# 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  $\hat{N} = n + ik$  of water at 27°C in the spectral range 5000-10 cm<sup>-1</sup>, corresponding to wavelengths in the range 2 µm to 1 mm. Values of *n*, *k*, and the Lambert absorption coefficient  $\alpha$ , 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.

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  $\hat{N} = n + ik$ . 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<sup>-1</sup> 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<sup>-1</sup>, 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  $\alpha$  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<sup>-1</sup>. 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 lowfrequency region by *Robertson et al.* [1973], who used a far infrared grating instrument to determine  $\alpha$  in the spectral range between 800 and 50 cm<sup>-1</sup>; these authors also obtained values of n by means of a KK analysis of measured values of  $\alpha$ .

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<sup>-1</sup>; 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<sup>-1</sup> region and results taken from Ray's survey in the frequency range below 20 cm<sup>-1</sup>. In spectral 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

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

where  $\alpha$  represents the Lambert absorption coefficient, for which we have values in the range between the radiofrequency region and 14,500 cm<sup>-1</sup> 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<sup>-1</sup> in agreement with all our own earlier measurements.

Copyright © 1975 by the American Geophysical Union.

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<sup>-1</sup>; these calculated values of *R* served to check Rusk's values in the 800- to 350-cm<sup>-1</sup> range and to provide values of *R* in the 350- to 120-cm<sup>-1</sup> range, where no reflectance measurements have been made. In the 120- to 90-cm<sup>-1</sup> range we joined our calculated values to a reflectance curve for the 90- to 10-cm<sup>-1</sup> 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

$$\phi(\nu) = (2\nu/\pi) P \int_0^\infty \frac{\ln [R(\nu')]^{1/2}}{\nu^2 - {\nu'}^2} d\nu'$$
(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  $\phi$  and R the values of n and k at any frequency are given by the relations

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

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

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<sup>-1</sup> except in the vicinity of the singularity at  $\nu$ , where analytic solutions involving quadratic approximations of  $\alpha(\nu)$  and ln  $[R(\nu)]^{1/2}$  were used. The 10-cm<sup>-1</sup> 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  $\alpha$  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<sup>-1</sup>, 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<sup>-1</sup>.

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  $\alpha$  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<sup>-1</sup> are based entirely on



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

ν

3600

3590

3580

3570

n(v)

1,141 1,144 1,149 1,154

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.	(continued)
----------	-------------

α(ν)

4070.0

4420.0

4750.0

5110.0

5530.0

k(v)

