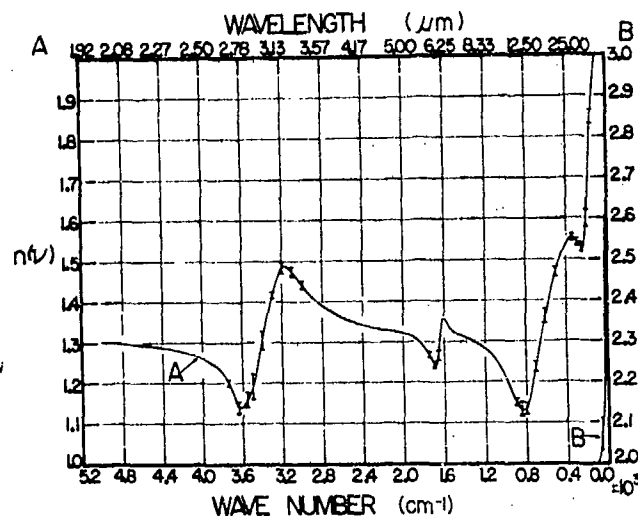


Fig. 2. Refractive index n as a function of wave number and wavelength.

ternal consistency of our work. In general, the actual uncertainties, which have been estimated in our earlier papers, are comparable with those given by the error bars except in the vicinity of the strong absorption band near 3400 cm^{-1} , for which Robertson and Williams [1971] list an uncertainty of $\pm 4\%$ in k ; thus since transmission measurements tend to give an underestimate of k at the centers of strong absorption bands, our results indicate that k may be as large as 0.294 at 3390 cm^{-1} .

Our final values of the refractive index n are plotted as a function of wave number and wavelength in Figure 2. The curve shown represents a weighted average of direct determinations in regions where α and R have been determined directly by experiment, of KK determinations from (1), and of KK determinations from (2) and (3); greater weight has been accorded to direct determinations. It should be noted that our values of n in the range 350–120 cm^{-1} are based entirely on

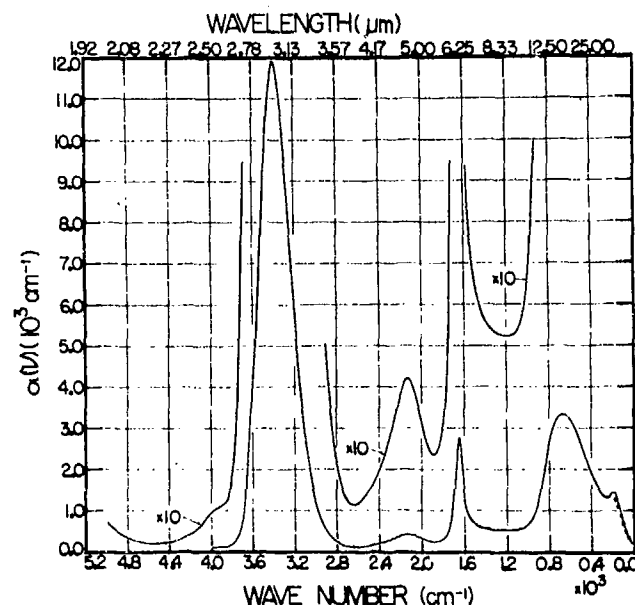


Fig. 3. Lambert absorption coefficient α as a function of wave number and wavelength. Values shown are based on direct measurement of absorption.

KK analyses, since we have made no reflection measurements in this range. The error bars on the curve in the figure are a measure of the self-consistency of our work and at a given frequency represent the maximum differences between n as determined by various techniques; the large uncertainties in spectral regions where n is changing rapidly are probably due in part to spectrometer calibration problems and in part to the size of the increments employed in the KK analysis.

TABLE 1. Optical Constants of Water in the Infrared

ν	$n(\nu)$	$k(\nu)$	$\alpha(\nu)$	λ
5000	1.303	0.00110	69.2	2.000
4950	1.301	0.000900	56.0	2.020
4900	1.301	0.000731	45.0	2.041
4850	1.300	0.000617	37.6	2.062
4800	1.298	0.000514	31.0	2.083
4750	1.298	0.000452	27.0	2.105
4700	1.296	0.000400	23.6	2.128
4650	1.295	0.000359	21.0	2.151
4600	1.294	0.000341	19.7	2.174
4550	1.293	0.000338	19.3	2.198
4500	1.291	0.000345	19.5	2.222
4450	1.289	0.000376	21.0	2.247
4400	1.287	0.000416	23.0	2.273
4350	1.285	0.000465	25.4	2.299
4300	1.282	0.000542	29.3	2.326
4250	1.280	0.000652	34.8	2.353
4200	1.277	0.000792	41.8	2.381
4150	1.274	0.000963	50.5	2.410
4100	1.270	0.00123	63.5	2.439
4050	1.265	0.00156	79.5	2.469
4000	1.261	0.00190	95.7	2.500
3990	1.260	0.00195	97.5	2.506
3980	1.259	0.00200	100.0	2.513
3970	1.257	0.00205	102.0	2.519
3960	1.256	0.00207	103.0	2.525
3950	1.255	0.00210	104.0	2.532
3940	1.254	0.00212	105.0	2.538
3930	1.252	0.00215	106.0	2.545
3920	1.250	0.00219	108.0	2.551
3910	1.249	0.00224	110.0	2.558
3900	1.247	0.00227	111.0	2.564
3890	1.246	0.00231	113.0	2.571
3880	1.243	0.00234	114.0	2.577
3870	1.241	0.00239	116.0	2.584
3860	1.240	0.00243	118.0	2.591
3850	1.238	0.00248	120.0	2.597
3840	1.235	0.00257	124.0	2.604
3830	1.232	0.00270	130.0	2.611
3820	1.230	0.00298	143.0	2.618
3810	1.227	0.00330	158.0	2.625
3800	1.224	0.00402	192.0	2.632
3790	1.221	0.00437	208.0	2.639
3780	1.218	0.00482	229.0	2.646
3770	1.214	0.00536	254.0	2.653
3760	1.210	0.00627	296.0	2.660
3750	1.205	0.00732	345.0	2.667
3740	1.200	0.00855	402.0	2.674
3730	1.195	0.0105	490.0	2.681
3720	1.191	0.0127	593.0	2.688
3710	1.185	0.0145	677.0	2.695
3700	1.179	0.0164	762.0	2.703
3690	1.172	0.0186	862.0	2.710
3680	1.166	0.0205	946.0	2.717
3670	1.157	0.0282	1300.0	2.725
3660	1.149	0.0380	1930.0	2.732
3650	1.144	0.0462	2270.0	2.740
3640	1.139	0.0548	2600.0	2.747
3630	1.138	0.0649	2970.0	2.755
3620	1.138	0.0744	3340.0	2.762
3610	1.139	0.0836	3720.0	2.770

