# Optical properties of water in the near infrared*

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The real $n(\nu)$ and imaginary $k(\nu)$ parts of the complex refractive index $\hat{N} = n + ik$ of water at 27 °C have been determined from measurements of spectral reflectance at near-normal incidence and from measurements of the transmittance of water in carefully constructed absorption cells. Values of $n(\nu)$ are reported in graphical and tabular form for the spectral region 3800–27 800 $cm^{-1}$; values of the Lambert absorption coefficient $\alpha(\nu)$ are presented graphically and in tabular form, along with $k(\nu)$ for the region 3800–14 500 $cm^{-1}$. Upper limits of $k(\nu)$ are established for the region 14 500–27 800 $cm^{-1}$. The results are compared with earlier studies.

Index Headings: Refractive index; Absorption; Water; Reflectance; Infrared; Spectra.

Since the time of the Irvine–Pollack survey,[1] which emphasized the dearth of reliable values of the optical constants $\hat{N}(\nu) = n(\nu) + ik(\nu)$ for water, there have been numerous studies[2–8] of the spectrum of water in the frequency range below 4000 $cm^{-1}$. In the present paper, we report new results for $n(\nu)$ in the range 3800–27 800 $cm^{-1}$; these are based primarily on reflectance measurements. We also give values for the Lambert absorption coefficient $\alpha(\nu)$ based on transmittance measurements and list the corresponding values of $k(\nu) = \lambda\alpha(\nu)/4\pi$.

In the course of our work, we employed a double-pass prism monochromator equipped with a type DF-2 glass prism calibrated in terms of atomic emission lines in the visible region and water-vapor bands in the near infrared. A Reeder thermocouple was employed as a detector. We used a carefully monitored tungsten iodide lamp as a source.

## REFLECTANCE MEASUREMENTS

The general procedures that we employed for the near-normal reflectance measurements were similar to those described in earlier reports[5,6]; we measured the ratio of the reflectance of water at 27°C to that of a reference mirror, the absolute reflectance of which was determined in an auxiliary experiment by use of a Strong reflectometer. Because water is relatively transparent in the visible and near infrared, we used water samples contained in a glass optical horn, the exterior of which was painted dull black in order to minimize spurious reflections from the walls of the container; the curved horn was constructed of 6-cm-o.d. Pyrex, had a tapered length of 16 cm, and ended in a point. We were unable to detect radiant flux reflected from the interior of the horn. As in the earlier work, we used a rapidly rotating sector disk when measuring radiant flux from the reference mirror; use of such a calibrated optical attenuator eliminates the necessity of undesirable changes of amplifier gain-control adjustments.

A plot of measured fractional spectral reflectance $R(\nu)$ as a function of wave number is given in the curve labeled $R$ in Fig. 1; the curve has a slope that is small and nearly constant over most of the indicated spectral range. However, the spectral reflectance decreases rapidly in the region of 4000 $cm^{-1}$, owing to the proximity of the strong fundamental water bands near 3400 $cm^{-1}$. The reflectance curve shown in the figure is the smooth curve drawn through points representing many individual determinations; we believe that the fractional uncertainty $\delta R/R$ is 0.02 over most of the range, where $\delta R$ includes the standard deviation of the measurements of samples and reference mirror and the restrictions imposed by the calibration of the sector wheels.

## TRANSMITTANCE MEASUREMENTS

In order to obtain accurate values of the Lambert absorption coefficient $\alpha(\nu)$, it is necessary to have accurately measured values of the thickness $x$ of the absorbing layers of water and to eliminate the effects of reflection and absorption by the windows of the absorption cell.[7] In the present study, in the 5500–14 500 $cm^{-1}$ region, we employed a set of precision absorption cells

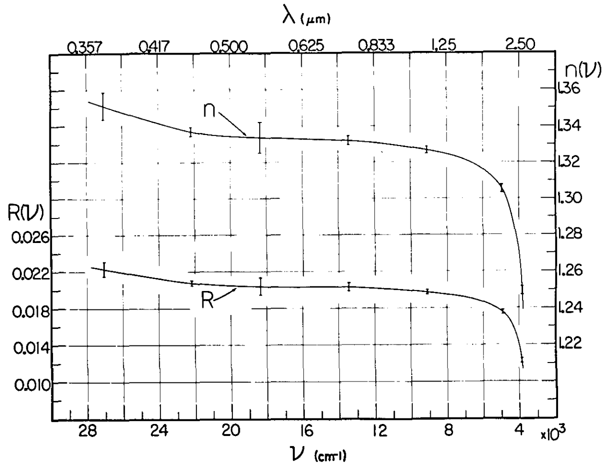


FIG. 1. Curve $R$ gives fractional reflectance at near-normal incidence as a function of frequency in $cm^{-1}$. Curve $n$ gives a plot of refractive index $n(\nu)$ as a function of frequency.