0.0927

0.102 0.112 0.121 λ

2.778

2.786

2,793

2,801

2.809

size of	the increment	its employed in	the KK analys	SIS.	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
				•	7570	1 171	0 167	7070 0	7 977
TAB	LE 1. Optic	al Constants of	Water in the In	nfrared	3530	1,1/1	0.107	7070.0	2.033
					3520	1.1//	0.180 .	/6/0.0	2.841
					3510	1.183	0.194	8230.0	2,849
ν	n(v)	k(v)	α(ν)	λ	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
5000	1 307	0.00110	60 2	2 000	3470	1 220	0 230	10120 0	2 882
3000	1.303	0.00110	56.0	2.000	3470	1.220	0.239	10120.0	2.002
4950	1.301	0.000900	56.0	2.020	3460	1.233	0.249	10500.0	2.890
4900	1.301	0.000731	45.0	2.041	3450	1.246	0.258	10850.0	2.899
4850	1.300	0.000617	37.6	2.062	3440	1.258	0.265	11150.0	2.907
4800	1.298	0.000514	31.0	2.083	3430	1.271	0.271	11370.0	2.915
4750	1 209	0 000452	27 0	2 105	3420	1 282	0 276	11600 0	2 924
4730	1.206	0.000452	27.0	2,100	7410	1.202	0.200	11000.0	2.027
4700	1.290	0.000400	23.0	2.120	3410	1.295	0.280	11/80.0	2.933
4650	1.295	0,000359	21.0	2.151					
4600	1,294	0.000341	19.7	2.174	3400	1.305	0.281	11850.0	2.941
4550	1,293	0,000338	19.3	2.198	3390	1.317	0.282	11900.0	2.950
					3380	1 329	0 282	11870.0	2.959
45.00	1 201	0.000745	10 E	2 222	7770	1 740	0.270	11720 0	2.067
4500	1.291	0.000345	19.5	2.222	3370	1.342	0.279	11/20.0	2.90/
4450	1.289	0.000376	21.0	2.247	3360	1.353	0.276	11600.0	2.976
4400	1.287	0.000416	23.0	2.273	3350	1.364	0.272	11400.0	2.985
4350	1.285	0.000465	25.4	2.299	3340	1.376	0.267	11150.0	2.994
4300	1 292	0 000542	29 3	2 326	3330	1 386	0.262	10920-0	3.003
4300	1 202	0.000542	74 0	2.520	7720	1 709	0.202	1052010	7 012
4250	1.280	0.000652	34.0	2,333	3320	1.390	0.233	10370.0	3.012
4200	1.277	0.000792	41.8	2.381	3310	1.407	0.250	10300.0	3.021
4150	1.274	0,000968	50.5	2,410					
4100	1.270	0.00123	63.5	2.439	3300	1.417	0.243	10000.0	3,030
4050	1 265	0.00156	79.5	2,469	3290	1.426	0.236	9670.0	3.040
4030	1.205	0100100	/010		7290	1 474	0 229	9300 0	3 040
	1 0/1	0.00100	05 7	2 500	3200	1 442	0.220	8050.0	7 059
4000	1.201	0.00190	95.7	2.500	3270	1.442	0.220	8950.0	3.058
3990	1.260	0.00195	97.5	2,506	3260	1.450	0.212	8570.0	3.067
3980	1.259	0.00200	100.0	2.513	3250	1.457	0.204	8270.0	3.077
3970	1.257	0.00205	102.0	2.519	3240	1.465	0.195	7820.0	3.086
3960	1 256	0 00207	103 0	2 525	3230	1 471	0 183	7320.0	3,096
3300	1.250	0.00210	104.0	2.020	7220	1 476	0.177	6970 0	7 106
3950	1.255	0.00210	104.0	2.332	3220	1.4/0	0.1/5	6400.0	3,100