TABLE 1. (continued)

ν	$n(\nu)$	$k(\nu)$	$\alpha(\nu)$	λ
3600	1.141	0.0927	4070.0	2.778
3590	1.144	0.102	4420.0	2.786
3580	1.149	0.112	4750.0	2.793
3570	1.154	0.121	5110.0	2.801
3560	1.158	0.131	5530.0	2.809
3550	1.161	0.142	6020.0	2.817
3540	1.165	0.154	6510.0	2.825
3530	1.171	0.167	7070.0	2.833
3520	1.177	0.180	7670.0	2.841
3510	1.183	0.194	8230.0	2.849
3500	1.191	0.206	8750.0	2.857
3490	1.199	0.218	9270.0	2.865
3480	1.212	0.229	9660.0	2.874
3470	1.220	0.239	10120.0	2.882
3460	1.233	0.249	10500.0	2.890
3450	1.246	0.258	10850.0	2.899
3440	1.258	0.265	11150.0	2.907
3430	1.271	0.271	11370.0	2.915
3420	1.282	0.276	11600.0	2.924
3410	1.293	0.280	11780.0	2.933
3400	1.305	0.281	11850.0	2.941
3390	1.317	0.282	11900.0	2.950
3380	1.329	0.282	11870.0	2.959
3370	1.342	0.279	11720.0	2.967
3360	1.353	0.276	11600.0	2.976
3350	1.364	0.272	11400.0	2.985
3340	1.376	0.267	11150.0	2.994
3330	1.386	0.262	10920.0	3.003
3320	1.398	0.255	10570.0	3.012
3310	1.407	0.250	10300.0	3.021
3300	1.417	0.243	10000.0	3.030
3290	1.426	0.236	9670.0	3.040
3280	1.434	0.228	9300.0	3.049
3270	1.442	0.220	8950.0	3.058
3260	1.450	0.212	8570.0	3.067
3250	1.457	0.204	8270.0	3.077
3240	1.465	0.195	7820.0	3.086
3230	1.471	0.183	7320.0	3.096
3220	1.476	0.173	6830.0	3.106
3210	1.480	0.163	6400.0	3.115
3200	1.483	0.153	6010.0	3.125
3190	1.486	0.144	5610.0	3.135
3180	1.487	0.134	5210.0	3.145
3170	1.487	0.125	4840.0	3.155
3160	1.487	0.117	4550.0	3.165
3150	1.486	0.110	4320.0	3.175
3140	1.485	0.0994	3890.0	3.185
3130	1.482	0.0920	3620.0	3.195
3120	1.479	0.0855	3390.0	3.205
3110	1.477	0.0785	3120.0	3.215
3100	1.474	0.0716	2840.0	3.226
3090	1.472	0.0653	2590.0	3.236
3080	1.467	0.0600	2390.0	3.247
3070	1.464	0.0550	2190.0	3.257
3060	1.461	0.0504	2010.0	3.268
3050	1.457	0.0462	1840.0	3.279
3040	1.454	0.0422	1680.0	3.289
3030	1.451	0.0385	1530.0	3.300
3020	1.448	0.0348	1390.0	3.311
3010	1.444	0.0315	1260.0	3.322
3000	1.441	0.0297	1120.0	3.333
2990	1.437	0.0279	1050.0	3.344
2980	1.434	0.0262	980.0	3.356
2970	1.431	0.0250	933.0	3.367
2960	1.427	0.0229	850.0	3.378
2950	1.425	0.0210	780.0	3.390
2940	1.421	0.0193	713.0	3.401
2930	1.418	0.0177	650.0	3.413
2920	1.415	0.0163	599.0	3.425
2910	1.413	0.0151	551.0	3.436
2900	1.410	0.0138	503.0	3.448
2890	1.407	0.0128	466.0	3.460

TABLE 1. (continued)

ν	$n(\nu)$	$k(\nu)$	$\alpha(\nu)$	λ
2880	1.405	0.0118	428.0	3.472
2870	1.403	0.0110	398.0	3.484
2860	1.400	0.0101	363.0	3.497
2850	1.398	0.00941	337.0	3.509
2840	1.396	0.00866	309.0	3.521
2830	1.394	0.00807	287.0	3.534
2820	1.392	0.00737	261.0	3.546
2810	1.390	0.00683	241.0	3.559
2800	1.388	0.00625	220.0	3.571
2790	1.387	0.00579	203.0	3.584
2780	1.385	0.00538	188.0	3.597
2770	1.383	0.00506	176.0	3.610
2760	1.382	0.00473	164.0	3.623
2750	1.379	0.00449	155.0	3.636
2740	1.378	0.00424	146.0	3.650
2730	1.377	0.00405	139.0	3.663
2720	1.375	0.00389	133.0	3.676
2710	1.374	0.00376	128.0	3.690
2700	1.372	0.00363	123.0	3.704
2690	1.371	0.00355	120.0	3.717
2680	1.370	0.00347	117.0	3.731
2670	1.369	0.00340	114.0	3.745
2660	1.367	0.00335	112.0	3.759
2650	1.366	0.00336	112.0	3.774
2640	1.365	0.00335	111.0	3.788
2630	1.363	0.00339	112.0	3.802
2620	1.361	0.00340	112.0	3.817
2610	1.361	0.00348	114.0	3.831
2600	1.360	0.00352	115.0	3.846
2590	1.358	0.00363	118.0	3.861
2580	1.358	0.00370	120.0	3.876
2570	1.357	0.00378	122.0	3.891
2560	1.355	0.00389	125.0	3.906
2550	1.354	0.00399	128.0	3.922
2540	1.353	0.00410	131.0	3.937
2530	1.352	0.00422	134.0	3.953
2520	1.351	0.00433	137.0	3.968
2510	1.350	0.00450	142.0	3.984
2500	1.349	0.00465	146.0	4.000
2490	1.348	0.00479	150.0	4.016
2480	1.348	0.00494	154.0	4.032
2470	1.347	0.00512	159.0	4.049
2460	1.346	0.00531	164.0	4.065
2450	1.345	0.00549	169.0	4.082
2440	1.344	0.00568	174.0	4.098
2430	1.344	0.00586	179.0	4.115
2420	1.343	0.00608	185.0	4.132
2410	1.342	0.00631	191.0	4.149
2400	1.341	0.00653	197.0	4.167
2390	1.340	0.00673	202.0	4.184
2380	1.340	0.00696	208.0	4.202
2370	1.338	0.00722	215.0	4.219
2360	1.337	0.00749	222.0	4.237
2350	1.337	0.00779	230.0	4.255
2340	1.335	0.00806	237.0	4.274
2330	1.334	0.00833	244.0	4.292
2320	1.334	0.00864	252.0	4.310
2310	1.333	0.00896	260.0	4.329
2300	1.332	0.00927	268.0	4.348
2290	1.332	0.00966	278.0	4.367
2280	1.331	0.0100	287.0	4.386
2270	1.330	0.0104	297.0	4.405
2260	1.330	0.0108	308.0	4.425
2250	1.330	0.0112	318.0	4.444
2240	1.329	0.0117	330.0	4.464
2230	1.329	0.0122	342.0	4.484
2220	1.329	0.0126	352.0	4.505
2210	1.328	0.0131	364.0	4.525
2200	1.328	0.0136	376.0	4.545
2190	1.327	0.0140	386.0	4.566