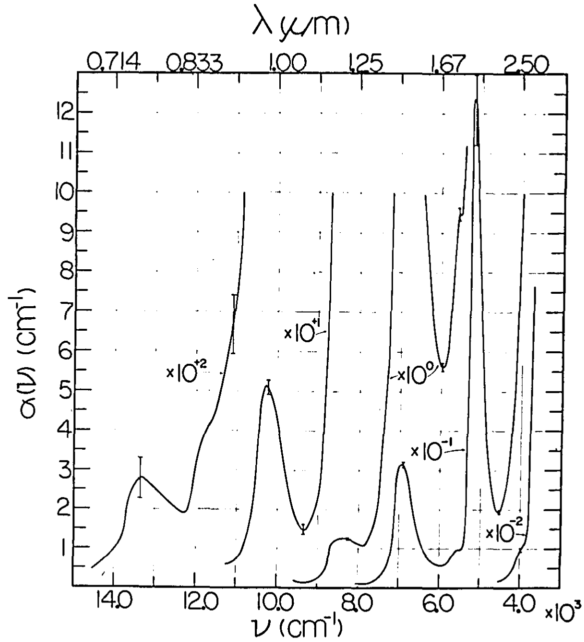


FIG. 2. Lambert absorption coefficient $\alpha(\nu)$ as a function of frequency expressed in $cm^{-1}$.

of Infrasil quartz that provided path lengths of 1, 2, 5, 10, 20, 30, 40, and 50 mm; these cells, which were supplied by Markson Science, Inc., were fabricated from a single batch of fused silica in order to avoid differences of optical properties of the cell windows. In measuring the transmittance of water samples in these cells, we used a collimated beam of radiant flux.

The measured spectral transmittance $T(\nu)$ of water in an absorption cell of length $x$ is given by the expression

$$T(\nu)=[1-R'(\nu)][1-A'(\nu)]\exp[-\alpha(\nu)x], \quad (1)$$

where $R'(\nu)$ is fraction of the incident radiant flux reflected from the inner and outer window surfaces of the filled cells and $A'(\nu)$ is the fraction of the flux absorbed by the windows. By taking the ratios of the spectral transmittances of water-filled cells of different lengths, we eliminated the influence of $R'(\nu)$ and $A'(\nu)$ and obtained accurate values of the Lambert coefficient $\alpha(\nu)$.

In the range 3800–5500 $cm^{-1}$, we used a Beckmann variable-path-length cell with fused-silica windows; the path length can be accurately and continuously adjusted in the range 6 mm to 30 $\mu$m.

The values of the Lambert absorption coefficient that we derived from our measurements are shown in Fig. 2. As indicated in the figure, the values of $\alpha(\nu)$ at 14 000 and 4000 $cm^{-1}$ differ by a factor of $10^4$; uncertainty bars for various spectral regions are indicated in the figure. Values of $\alpha(\nu)$ are listed in Table I. In arriving at each value of $\alpha(\nu)$ given in the table we measured the transmittance of 6 to 12 absorbing layers that had different thicknesses $x$. The fractional uncertainty $\delta\alpha(\nu)/\alpha(\nu)$, based on the standard deviation $\delta\alpha(\nu)$, is fairly small in the range 1000–5500 $cm^{-1}$; at higher frequencies $\alpha(\nu)$ becomes smaller and the measured absorptance $A(\nu)=1-T(\nu)$ of the water for the absorption cells employed becomes too small to provide accurate values of $\alpha(\nu)$; thus, the fractional uncertainty increases. At frequencies less than 4000 $cm^{-1}$, the values of $\alpha(\nu)$ are so great that even with the thinnest cell employed $A(\nu)$ becomes too great for accurate determination of $\alpha(\nu)$; for these low frequencies, the wedge-cell techniques described by Robertson[7] are to be preferred.