3940	1.254	0.00212	105.0	2.538	3210	1.480	0.163	6400.0	3.115
3930	1.252	0.00215	106.0	2.545					
3920	1,250	0.00219	108.0	2.551	3200	1.483	0.153	6010.0	3.125
3910	1,249	0.00224	110.0	2.558	3190	1.486	0.144	5610.0	3.135
0010					3180	1 487	0.134	5210.0	3 145
7000	1 247	0 00227	111 0	2 564	7170	1 407	0 125	4840 0	7 155
3900	1.24/	0.00227	111.0	2.304	3170	1.407	0.125	4840.0	3.133
3890	1.246	0.00231	113.0	2.5/1	3160	1.48/	0.117	4550.0	3.105
3880	1.243	0.00234	114.0	2.577	3150	1.486	0.110	4320.0	3.175
3870	1.241	0.00239	116.0	2.584	3140	1.485	0.0994	3890.0	3.185
3860	1.240	0.00243	118.0	2.591	3130	1.482	0.0920	3620.0	3,195
3850	1 238	0 00248	120 0	2 597	3120	1 479	0 0855	3390 0	3 205
7040	1 275	0.00240	124.0	2.50/	7110	1 477	0.0000	7120.0	7 215
3840	1.235	0.00257	124.0	2.004	3110	1.4//	0.0/05	3120.0	3.215
3830	1.232	0.00270	130.0	2.011					
3820	1.230	0.00298	143.0	2,618	3100	1.474	0.0716	2840.0	3.226
3810	1.227	0.00330	158.0	2.625	3090	1.472	0.0653	2590.0	3.236
					3080	1.467	0.0600	2390.0	3.247
3800	1 224	0 00402	192 0	2 632	3070	1 464	0.0550	2190 0	3 257
7700	1 221	0.00472	200 0	2 6 7 0	7060	1 461	0.0530	2130.0	7 260
3790	1.221	0.00437	200.0	2.039	3000	1.401	0.0304	2010.0	3.200
3780	1.218	0.00482	229.0	2.046	3050	1.457	0.0462	1840.0	3.279
3770	1.214	0.00536	254.0	2.653	3040	1.454	0.0422	1680.0	3.289
3760	1.210	0.00627	296.0	2.660	3030	1.451	0.0385	1530.0	3.300
3750	1.205	0.00732	345.0	2.667	3020	1.448	0.0348	1390.0	3.311
3740	1 200	0 00855	402 0	2 674	3010	1 111	0 0315	1260 0	3 322
3740	1.105	0.00055	400.0	2.074	3010	1.444	0.0315	1200.0	3.322
3/30	1.195	0.0105	490.0	2.001					
3720	1.191	0.0127	593.0	2.688	3000	1.441	0.0297	1120.0	3,333
3710	1.185	0.0145	677.0	2.695	2990	1.437	0.0279	1050.0	3.344
					2980	1.434	0.0262	980.0	3.356
3700	1,179	0.0164	762.0	2.703	2970	1.431	0.0250	933-0	3.367
3600	1 170	0 0196	867 D	2 710	2060	1 427	0 0220	820 O	2 270
3030	1.1/2	0.0100	004.0	2.710	2000	1 405	0.0223	700.0	3.3/0
3080	1.100	0.0205	940.0	2./17	2950	1.425	0.0210	/80.0	3.390
3670	1.157	0.0282	1300.0	2.725	2940	1.421	0.0193	713.0	3.401
3660	1.149	0.0380	1930.0	2.732	2930	1.418	0.0177	650.0	3.413
3650	1.144	0.0462	2270.0	2.740	2920	1,415	0.0163	599.0	3.425
3640	1,139	0.0548	2600.0	2.747	2910	1.413	0.0151	551.0	3 436
2620	1 1 7 0	0 0640	2070 0	2007EE	2010	1.110	0.0101	551.0	51450
3030	1.130	0.0049	47/0.0	2./30	2000	1 110	0.0170	<b>F A H</b>	
3020	1.138	0.0/44	3340.0	2./62	2900	1.410	0.0138	503.0	3.448
3610	1.139	0.0836	3720.0	2.770	2890	1.407	0.0128	466.0	3.460