TABLE 1. (continued)

ν	$n(\nu)$	$k(\nu)$	$\alpha(\nu)$	λ
2180	1.327	0.0145	396.0	4.587
2170	1.327	0.0149	406.0	4.608
2160	1.327	0.0152	412.0	4.630
2150	1.327	0.0154	417.0	4.651
2140	1.326	0.0156	419.0	4.673
2130	1.326	0.0157	419.0	4.695
2120	1.326	0.0157	418.0	4.717
2110	1.325	0.0157	416.0	4.739
2100	1.325	0.0155	410.0	4.762
2090	1.325	0.0153	402.0	4.785
2080	1.325	0.0151	394.0	4.808
2070	1.325	0.0148	386.0	4.831
2060	1.325	0.0146	377.0	4.854
2050	1.324	0.0143	368.0	4.878
2040	1.324	0.0140	359.0	4.902
2030	1.323	0.0137	349.0	4.926
2020	1.322	0.0133	338.0	4.950
2010	1.322	0.0129	327.0	4.975
2000	1.321	0.0126	317.0	5.000
1990	1.320	0.0122	306.0	5.025
1980	1.319	0.0118	294.0	5.051
1970	1.318	0.0115	284.0	5.076
1960	1.318	0.0110	272.0	5.102
1950	1.317	0.0108	264.0	5.128
1940	1.316	0.0105	255.0	5.155
1930	1.314	0.0103	249.0	5.181
1920	1.313	0.0101	244.0	5.201
1910	1.311	0.0100	240.0	5.236
1900	1.310	0.00993	237.0	5.263
1890	1.308	0.00990	235.0	5.291
1880	1.306	0.00995	235.0	5.319
1870	1.304	0.0100	236.0	5.348
1860	1.302	0.0102	238.0	5.376
1850	1.299	0.0104	242.0	5.405
1840	1.297	0.0107	247.0	5.435
1830	1.294	0.0110	253.0	5.464
1820	1.291	0.0115	262.0	5.495
1810	1.288	0.0120	274.0	5.525
1800	1.285	0.0128	289.0	5.556
1790	1.282	0.0138	311.0	5.587
1780	1.278	0.0150	336.0	5.618
1770	1.275	0.0166	370.0	5.650
1760	1.271	0.0185	409.0	5.682
1750	1.267	0.0205	451.0	5.714
1740	1.262	0.0242	529.0	5.747
1730	1.256	0.0293	637.0	5.780
1720	1.251	0.0332	734.0	5.814
1710	1.247	0.0429	947.0	5.848
1700	1.242	0.0544	1200.0	5.882
1690	1.241	0.0688	1515.0	5.917
1680	1.241	0.0840	1840.0	5.952
1670	1.247	0.1021	2175.0	5.988
1660	1.265	0.117	2430.0	6.024
1650	1.289	0.130	2670.0	6.061
1640	1.311	0.132	2738.0	6.098
1630	1.332	0.124	2566.0	6.135
1620	1.349	0.106	2139.0	6.173
1610	1.354	0.0880	1760.0	6.211
1600	1.356	0.0740	1465.0	6.250
1590	1.354	0.0618	1200.0	6.289
1580	1.350	0.0535	1025.0	6.329
1570	1.345	0.0484	934.0	6.369
1560	1.341	0.0447	863.0	6.410
1550	1.337	0.0420	806.0	6.452
1540	1.333	0.0398	758.0	6.494
1530	1.330	0.0383	726.0	6.536
1520	1.326	0.0373	703.0	6.579
1510	1.324	0.0370	683.0	6.623
1500	1.322	0.0366	666.0	6.667

TABLE 1. (continued)

ν	$n(\nu)$	$k(\nu)$	$\alpha(\nu)$	λ
1490	1.320	0.0363	652.0	6.711
1480	1.319	0.0360	638.0	6.757
1470	1.318	0.0357	624.0	6.803
1460	1.317	0.0355	612.0	6.849
1450	1.316	0.0352	602.0	6.897
1440	1.315	0.0350	593.0	6.944
1430	1.314	0.0347	582.0	6.993
1420	1.313	0.0346	575.0	7.042
1410	1.311	0.0343	564.0	7.092
1400	1.310	0.0342	558.0	7.143
1390	1.309	0.0342	554.0	7.194
1380	1.308	0.0342	550.0	7.246
1370	1.307	0.0343	547.0	7.299
1360	1.306	0.0342	543.0	7.355
1350	1.305	0.0342	540.0	7.407
1340	1.303	0.0342	537.0	7.463
1330	1.302	0.0342	535.0	7.519
1320	1.301	0.0342	532.0	7.576
1310	1.300	0.0344	530.0	7.634
1300	1.298	0.0345	530.0	7.692
1290	1.296	0.0346	529.0	7.752
1280	1.295	0.0349	528.0	7.813
1270	1.294	0.0351	527.0	7.874
1260	1.293	0.0351	526.0	7.937
1250	1.291	0.0351	525.0	8.000
1240	1.288	0.0352	524.0	8.065
1230	1.286	0.0356	524.0	8.130
1220	1.285	0.0359	523.0	8.197
1210	1.283	0.0361	523.0	8.264
1200	1.281	0.0362	522.0	8.333
1190	1.279	0.0366	522.0	8.403
1180	1.276	0.0370	523.0	8.475
1170	1.274	0.0374	523.0	8.547
1160	1.271	0.0378	523.0	8.621
1150	1.269	0.0383	524.0	8.696
1140	1.267	0.0387	525.0	8.772
1130	1.264	0.0392	527.0	8.850
1120	1.261	0.0398	529.0	8.929
1110	1.259	0.0405	532.0	9.009
1100	1.256	0.0411	536.0	9.091
1090	1.253	0.0417	540.0	9.174
1080	1.249	0.0424	546.0	9.259
1070	1.246	0.0434	553.0	9.346
1060	1.242	0.0443	561.0	9.434
1050	1.238	0.0453	571.0	9.524
1040	1.234	0.0467	583.0	9.615
1030	1.230	0.0481	596.0	9.709
1020	1.224	0.0497	613.0	9.804
1010	1.220	0.515	631.0	9.901
1000	1.214	0.0534	651.0	10.000
990	1.208	0.0557	673.0	10.101
980	1.202	0.0589	702.0	10.204
970	1.194	0.0622	733.0	10.309
960	1.189	0.0661	770.0	10.417
950	1.181	0.0707	817.0	10.526
940	1.174	0.0764	866.0	10.638
930	1.168	0.0828	927.0	10.753
920	1.162	0.0898	993.0	10.870
910	1.156	0.0973	1064.0	10.989
900	1.149	0.107	1165.0	11.111
890	1.143	0.118	1270.0	11.236
880	1.139	0.130	1396.0	11.364
870	1.135	0.144	1533.0	11.494
860	1.132	0.159	1682.0	11.628
850	1.132	0.176	1833.0	11.765
840	1.131	0.192	1987.0	11.905
830	1.132	0.208	2143.0	12.048
820	1.130	0.226	2309.0	12.195
810	1.130	0.243	2467.0	12.346
800	1.134	0.260	2618.0	12.500
790	1.138	0.277	2760.0	12.658