## OPTICAL CONSTANTS

Values of the imaginary part $k(\nu)$ of the complex refractive index based on measured values of $\alpha(\nu)$ are listed in Table I. A plot of $k(\nu)$ vs $\nu$ for the region covered in the present study joins smoothly with the curve based on Robertson's results[7] for lower frequency ranges.

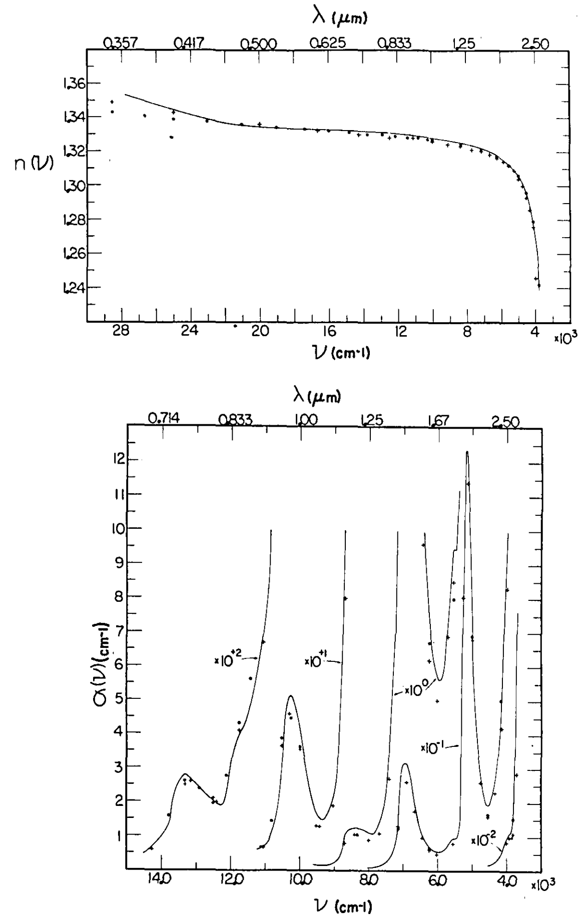


FIG. 3. The continuous curve in the upper panel gives values of $n(\nu)$ obtained in the present study; the continuous curve in the lower panel gives values of $\alpha(\nu)$ obtained in the present study. The crosses indicate values tabulated by Irvine and Pollack; the circles indicate values tabulated by Hale and Querry.

TABLE I. Optical constants of liquid water from the near infrared to the ultraviolet.