,

,

TABLE 1. (continued)			TABLE 1. (continued)						
ν	n(v)		α(ν)	λ	ν	n(v)	<i>k</i> (ν)	α(ν)	λ
2880	1.405	0.0118	428.0	3,472	2180	1.327	0.0145	396.0	4.587
2870	1 403	0.0110	398.0	3,484	2170	1.327	0.0149	406.0	4.608
2860	1 400	0 0101	363.0	3,497	2160	1.327	0.0152	412.0	4.630
2800	1 209	0.00041	337 0	3 509	2150	1.327	0.0154	417.0	4.651
2830	1 706	0.00941	700 0	2 521	2140	1 326	0 0156	A10 0	4 673
2840	1,390	0,00000	303.0	7 574	2140	1 726	0.0157	410.0	4.605
2830	1,394	0.00807	287.0	2.234	2130	1 774	0.0157	419.0	4.033
2820	1.392	0.00737	261.0	3,540	2120	1.320	0.0157	416.0	4./1/
2810	1.390	0,0085	241.0	3.335	2110	1.525	0.0137	410.0	4.755
2800	1.388	0.00625	220.0	3,571	2100	1.325	0.0155	410.0	4.762
2790	1.387	0.00579	203.0	3,584	2090	1.325	0.0155	402.0	4./05
2780	1.385	0.00538	188.0	3.59/	2080	1.325	0.0151	394.0	4.000
2770	1.383	0,00506	176.0	3,610	2070	1.325	0.0148	380.0	4.831
2760	1.382	0.00473	164.0	3.623	2060	1.325	0.0146	3/7.0	4.854
2750	1.379	0,00449	155.0	3.636	2050	1.324	0.0143	368.0	4.878
2740	1.378	0.00424	146.0	3.650	2040	1.324	0.0140	359.0	4.902
2730	1.377	0.00405	139.0	3.663	2030	1.323	0.0137	349.0	4.926
2720	1.375	0.00389	133.0	3.676	2020	1.322	0.0133	338.0	4.950
2710	1.374	0.00376	128.0	3.690	2010	1.322	0.0129	327.0	4.975
2700	1.372	0.00363	123.0	3.704	2000	1.321	0.0126	317.0	5.000
2690	1.371	0.00355	120.0	3.717	1990	1.320	0.0122	306.0	5.025
2680	1.370	0.00347	117.0	3.731	1980	1.319	0.0118	294.0	5.051
2670	1.369	0.00340	114.0	3.745	1970	1.318	0.0115	284.0	5.076
2660	1.367	0.00335	112.0	3.759	1960	1.318	0,0110	272.0	5.102
2650	1.366	0.00336	112.0	3.774	1950	1.317	0.0108	264.0	5.128
2640	1.365	0.00335	111.0	3.788	1940	1.316	0.0105	255.0	5.155
2630	1.363	0.00339	112.0	3.802	1930	1.314	0.0103	249.0	5.181
2620	1.361	0.00340	112.0	3.817	1920	1.313	0.0101	244.0	5.208
2610	1.361	0.00348	114.0	3.831	1910	1.311	0.0100	240.0	5.236
2600	1.360	0.00352	115.0	3.846	1900	1.310	0.00993	237.0	5.263
2590	1,358	0.00363	118.0	3.861	1890	1.308	0.00990	235.0	5.291
2580	1.358	0.00370	120.0	3,876	1880	1.306	0.00995	235.0	5.319
2570	1.357	0.00378	122.0	3.891	1870	1.304	0.0100	236.0	5.348
2560	1.355	0.00389	125.0	3,906	1860	1.302	0.0102	238.0	5.376
2550	1.354	0.00399	128.0	3.922	1850	1.299	0.0104	242.0	5.405