TABLE 1. (continued)

ν	$n(\nu)$	$k(\nu)$	$\alpha(\nu)$	λ
780	1.142	0.292	2883.0	12.821
770	1.157	0.305	2969.0	12.987
760	1.171	0.317	3040.0	13.158
750	1.182	0.328	3100.0	13.333
740	1.189	0.338	3150.0	13.514
730	1.201	0.347	3192.0	13.699
720	1.213	0.356	3231.0	13.889
710	1.223	0.365	3263.0	14.085
700	1.236	0.373	3287.0	14.286
690	1.249	0.379	3298.0	14.493
680	1.264	0.386	3307.0	14.706
670	1.277	0.392	3308.0	14.925
660	1.289	0.397	3307.0	15.152
650	1.303	0.403	3301.0	15.385
640	1.313	0.408	3291.0	15.625
630	1.324	0.412	3276.0	15.873
620	1.335	0.417	3259.0	16.129
610	1.348	0.420	3234.0	16.393
600	1.361	0.423	3203.0	16.667
590	1.372	0.425	3167.0	16.949
580	1.385	0.427	3126.0	17.241
570	1.396	0.428	3077.0	17.544
560	1.407	0.427	3022.0	17.857
550	1.419	0.427	2964.0	18.182
540	1.431	0.426	2903.0	18.519
530	1.441	0.425	2842.0	18.868
520	1.451	0.423	2779.0	19.231
510	1.462	0.421	2709.0	19.608
500	1.470	0.418	2638.0	20.000
490	1.480	0.415	2565.0	20.408
480	1.488	0.411	2494.0	20.833
470	1.496	0.408	2423.0	21.277
460	1.504	0.404	2347.0	21.739
450	1.510	0.401	2280.0	22.222
440	1.515	0.397	2210.0	22.727
430	1.521	0.394	2143.0	23.256
420	1.527	0.390	2072.0	23.810
410	1.532	0.386	2004.0	24.390
400	1.537	0.382	1933.0	25.000
390	1.541	0.377	1862.0	25.641
380	1.545	0.372	1793.0	26.316
370	1.549	0.368	1724.0	27.027
360	1.552	0.363	1658.0	27.778
350	1.552	0.359	1593.0	28.571
340	1.552	0.356	1532.0	29.412
330	1.550	0.352	1472.0	30.303
320	1.546	0.353	1432.0	31.250
310	1.543	0.357	1401.0	32.258
300	1.541	0.361	1374.0	33.333
290	1.539	0.368	1351.0	34.483
280	1.537	0.375	1331.0	35.714
270	1.534	0.385	1317.0	37.037
260	1.532	0.398	1311.0	38.462
250	1.529	0.414	1310.0	40.000
240	1.525	0.436	1323.0	41.667
230	1.528	0.469	1364.0	43.478
220	1.542	0.505	1407.0	45.455
210	1.567	0.539	1434.0	47.619
200	1.600	0.571	1445.0	50.000
190	1.640	0.597	1437.0	52.632
180	1.689	0.618	1412.0	55.556
170	1.746	0.629	1358.0	58.824
160	1.801	0.622	1266.0	62.500
150	1.848	0.608	1165.0	66.667
140	1.890	0.593	1065.0	71.429
130	1.929	0.577	967.0	76.923
120	1.960	0.557	872.0	83.333
110	1.982	0.532	773.0	90.909
100	1.997	0.507	678.0	100.000
90	2.000	0.487	594.0	111.111
80	2.010	0.466	509.0	125.000

TABLE 1. (continued)

ν	$n(\nu)$	$k(\nu)$	$\alpha(\nu)$	λ
70	2.020	0.450	429.0	142.857
60	2.040	0.444	360.0	166.667
50	2.070	0.438	290.0	200.000
40	2.110	0.460	240.0	250.000
30	2.150	0.527	210.0	333.333
20	2.225	0.718	192.0	500.000
10	2.600	1.0902	137.0	1000.000

Frequencies ν are expressed in waves per centimeter (cm^{-1}), $n(\nu)$ and imaginary $k(\nu)$ parts of the dielectric constant $N = n + ik$ are dimensionless, the Lambert absorption coefficient $\alpha(\nu)$ defined by the relation $I = I_0 \exp [-\alpha x]$ is expressed in waves per centimeter (cm^{-1}), and wavelengths λ are given in micrometers (μm). The values of $n(\nu)$, $k(\nu)$, and $\alpha(\nu)$ are given for water at 27°C.

Although the values of n and k provide all the information actually required for a quantitative description of the optical properties of water, a set of values of the Lambert coefficient α is of direct use in providing information of importance to studies of radiative heat balance at horizontal water surfaces. We have therefore included a plot of α versus ν in Figure 3; values of α given in the plot are based entirely on direct measurements and thus differ slightly from α values calculated from our averaged values of k . The values of α given in Figure 3 would apply in good approximation to clear freshwater lakes and can provide rough approximations of the properties of clear seawater, as suggested by *Hobson and Williams* [1971].