| $\nu$ in $cm^{-1}$ | $\alpha(\nu)$ in $cm^{-1}$ | $k(\nu)$ | $n(\nu)$ | $\lambda$ in $\mu m$ |
|---|---|---|---|---|
| 3 800 | $1.93\times10^{2}$ | $4.04\times10^{-3}$ | 1.239 | 2.632 |
| 3 900 | 1.11 | 2.26 | 1.257 | 2.564 |
| 4 000 | $9.57\times10^{1}$ | 1.90 | 1.268 | 2.500 |
| 4 100 | 6.35 | 1.23 | 1.276 | 2.439 |
| 4 200 | 4.18 | $7.92\times10^{-4}$ | 1.281 | 2.381 |
| 4 300 | 2.93 | 5.42 | 1.285 | 2.326 |
| 4 400 | 2.30 | 4.16 | 1.291 | 2.273 |
| 4 550 | 1.93 | 3.38 | 1.296 | 2.198 |
| 4 700 | 2.36 | 4.00 | 1.301 | 2.128 |
| 4 800 | 3.10 | 5.14 | 1.303 | 2.083 |
| 4 900 | 4.50 | 7.31 | 1.305 | 2.041 |
| 5 000 | 6.92 | $1.10\times10^{-3}$ | 1.306 | 2.000 |
| 5 100 | $1.09\times10^{2}$ | 1.70 | 1.307 | 1.961 |
| 5 190 | 1.24 | 1.90 | 1.309 | 1.927 |
| 5 300 | $5.75\times10^{1}$ | $8.63\times10^{-4}$ | 1.310 | 1.887 |
| 5 400 | 1.08 | 1.59 | 1.311 | 1.852 |
| 5 500 | $9.44\times10^{0}$ | 1.37 | 1.312 | 1.818 |
| 5 550 | 9.48 | 1.36 | 1.312 | 1.802 |
| 5 600 | 9.18 | 1.30 | 1.313 | 1.786 |
| 5 700 | 7.60 | 1.06 | 1.314 | 1.754 |
| 5 800 | 6.23 | $8.55\times10^{-5}$ | 1.314 | 1.724 |
| 5 900 | 5.65 | 7.62 | 1.315 | 1.695 |
| 6 000 | 5.65 | 7.49 | 1.316 | 1.667 |
| 6 100 | 6.07 | 7.92 | 1.317 | 1.639 |
| 6 200 | 6.80 | 8.73 | 1.318 | 1.613 |
| 6 300 | 8.07 | $1.02\times10^{-4}$ | 1.318 | 1.587 |
| 6 400 | 9.68 | 1.20 | 1.319 | 1.563 |
| 6 500 | $1.21\times10^{1}$ | 1.48 | 1.319 | 1.538 |
| 6 600 | 1.56 | 1.88 | 1.320 | 1.515 |
| 6 700 | 2.17 | 2.58 | 1.320 | 1.493 |
| 6 800 | 2.85 | 3.34 | 1.321 | 1.471 |
| 6 930 | 3.17 | 3.64 | 1.321 | 1.443 |
| 7 000 | 3.10 | 3.52 | 1.321 | 1.429 |
| 7 100 | 2.15 | 2.41 | 1.322 | 1.408 |
| 7 200 | $9.13\times10^{0}$ | 1.01 | 1.322 | 1.389 |
| 7 300 | 5.45 | $5.94\times10^{-5}$ | 1.323 | 1.370 |
| 7 400 | 3.87 | 4.16 | 1.323 | 1.351 |
| 7 500 | 2.25 | 2.39 | 1.323 | 1.333 |
| 7 600 | 1.67 | 1.75 | 1.324 | 1.316 |
| 7 700 | 1.34 | 1.38 | 1.324 | 1.299 |
| 7 800 | 1.13 | 1.15 | 1.324 | 1.282 |
| 7 900 | 1.07 | 1.08 | 1.324 | 1.266 |
| 8 000 | 1.11 | 1.10 | 1.325 | 1.250 |
| 8 100 | 1.17 | 1.15 | 1.325 | 1.235 |
| 8 200 | 1.22 | 1.18 | 1.325 | 1.220 |
| 8 300 | 1.25 | 1.20 | 1.325 | 1.205 |
| 8 400 | 1.25 | 1.18 | 1.325 | 1.190 |
| 8 500 | 1.23 | 1.15 | 1.326 | 1.176 |
| 8 600 | 1.18 | 1.09 | 1.326 | 1.163 |
| 8 700 | $9.70\times10^{-1}$ | $8.87\times10^{-6}$ | 1.326 | 1.149 |
| 8 800 | 5.48 | 4.96 | 1.326 | 1.136 |
| 8 900 | 3.23 | 2.89 | 1.327 | 1.124 |
| 9 000 | 2.32 | 2.05 | 1.327 | 1.111 |
| 9 100 | 1.92 | 1.68 | 1.327 | 1.099 |
| 9 200 | 1.66 | 1.44 | 1.327 | 1.087 |
| 9 350 | 1.48 | 1.26 | 1.328 | 1.070 |
| 9 500 | 1.64 | 1.37 | 1.328 | 1.053 |
| 9 600 | 1.90 | 1.57 | 1.328 | 1.042 |
| 9 700 | 2.31 | 1.90 | 1.328 | 1.031 |
| 9 800 | 2.85 | 2.31 | 1.328 | 1.020 |
| 9 900 | 3.51 | 2.82 | 1.328 | 1.010 |
| 10 000 | 4.16 | 3.31 | 1.328 | 1.000 |
| 10 100 | 4.69 | 3.70 | 1.328 | 0.990 |
| 10 200 | 5.02 | 3.92 | 1.328 | 0.980 |
| 10 280 | 5.14 | 3.98 | 1.328 | 0.973 |
| 10 400 | 4.71 | 3.60 | 1.328 | 0.962 |
| 10 500 | 3.22 | 2.44 | 1.328 | 0.952 |
| 10 600 | 2.14 | 1.61 | 1.329 | 0.943 |
| 10 700 | 1.58 | 1.18 | 1.329 | 0.935 |
| 10 800 | 1.19 | $8.77\times10^{-7}$ | 1.329 | 0.926 |
| 11 000 | $7.50\times10^{-2}$ | 5.43 | 1.329 | 0.909 |
| 11 200 | 6.09 | 4.33 | 1.329 | 0.893 |
| 11 400 | 5.06 | 3.53 | 1.330 | 0.877 |
| 11 600 | 4.28 | 2.94 | 1.330 | 0.862 |
| 11 800 | 3.87 | 2.61 | 1.330 | 0.847 |
| 12 000 | 3.08 | 2.04 | 1.330 | 0.833 |
| 12 200 | 1.99 | 1.30 | 1.330 | 0.820 |
| 12 300 | 1.91 | 1.24 | 1.331 | 0.813 |
| 12 400 | 1.95 | 1.25 | 1.331 | 0.806 |
| 12 600 | 2.10 | 1.33 | 1.331 | 0.794 |
| 12 800 | 2.30 | 1.43 | 1.331 | 0.781 |
| 13 000 | 2.51 | 1.54 | 1.331 | 0.769 |
| 13 200 | 2.72 | 1.64 | 1.332 | 0.758 |
| 13 300 | 2.81 | 1.68 | 1.332 | 0.752 |
| 13 400 | 2.75 | 1.63 | 1.332 | 0.746 |
| 13 600 | 2.38 | 1.39 | 1.332 | 0.735 |
| 13 800 | 1.34 | $7.73\times10^{-8}$ | 1.332 | 0.725 |
| 14 000 | $9.8\times10^{-3}$ | 5.6 | 1.332 | 0.714 |
| 14 250 | 6.9 | 3.8 | 1.332 | 0.702 |
| 14 500 | 4.9 | 2.7 | 1.332 | 0.690 |
| 18 000 | | | 1.333 | 0.556 |
| 22 250 | | | 1.337 | 0.449 |
| 24 500 | | | 1.344 | 0.408 |
| 27 800 | | | 1.353 | 0.360 |