2540	1 353	0.00410	131.0	3,937	1840	1.297	0.0107	247.0	5.435
2530	1 352	0 00422	134 0	3 953	1830	1.294	0.0110	253.0	5,464
2530	1 751	0.00422	137 0	3 968	1820	1.291	0.0115	262.0	5.495
2510	1.350	0.00450	142.0	3.984	1810	1.288	0.0120	274.0	5.525
2500	1.349	0,00465	146.0	4.000	1800	1,285	0.0128	289.0	5.556
2490	1.348	0.00479	150.0	4.016	1790	1.282	0.0138	311.0	5.587
2490	1 7/9	0.00494	154 0	4 032	1780	1.278	0.0150	336.0	5.618
2480	1 747	0.00512	159.0	4.032	1770	1 275	0 0166	370.0	5.650
2470	1 746	0.00512	164 0	4.045	1760	1 271	0.0185	409 0	5 682
2400	1.340	0.00531	160.0	4.003	1750	1 267	0.0205	451 0	5 714
2450	1,343	0.00549	103.0	4.002	1740	1 262	0.0200	520 0	5 747
2440	1.344	0.00508	174.0	4.050	1770	1 256	0.0242	637 0	5 780
2430	1.344	0.00580	19.0	4.115	1720	1.250	0.0233	734 0	5 914
2420	1.343	0.00631	191.0	4.132	1710	1.247	0.0429	947.0	5.848
2400	1,341	0,00653	197.0	4.167	1700	1.242	0.0544	1200.0	5,882
2390	1.340	0.00673	202.0	4.184	1690	1.241	0.0688	1515.0	5.917
2380	1 340	0.00696	208.0	4.202	1680	1.241	0.0840	1840.0	5.952
2370	1 220	0.00030	215 0	1 210	1670	1.247	0.1021	2175.0	5.988
23/0	1.330	0.00722	213.0	4.213	1660	1 265	0.117	2430 0	6 024
2300	1.33/	0.00749	222.0	4.237	1650	1 280	0.130	2670 0	6 061
2350	1.33/	0.00//9	230.0	4.233	1640	1.205	0.130	2070.0	6 008
2340	1.335	0.00806	237.0	4.2/4	1670	1.311	0.132	2738.0	6 175
2330	1.334	0.00833	244.0	4.292	1630	1.332	0.124	2300.0	6.133
2320	1.334	0.00864	252.0	4.310	1620	1.349	0.100	2139.0	0.1/3
2310	1.333	0,00896	260.0	4.329	1610	1.354	0.0880	1760.0	0,211
2300	1.332	0.00927	268.0	4.348	1600	1.356	0,0740	1465.0	6.250
2290	1.332	0.00966	278.0	4.367	1590	1.354	0.0618	1200.0	6.289
2280	1.331	0.0100	287.0	4.386	1580	1.350	0.0535	1025.0	6.329
2270	1,330	0.0104	297.0	4,405	1570	1.345	0.0484	934.0	6.369
2260	1.330	0.0108	308.0	4.425	1560	1.341	0.0447	863.0	6.410
2250	1.330	0.0112	318.0	4.444	1550	1.337	0.0420	806.0	6.452
2240	1.329	0.0117	330.0	4 464	1540	1.333	0.0398	758.0	6.494
2230	1 320	0.0122	342.0	4.484	1530	1.330	0.0383	726.0	6.536
2230	1 220	0.0122	372.0 357 A	1 EUE	1520	1.326	0.0373	703 0	6.579
2210	1.328	0.0131	364.0	4.505	1510	1.324	0.0370	683.0	6.623
2200	1 329	0, 01 36	376.0	4.545	1500	1.322	0,0366	666.0	6.667
2190	1.327	0.0140	386.0	4.566				•	/
	/								