Irvine and Pollack have emphasized the importance of presenting optical constants in tabular as well as graphical form. In Table 1 we list our best values of k , n , and α at frequency intervals of 10 cm^{-1} over most of the range between 5000 and 10 cm^{-1} ; the values in the table correspond to those plotted in Figures 1-3 and involve the same uncertainties. These values apply to water at a laboratory temperature of approximately 27°C; values at other temperatures can be estimated from the plots given by *Hale et al.* [1972]. A molecular interpretation of the water spectrum was given by *Robertson et al.* [1973].

COMPARISON WITH OTHER STUDIES

Our values for the optical constants can be compared with those obtained in earlier studies by *Pontier and Dechambenoy* [1965, 1966] in France and by *Zolotarev et al.* [1969] in Russia. The present results for k are in excellent agreement with both of these studies in the range 5000-4000 cm^{-1} but are in somewhat serious disagreement in the vicinity of the strong absorption band near 3400 cm^{-1} , where plots of the earlier studies differ by several percent from those in Figure 1. The peak values of k in the two studies are 0.305, a value somewhat higher than our present highest estimate and 8% higher than the value given in our plot; the absorption band obtained by the French workers is centered at a slightly lower frequency than the frequency given in the other studies.

In the frequency range 2800-800 cm^{-1} there is truly excellent agreement between the present k values and those reported by the Russian group; throughout most of this region the French values of k are significantly higher than our values. At frequencies lower than 800 cm^{-1} the French values are generally

greater than ours, and the Russian values generally lower; through the entire region below 800 cm^{-1} the k values reported by the other groups fall within $\pm 10\%$ of the values we give in Figure 1.

In comparing our present values for n with the earlier studies we find that in the 5000- to 3600- cm^{-1} region our values are in good agreement with the values obtained in the French study; throughout this region the Russian values are considerably lower than ours and are in serious disagreement in the 3800- to 3600- cm^{-1} range, where the Russian values are much lower than ours. In the range 3200-400 cm^{-1} the n values obtained in the earlier studies generally fall within $\pm 1\%$ of our values as plotted in Figure 2; however, at the minimum near 840 cm^{-1} the earlier results are lower than ours by 1.5%. At frequencies below 400 cm^{-1} we have continued satisfactory agreement with the Russians, who based their values in this region on published results of others including *Draeger et al.* [1966] which are shown by the points in Figures 1 and 3 for $\nu < 200 \text{ cm}^{-1}$. In the region $\nu < 400 \text{ cm}^{-1}$ the French results fall below our values and are apparently in serious error; they are based on prism spectrograph results, which we find are subject to stray radiation problems in the low-frequency region.

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Optical properties of sea water in the infrared²:

Lary W. Pinkley and Dudley Williams
Kansas State University, Manhattan, Kansas 66506
(Received 11 December 1975)

We have made quantitative measurements of the ratio of the infrared spectral reflectance of standard sea water at near-normal incidence to the corresponding spectral reflectance of pure water at 27°C. The infrared spectral reflectance of standard sea water was determined from the measured ratio and the known optical constants for pure water. The real $n(\nu)$ and the imaginary $k(\nu)$ parts of the complex index of refraction of standard sea water were then determined by Kramer-Kronig methods. The results obtained for the standard sea water are compared with previous results obtained for pure water and with previous studies of sea water.

In view of the fact that three-quarters of the earth's surface is covered by sea water, the optical properties of sea water have an important bearing on the earth's radiative heat balance; because the emission spectrum of the earth is largely in the intermediate infrared, a knowledge of the optical constants of sea water in this spectral region is of special importance. Detailed knowledge of these constants is also of importance to remote sensing of the earth's atmospheric and surface features from satellites and to infrared signal transmission through the atmosphere near the surface of the sea, where droplets of sea water are an important aerosol component of the atmosphere.

The present infrared study of sea water is a part of a research program dealing with the infrared properties of water, in which we have used quantitative measurements of absorption¹ and reflection² to determine the real n and imaginary k parts of the complex index of refraction $\hat{N} = n + ik$. In a critical summary³ of earlier work, we compare the n and k values obtained by Kramers-Kronig (KK) analyses of separate reflection and absorption measurements with the values of these constants based on a combination of absorption and reflec-

tion measurements. In general, KK analysis of reflection measurements provided excellent values of n and yielded good values of k in spectral regions of strong absorption. In the present study we have determined the reflectance R at near-normal incidence and have employed KK analysis to obtain n and k for sea water in the infrared.

In earlier studies we have investigated the influence of temperature⁴ and various inorganic solutes⁵ on the infrared reflectance of water; the results have a bearing on the spectrum of sea water, which, apart from its particulate and biologic components, is merely a dilute solution of certain salts. Hobson and Williams⁶ have compared the spectral reflectance of sea water from various geographical locations with the reflection of pure water and with the reflection of the solutions of salts known to be present in sea water; the presence of the SO_4^{2-} ion produces readily observable effects in sea water. Querry and his associates⁷ have also studied the reflection spectra of sea water from various sources and have made a detailed investigation of the influence of NaCl on the spectrum of water.

Because the concentration of the solutes in ocean

water varies with geographic location, various varieties of *standard sea water* (SSW) have been devised and used in laboratory studies. In the present investigation we have employed SSW prepared from the complete prescription of Lyman and Fleming,⁶ which provides an extremely close approximation to clean ocean water. Friedman⁹ has made a detailed study of SSW in which he measured spectral reflectance at large angles of incidence and, in certain spectral regions, made comparisons of the spectral transmittance of SSW and pure water. The SSW employed by Friedman included only $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NaCl , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and CaCl_2 , which are the major components of the Lyman-Fleming prescription; the concentration of minor components is so small that their contributions to the observable spectrum of sea water is probably completely negligible. In the course of his work, Friedman also employed solutions having 0.5 the normal solute concentration (SSW-0.5), along with multiples 1.5 (SSW-1.5) and 2 (SSW-2) of the normal concentration; the use of these solutions facilitated estimates of the effects of salinity on the spectral properties of sea water.

In the present study we made a careful comparison of the spectral reflectances of SSW and SSW-2 with that of pure water at near-normal incidence in the spectral range 350–6700 cm^{-1} . The results are shown in Fig. 1 in which we plot the measured ratios $R(\nu)_{\text{SSW}}/R(\nu)_w$ and $R(\nu)_{\text{SSW-2}}/R(\nu)_w$ as a function of wave number in the range 400–5200 cm^{-1} . The length of the uncertainty bars shown at selected wave numbers on the SSW curve also apply to the SSW-2 curve. In most spectral regions the uncertainty in the ratio plotted in Fig. 1 amounts to approximately ± 0.01 but becomes larger in regions of low spectral reflectance near 3700 and 900 cm^{-1} and in regions where spectral reflectance changes rapidly with frequency. The results shown in Fig. 1 indicate that the spectral reflectance of sea water is greater than that of pure water in most of the infrared region but is significantly lower in the vicinity of 800 cm^{-1} .