Values of the real part $n(\nu)$ of the complex refractive index can be obtained by use of the Fresnel expression for normal-incidence spectral reflectance

$$R=[(n-1)^2+k^2]/[(n+1)^2+k^2]. \quad (2)$$

Over much of the spectral region covered in the present work, $k(\nu)$ is so small that it can be neglected; in this case, $n(\nu)$ can be obtained in excellent approximation from

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

We plot $n(\nu)$ vs $\nu$ in curve $n$ in Fig. 1 and list values of $n(\nu)$ in Table I. The fractional uncertainty $\delta n(\nu)/n(\nu)$ is approximately $\pm0.01$ over most of the spectral region covered.

## DISCUSSION OF RESULTS

The present study covers a region intermediate between the region of extremely high absorption in the infrared and the region of great transparency in the visible and near ultraviolet. A portion of this region was covered in the Irvine–Pollack survey[1]; our results are in much closer agreement with the Irvine–Pollack values in this region than were our earlier results in the intermediate and far-infrared regions.[4–8]

Recently Hale and Querry[9] have made a critical survey of the existing literature dealing with the optical properties of water and have attempted to select a set of best values. In the region of present interest, these authors base their values on the work of

Kondratyev,[10] Curcio and Petty,[11] and Zolatarev *et al.*[3] In Fig. 3, we compare our values of $n$ and $\alpha$, as given by the continuous curves, with the results of the Irvine–Pollack survey given by crosses and the Hale–Querry survey given by circles. In general, there is fair agreement; some of the disagreements can possibly be attributed to slight differences of frequency calibration of the dispersing instruments, rather than to real differences of $n$ and $k$ values.

Although the values of the optical constants that we list in Table I are sufficiently accurate for use in Mie-theory calculations of scattering, more-precise values of $n(\nu)$ in much of the range covered can be obtained from measurements of the angular deviation of beams passing through a hollow prism filled with water. The values of $k(\nu)$ progressively decrease with increasing frequency in the visible region and attain a value of approximately $10^{-9}$ in the 20 000–22 000 $cm^{-1}$ range. Extremely long absorption path lengths must be employed, and extreme care must be taken to avoid spurious effects associated with scattering, if improved values of $k(\nu)$ are to be obtained in the frequency range above 15 000 $cm^{-1}$.

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