-

TABLE 1. (continued)			TABLE 1. (continued)						
ν	n(v)	<i>k</i> (ν)	α(ν)	λ	v	n(v)	k(v)	α(ν)	λ
1490	1.320	0.0363	652.0	6.711	780	1.142	0.292	2883.0	12.821
1480	1.319	0.0360	638.0	6.757	770	1,157	0.305	2969.0	12.987
1470	1.318	0.0357	624.0	6.803	760	1.171	0.317	3040.0	13.158
1460	1,317	0.0355	612.0	6.849	750	1.182	0.328	3100.0	13.333
1450	1.316	0.0352	602.0	6.897	740	1.189	0.338	3150.0	13.514
1440	1,315	0.0350	593.0	6.944	730	1.201	0.347	3192.0	13.699
1430	1.314	0.0347	582.0	6.993	720	1.213	0.356	3231.0	13.889
1420 1410	$1.313 \\ 1.311$	0.0346 0.0343	575.0 564.0	7.042 7.092	710	1.223	0.365	3263.0	14.085
1 4 9 9		0.0740		- 147	700	1.236	0.373	3287.0	14.286
1400	1,310	0.0342	558.0	7.143	690	1.249	0.379	3298.0	14.493
1390	1 309	0.0342	550 0	7.194	680	1.204	0.385	330/.0	14.706
1370	1 307	0.0342	547.0	7.299	670	1.2//	0.392	3308.0	14.923
1360	1,306	0.0342	543.0	7.353	650	1 303	0.397	3307.0	15,132
1350	1.305	0.0342	540.0	7.407	640	1.313	0.408	3291.0	15,625
1340	1.303	0.0342	537.0	7.463	630	1.324	0.412	3276.0	15.873
1330	1.302	0.0342	535.0	7.519	620	1.335	0.417	3259.0	16,129
1320	1.301	0.0342	532.0	7.576	610	1.348	0.420	3234.0	16.393
1310	1.300	0.0344	530.0	7.634	( 00	1 7/1	0.427	7307 0	16 667
1300	1 208	0 0345	530 0	7 692	600	1.361	0.423	3203.0	16.00/
1290	1.296	0.0346	529.0	7.752	590	1,3/2	0.425	3107.0	10.949
1280	1.295	0.0349	528.0	7.813	570	1 396	0.427	3077.0	17.544
1270	1.294	0.0351	527.0	7.874	560	1.407	0,427	3022.0	17.857
1260	1.293	0.0351	526.0	7.937	550	1.419	0.427	2964.0	18.182
1250	1.291	0.0351	525.0	8.000	540	1.431	0.426	2903.0	18.519
1240	1.288	0.0352	524.0	8.065	530	1.441	0.425	2842.0	18.868
1230	1.286	0.0356	524.0	8.130	520	1.451	0.423	2779.0	19,231
1220	1.285	0.0359	523.0 523.0	8,197 8,264	510	1.462	0.421	2709.0	19,608
1210	1.205	0.0001	52510	0.204	500	1.470	0.418	2638.0	20.000
1200	1.281	0.0362	522.0	8.333	490	1.480	0.415	2565.0	20.408
1190	1.279	0.0366	522.0	8.403	480	1.488	0.411	2494.0	20.833
1180	1.2/6	0.0370	523.0	8.4/5	470	1.496	0.408	2423.0	21.277
1160	1.2/4	0.0374	523.0	8.54/	460	1.504	0.404	2347.0	21./39
1150	1 269	0.0378	523.0	8 696	450	1.510	0.401	2280.0	22.222
1140	1.267	0.0387	525.0	8.772	440	1 521	0.397	21/13 0	22.727
1130	1.264	0.0392	527.0	8.850	430	1.527	0.390	2072.0	23.810
1120	1.261	0.0398	529.0	8.929	410	1.532	0.386	2004.0	24.390
1110	1.259	0.0405	532.0	9.009					
1100	1 254	0.0411	F76 0	0 001	400	1.537	0.382	1933.0	25.000
1000	1.250	0.0411	530.0	9.091	390	1.541	0.377	1862.0	25.641
1090	1 240	0.0417	546.0	9.1/4	380	1.545	0.3/2	1793.0	20.310
1070	1.246	0.0434	553.0	9.346	370	1.549	0.300	1/24.0	27.027
1060	1.242	0.0443	561.0	9.434	350	1 552	0.359	1593.0	28.571
1050	1.238	0.0453	571.0	9.524	340	1.552	0.356	1532.0	29.412
1040	1.234	0,0467	583.0	9.615	330	1.550	0.352	1472.0	30,303
1030	1.230	0.0481	596.0	9.709	320	1.546	0.353	1432.0	31,250
1020	1.224	0.0497	613.0	9.804	310	1.543	0.357	1401.0	32.258
1010	1.220	0.515	631.0	9.901	300	1 541	0 361	1374 0	22 222
1000	1.214	0.0534	651.0	10.000	290	1.539	0.368	1351.0	34,483
990	1.208	0.0557	673.0	10.101	280	1.537	0.375	1331.0	35.714
980	1.202	0.0589	702.0	10.204	270	1.534	0.385	1317.0	37.037
970	1.194	0,0622	733.0	10.309	260	1.532	0.398	1311.0	38.462
960	1.189	0.0661	770.0	10.417	250	1.529	0.414	1310.0	40.000
950	1.181	0.0707	817.0	10.526	240	1.525	0.436	1323.0	41.667
940	1.174	0.0764	866.0	10.638	230	1.528	0.469	1364.0	43.478
930	1.168	0.0828	927.0	10.753	220	1.542	0.505	1407.0	45.455
920	1.162	0,0898	993.0	10.870	210	1.567	0.539	1434.0	47.619
910	1.156	0.0973	1064.0	10.989	200	1.600	0.571	1445.0	50.000
900	1.149	0,107	1165.0	11.111	190	1.640	0.597	1437.0	52.632
890	1.143	0.118	1270.0	11.236	180	1.689	0.618	1412.0	55.556
880	1.139	0.130	1396.0	11.364	1/0	1.746	0.629	1358.0	58.824
870	1.135	0.144	1533.0	11.494	150	1.801	0.022	1200.0	02.500
860	1.132	0.159	1682.0	11.628	140	1.848	0.008	1105.0	71 420
850	1.132	0.176	1833.0	11.765	140	1 020	0.333	067 0	74 077
840	1.131	0.192	1987.0	11.905	120	1,929	0.577	907.0 877 n	10.923 QZ 222
830	1.132	0.208	2143.0	12.048	110	1.982	0.532	773.0	80° 800
820	1.130	0.226	2309.0	12.195		******	0.002	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	20.203
810	1.130	0.243	2467.0	12.346	100	1.997	0.507	678.0	100.000
000	1 174	0 260	2610 0	12 500	90	2.000	0.487	594.0	111.111
700	1,134	0.200	2018.U 2760 0	12.500	80	2.010	0.466	509.0	125.000
/ 30	1.130	0.2//	2/00.0	14,030					

ν	n(v)	<i>k</i> (ν)	α(ν)	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

TABLE 1. (continued)