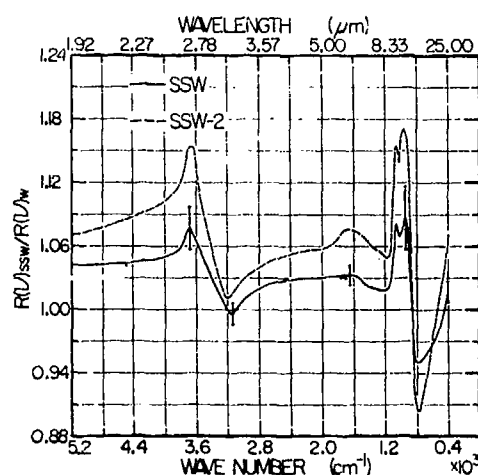


FIG. 1. Ratio of the near-normal-incidence spectral reflectances of SSW and SSW-2 to that of water. Samples were at 27°C.

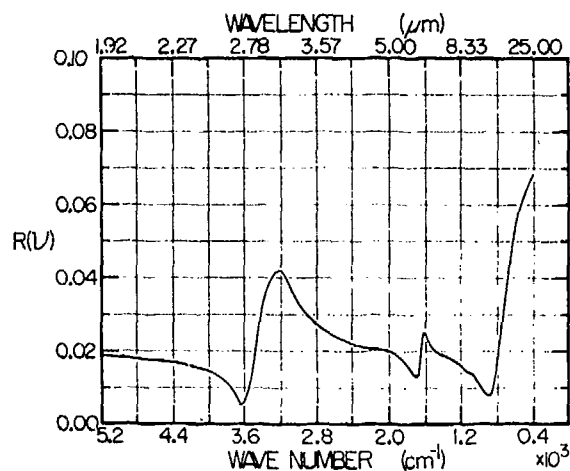


FIG. 2. Near-normal-incidence spectral reflectance $R(\nu)$ of standard sea water at 27°C.

The spectral reflectances $R(\nu)$ for SSW and SSW-2 were obtained by using the measured ratios of their reflectance to water reflectance. In arriving at values for the spectral reflectance $R(\nu)_w$ of water we used values of reflectance computed from tabulated values³ of $n(\nu)$ and $k(\nu)$, which in turn are based on numerous quantitative measurements of reflection and absorption covering the spectral range 28 000 to 1 cm^{-1} . The resulting values of $R(\nu)$ for SSW are shown in Fig. 2. The low values of $R(\nu)$ near 3600 and 900 cm^{-1} were verified by direct measurements involving a calibrated reference mirror. Except for small shifts in frequency, the major features of $R(\nu)$ for SSW bear a close resemblance to the reflectance spectrum of pure water. However, a clearly visible small feature near 1100 cm^{-1} has no counterpart in the spectrum of pure water. We also obtained the spectral reflectance spectrum of SSW-2, which as expected from Fig. 1 is also roughly comparable with the reflectance spectrum of pure water.

The values of $R(\nu)$ shown in Fig. 2 were used in KK analysis to calculate values of the optical constants $n(\nu)$ and $k(\nu)$ for SSW. In arriving at these values we employed the KK phase-shift theorem

$$\phi(\nu) = \frac{2\nu}{\pi} P \int_0^\infty \frac{\ln[R(\nu')^{1/2}]}{\nu'^2 - \nu^2} d\nu', \quad (1)$$

where $[R(\nu)]^{1/2}$ is the modulus of the complex reflectivity $\hat{R} = [R(\nu)]^{1/2} \exp[i\phi(\nu)]$. In terms of ϕ and R , calculated values of n and k at any frequency are given by the relations

$$n = (1 - R)/(1 + R - 2R^{1/2} \cos \phi), \quad (2)$$

$$k = (-2R^{1/2} \sin \phi)/(1 + R - 2R^{1/2} \cos \phi). \quad (3)$$

We have used Eqs. (1)–(3) to obtain values for $n(\nu)$ and $k(\nu)$ for SSW and SSW-2 in the range 400–5200 cm^{-1} . We have used a computer program based on Simpson's rule except in the vicinity of ν where quadratic approximations of $[R(\nu)]^{1/2}$ based on measured values of $R(\nu)$ in the vicinity were used. Beyond the spectral range of actual measurement, 6700 cm^{-1} to ∞ and 0 to 350 cm^{-1} , we employed extrapolations based on $R(\nu)$ for pure

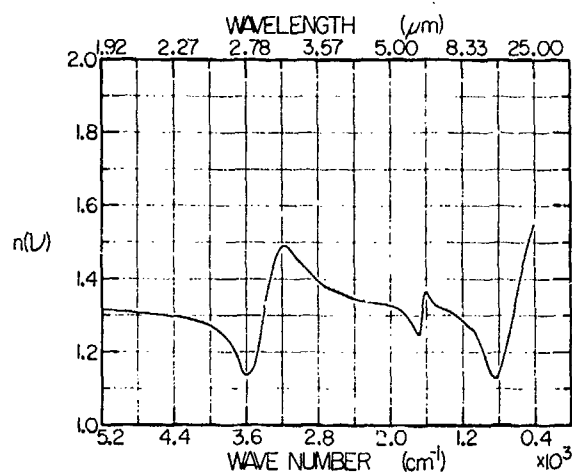


FIG. 3. Refractive index $n(\nu)$ of standard sea water at 27 °C.

water,^{3,10} which is known in the range 1 to 28 000 cm^{-1} .

The values of $n(\nu)$ for SSW are plotted as a function of wave number in Fig. 3. As in the case of $R(\nu)$, the general features of the $n(\nu)$ curve strongly resemble those of the corresponding curve for pure water. In most spectral regions $n(\nu)$ for SSW is slightly larger than the corresponding value for water. There are slight shifts in the major dispersion features near 3400 and 600 cm^{-1} with respect to the corresponding features for pure water. The small inflection near 1100 cm^{-1} is easily noted in Fig. 3. In general, the uncertainties in the values of $n(\nu)$ amount to approximately ± 0.005 .

The values of the absorption index $k(\nu)$ for SSW are plotted as a function of wave number in Fig. 4. The major absorption band near 3400 cm^{-1} is attributed to the ν_3 and ν_1 fundamentals of the water molecule along with some contribution from the overtone $2\nu_2$; the position and shape of this major band are strongly influenced by temperature changes⁴ and by the nature and concentration of solutes⁵ that modify the molecular surroundings of the water molecule. In SSW the band is shifted to slightly higher frequencies from its position in pure water. The sharp absorption band near 1650 cm^{-1} is due to the ν_2 fundamental of the water molecule; although slightly altered in shape, its frequency in SSW is the same as in pure water. The major absorption band near 600 cm^{-1} is associated with the librational or hindered rotational motion of the water molecule in the field of its neighbors; as in the case of the 3400 cm^{-1} band, the position of the librational band ν_L is dependent on water temperature⁴ and on the nature and concentration of solutes.⁵ In SSW it is shifted from its position in pure water to slightly lower frequencies.

The readily observable small absorption band near 1100 cm^{-1} can be attributed to the ν_3 fundamental of the SO_4^{2-} ion.¹¹ Comparison of the spectrum of SSW-2 with SSW reveals that absorption near 1100 cm^{-1} increases with increasing salt concentration. There are several small variations in $k(\nu)$ in the 1200–1500 cm^{-1} region but are not measurably different in the spectra of SSW-2.

In view of the direct dependence of the value of $k(\nu)$ on $\sin\phi(\nu)$ in (3), the absolute values of $k(\nu)$ in regions of low absorption are strongly influenced by uncertainties in $\phi(\nu)$ as determined by KK phase shift analysis (1). We have found that $k(\nu)$ values based on KK analysis are highly unreliable for $k(\nu) \leq 0.03$ but become increasingly reliable with increasing values of $k(\nu)$. The $k(\nu)$ values in Fig. 4 are virtually meaningless in the spectral ranges 3700–5200 cm^{-1} and 2900–1700 cm^{-1} ; in these regions absorption measurements are needed.

Because the spectrum of SSW so closely resembles the spectrum of pure water, Friedman has proposed that its optical properties can best be provided by the use of small corrections to the values of $n(\nu)$ and $k(\nu)$ that have been established for pure water. In view of the fact that we have measured the ratio of the reflectance of SSW and SSW-2 to pure water, we have adopted this procedure since the small corrections will remain applicable in good approximation when more exact values of the optical constants of water become available. In arriving at values of the small corrections we have compared our own values of the optical constants³ of pure water with those obtained for SSW and SSW-2 in the present study.

The curve shown in Fig. 5 gives the difference between $n(\nu)$ for SSW and $n(\nu)$ for pure water. In most spectral regions $n(\nu)$ for SSW is greater than that of water. The two major exceptions to this statement are associated with the minima near 3550 and 650 cm^{-1} , which are associated with changes in the frequency and contours of the major band near 3400 cm^{-1} and the librational band near 600 cm^{-1} , respectively. The corresponding curve for SSW-2 is shown in Fig. 6; the general features are similar to those for SSW except for larger differences between SSW-2 and water over much of the spectral range. Since the values of $n(\nu)$ for the solutions are based on the properties of water, the length of the uncertainty bars are closely related to those shown in Fig. 1. The influence of the SO_4^{2-} absorption band near 1100 cm^{-1} is clearly discernable in Figs. 5 and 6.

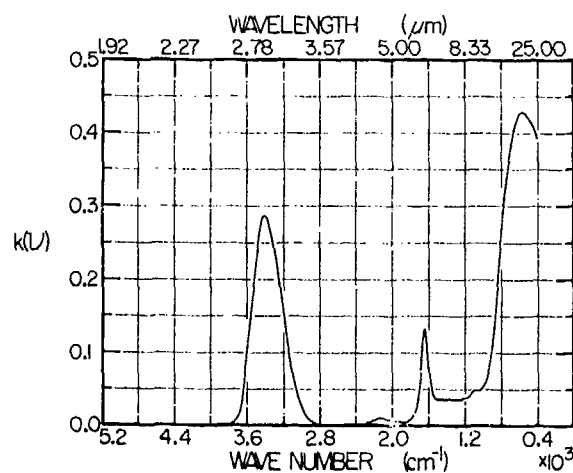


FIG. 4. Absorption index $k(\nu)$ of standard sea water at 27 °C.

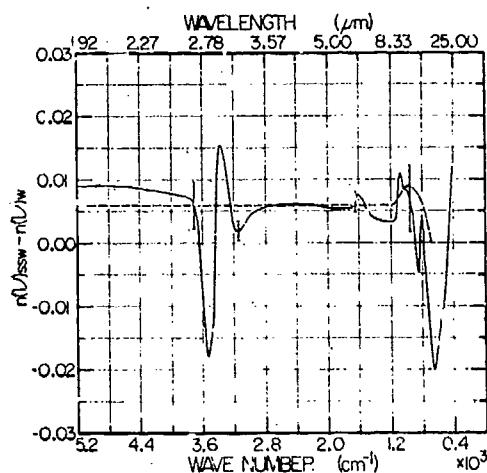


FIG. 5. Difference between the refractive index $n(\nu)$ for SSW and that of pure water.

The dashed curves shown in Figs. 5 and 6 represent Friedman's proposed corrections to the $n(\nu)$ for water that would give values of $n(\nu)$ for SSW and SSW-2. The present results are in close agreement with those of Friedman between 3000 and 1500 cm^{-1} ; our slightly larger values in the 5000–3800 cm^{-1} region may be due to the fact that Friedman's values are based on the $n(\nu)$ values of Pontier and Dechambeno¹² that differ from our values in this region. Friedman's corrections do not include those associated with changes in the 3400 cm^{-1} water band produced by the solutes.

In view of our criticism of the absolute values of $k(\nu)$ based on KK analysis (1) and (3) in regions where $k(\nu)$ is small, it would appear that the present study would provide little basis for establishing corrections of $k(\nu)$ for water to give corresponding values of $k(\nu)$ for SSW. Closer examination of the actual computation of $\phi(\nu)$ from (1) indicates that it is possible to provide significant corrections. In arriving at $\phi(\nu)$ from (1), we ob-

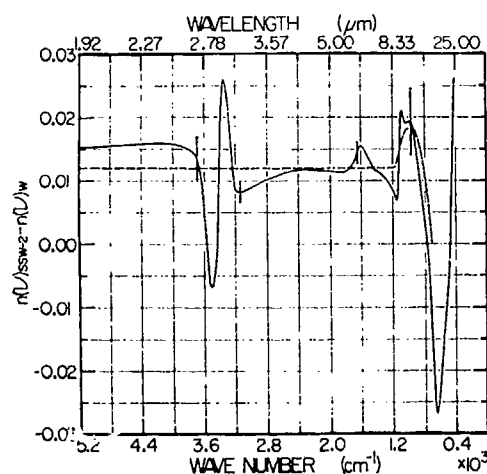


FIG. 6. Difference between the refractive index $n(\nu)$ for double-concentration standard sea water (SSW-2) and that of pure water.