Frequencies v are expressed in waves per centimeter  $(cm^{-1})$ , n(v) and imaginary k(v) parts of the dielectric constant N = n + ik are dimensionless, the Lambert absorption coefficient  $\alpha(v)$  defined by the relation  $I = I_0 \exp[-\alpha x]$  is expressed in waves per centimeter  $(cm^{-1})$ , and wavelengths  $\lambda$  are given in micrometers (um). The values of n(v), k(v), and  $\alpha(v)$  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  $\alpha$  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  $\alpha$  versus  $\nu$  in Figure 3; values of  $\alpha$  given in the plot are based entirely on direct measurements and thus differ slightly from  $\alpha$  values calculated from our averaged values of k. The values of  $\alpha$  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  $\alpha$  at frequency intervals of 10 cm<sup>-1</sup> over most of the range between 5000 and 10 cm<sup>-1</sup>; 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 *Zolatarev 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<sup>-1</sup> but are in somewhat serious disagreement in the vicinity of the strong absorption band near 3400 cm<sup>-1</sup>, 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  $2800-800 \text{ cm}^{-1}$  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<sup>-1</sup> the French values are generally greater than ours, and the Russian values generally lower; through the entire region below 800 cm<sup>-1</sup> 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<sup>-1</sup> 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<sup>-1</sup> range, where the Russian values are much lower than ours. In the range 3200-400 cm<sup>-1</sup> 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<sup>-1</sup> the earlier results are lower than ours by 1.5%. At frequencies below 400 cm<sup>-1</sup> we have continued satisfactory agreement with the Russians, who based their values in this region on published results of others including Draegert et al. [1966] which are shown by the points in Figures 1 and 3 for v  $< 200 \text{ cm}^{-1}$ . 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.

Acknowledgments. We wish to acknowledge our debt to all the participants in our laboratory studies and to generous support by the Office of Naval Research. We should also like to express our appreciation to the late John Chamberlain and his associates at the NPL and to Peter Ray for their generous cooperation.

#### REFERENCES

- Davies, M., G. W. Pardoe, J. Chamberlain, and H. A. Gebbie, Submillimetre- and millimetre-wave absorption of some polar and non-polar liquids, *Trans. Faraday Soc.*, 66, 273, 1970.
- Draegert, D. A., N. W. B. Stone, B. Curnutte, and D. Williams, Farinfrared spectrum of liquid water, J. Opt. Soc. Amer., 56, 64, 1966.
- Hale, G. M., M. R. Querry, A. N. Rusk, and D. Williams, Influence of temperature on the spectrum of water, J. Opt. Soc. Amer., 62, 1103, 1972.
- Hobson, D. E., and D. Williams, Infrared spectral reflectance of sea water, *Appl. Opt.*, 10, 2372, 1971.
- Irvine, W. M., and J. B. Pollack, Infrared optical properties of water and ice spheres, *Icarus*, 8, 324, 1968.
- Palmer, K. F., and D. Williams, Optical properties of water in the near infrared, J. Opt. Soc. Amer., 64, 1107, 1974.
- Pontier, L., and C. Dechambenoy, Mesure du pouvoir reflecteur de l'eau; Ann. Geophys., 21, 462, 1965.
- Pontier, L., and C. Dechambenoy, Détermination des constantes optiques de l'eau, Ann. Geophys., 22, 633, 1966.
- Querry, M. R., B. Curnutte, and D. Williams, Refractive index of water in the infrared, J. Opt. Soc. Amer., 59, 1299, 1969.
- Ray, P. S., Broadband complex refractive indices of ice and water, Appl. Opt., 11, 1836, 1972.
- Robertson, C. W., and D. Williams, Lambert absorption coefficients of water in the infrared, J. Opt. Soc. Amer., 61, 1316, 1971.
- Robertson, C. W., B. Curnutte, and D. Williams, The infra-red spectrum of water, *Mol. Phys.*, 26, 183, 1973.
- Rusk, A. N., D. Williams, and M. R. Querry, Optical constants of water in the infrared, J. Opt. Soc. Amer., 61, 895, 1971.
- Zafar, M. S., J. B. Hasted, and J. Chamberlain, Submillimetre-wave dielectric dispersion in water, *Nature London Phys. Sci.*, 243, 106, 1973.
- Zolatarev, V. M., B. A. Mikhailov, L. I. Aperovich, and S. I. Popov, Dispersion and absorption of water in the infrared, *Opt. Spectrosk.*, 27, 790, 1969. (*Opt. Spectrosc.*, Engl. Transl., 27, 430, 1969.)

(Received September 11, 1974; accepted November 25, 1974.)