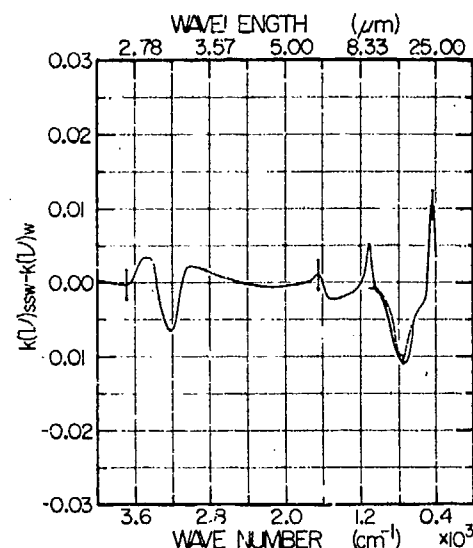


FIG. 7. Difference between the absorption index $k(\nu)$ of SSW and that of pure water.

tain a value of $\phi(\nu)$ that is the sum of $\phi(\nu)_{\text{HFE}}$ based on high-frequency extrapolation, $\phi(\nu)_M$ based on measured values of $R(\nu)$, and $\phi(\nu)_{\text{LFE}}$ based on low-frequency extrapolation. In spectral regions where $\phi(\nu)$ is small, its value given by (1) is strongly influenced by the extrapolations; this fact accounts for the large uncertainties in the absolute values of $k(\nu)$ in regions of low absorption. In spectral regions where ϕ is large, the magnitudes of $\phi(\nu)_{\text{HFE}}$ and $\phi(\nu)_{\text{LFE}}$ are small as compared with that of $\phi(\nu)_M$.

However, if we employ identical extrapolations for water and for SSW, we can obtain significant differences $k(\nu)_{\text{SSW}} - k(\nu)_W$ even though the calculated values of these separate absorption indices may be unreliable. In establishing these corrections, we note that $\phi(\nu)_{\text{SSW}} - \phi(\nu)_W = [\phi(\nu)_{\text{HFE}} + \phi(\nu)_M + \phi(\nu)_{\text{LFE}}]_{\text{SSW}} - [\phi(\nu)_{\text{HFE}} + \phi(\nu)_M + \phi(\nu)_{\text{LFE}}]_W = \phi(\nu)_{M-\text{SSW}} - \phi(\nu)_{M-W}$ provided identical high-frequency and low-frequency extrapolations are employed.

In Figs. 7 and 8 we show the results of values of $k(\nu)_{\text{SSW}} - k(\nu)_W$ and $k(\nu)_{\text{SSW-2}} - k(\nu)_W$, respectively. In arriving at the values shown in these figures we used extrapolations based on $R(\nu)_{\text{SSW}} = R(\nu)_W$ for $\nu > 8000 \text{ cm}^{-1}$ and $\nu < 350 \text{ cm}^{-1}$. On the basis of uncertainties ± 0.01 $R(\nu)$ in measured values of the spectral reflectance of SSW, we estimate that the uncertainties in the differences in absorption indices plotted in Figs. 7 and 8 amount to less than ± 0.002 over most of the spectral range between 4000 and 400 cm^{-1} . For $\nu > 4000 \text{ cm}^{-1}$, the calculated differences in absorption indices are influenced by the way in which the measured reflectance curves for sea water are merged with the values of $R(\nu)_W$ used in the high-frequency extrapolation.

Over most of the spectral region 4000–400 cm^{-1} the differences between $k(\nu)$ values for SSW-1 and SSW-2 and the values of $k(\nu)$ for water are small and the difference amounts to less than ± 0.002 . Differences larger than this occur in the 3400 cm^{-1} region and in-

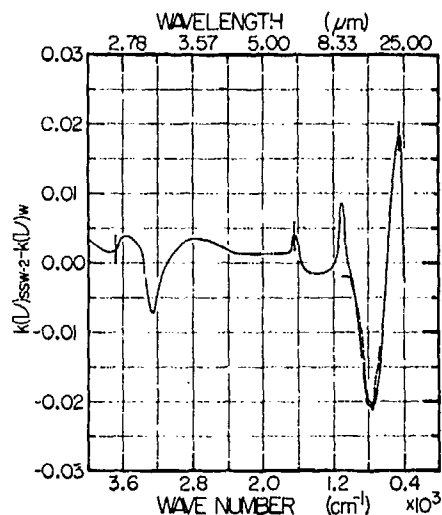


FIG. 8. Difference between the absorption index $k(\nu)$ of double-concentration standard sea water (SSW-2) and that of pure water.

dicates a slight shift to higher frequency and possible changes in the contours of the water band caused by the influence of the solutes. Similar but larger differences are noted in the 600 cm^{-1} region and are associated with a shift of the librational band to lower frequencies; the dashed curve in this region represents the differences in absorption index reported by Friedman on the basis of absorption measurements. The sharp peak near 1100 cm^{-1} is associated with the SO_4^{2-} absorption band mentioned earlier; the total absorption $\int k(\nu) d\nu$ associated with this band is roughly proportional to concentration.

It is gratifying to note the general agreement between the present results based on reflection measurements at near-normal incidence and the earlier results of Friedman,⁹ who measured reflectance at large angles of incidence along with transmission measurements in certain restricted spectral ranges. In the present

study we have extended quantitative measurements to lower frequencies and have detected shifts in the 3400 cm^{-1} water band not reported in Friedman's study.

On the basis of the refractive-index differences plotted in Fig. 5 and the absorption-index differences plotted in Fig. 7 one may obtain values of $n(\nu)$ and $k(\nu)$ for standard sea water by adding these differences to the values of these quantities tabulated by Downing and Williams.³ Comparisons of Figs. 5 and 7 with Figs. 6 and 8 provide a measure of the variations in $n(\nu)$ and $k(\nu)$ with salinity. We emphasize that comparisons of the reflection and emission of real sea water may be somewhat different from those computed on the basis of the present values of the optical constants for standard sea water, which contains no particulate or biologic constituents.

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2. "Explicit Solution of Generalized Fresnel Reflection Equations" (Marvin Querry), J. Opt. Soc. Amer. 58, 1560 (1968). P*.
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Technical Reports

Reprints of publications 1, 4, and 7 are listed above and have been distributed as Technical Reports No. 1, No. 2, and No. 3, respectively. A reprint of publication 12 was distributed as Technical Report No. 4 and was assigned No. AD730204 by DDC; a reprint of publication 14 as Technical Report No. 5 was assigned No. AD733820 and a reprint of publication 16 as Technical Report No. 6 was assigned No. AD733821 by DDC.