

Infrared Intensities of Liquids XX: The Intensity of the OH Stretching Band of Liquid Water Revisited, and the Best Current Values of the Optical Constants of H₂O(l) at 25 °C between 15,000 and 1 cm⁻¹

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The previously reported nonreproducibility of the intensity of the OH stretching band of liquid water has been explored. It was found that it can be eliminated in measurements with the Circle® multiple ATR cell by ensuring that the ATR rod is coaxial with the glass liquid holder. It was also found that normal laboratory temperature variations of a few degrees change the intensity by $\leq \sim 1\%$ of the peak height. A new imaginary refractive index spectrum of water has been determined between 4000 and 700 cm⁻¹ as the average of spectra calculated from ATR spectra recorded by four workers in our laboratory over the past seven years. It was obtained under experimental and computational conditions superior to those used previously, but is only marginally different from the spectra reported in 1989. In particular, the integrated intensities of the fundamentals are not changed significantly from those reported in 1989. The available imaginary refractive index, k , values between 15,000 and 1 cm⁻¹ have been compared. The values that are judged to be the most reliable have been combined into a recommended k spectrum of H₂O(l) at 25 °C between 15,000 and 1 cm⁻¹, from which the real refractive index spectrum has been calculated by Kramers–Kronig transformation. The recommended values of the real and imaginary refractive indices and molar absorption coefficients of liquid water at 25 ± 1 °C are presented in graphs and tables. The real and imaginary dielectric constants and the real and imaginary molar polarizabilities in this wavenumber range can be calculated from the tables. Conservatively estimated probable errors of the recommended k values are given. The precision with which the values can be measured in one laboratory and the relative errors between regions are, of course, far smaller than these probable errors. The recommended k values should be of considerable value as interim standard intensities of liquid water, which will facilitate the transfer of intensities between laboratories.

Index Headings: Water; Infrared intensity; Optical constant; Refractive index.

INTRODUCTION

In 1989 optical constants of H₂O(l) at 22 °C were reported,¹ on the basis of calibrated multiple ATR measurements in this laboratory. The reported values of the real, n , and imaginary, k , refractive indices of H₂O covered the range 9000 to 1250 cm⁻¹, although above 5300 cm⁻¹ the reported k values were all zero, meaning ≤ 0.0003 . The precision of the k values was reported to be “within $\pm 1\%$ of the value below 3300 cm⁻¹, $\pm 3.5\%$ at the peak of the OH stretching band, which is notoriously nonreproducible;^{2,3} and $\sim \pm 5\text{--}10\%$ for k values between 0.002 and 0.009 in the region above 3700 cm⁻¹”.

It was also noted¹ that k values of less than 0.001 were only determined qualitatively.

The nonreproducibility of the OH stretching band was much greater than that observed for other liquids, with methanol⁴ being of particular relevance. This nonreproducibility of the k values had been observed and discussed previously.^{2,3,5,6} Differences of up to 30% have been reported since 1960 (Ref. 3 and citations therein) and differences of up to 8% since 1969 (Refs. 1–3 and 5–7 and citations therein). Zolotarev and Demin³ have attempted to correlate the differences with the method of measurement used—whether transmission, specular reflection from an air/water interface, or attenuated total reflection (ATR)—and have concluded that the three methods yield the same results.

In an effort to seek the origin of this nonreproducibility, a further study was made⁸ in 1989 of the effect of impurities, and of dissolved N₂, O₂, Ar, and CO₂ gases, in the water. The result of this study was summarized⁸ as “There is no effect greater than $\pm 1.5\%$ of either the gas content or the water purity on the intensity of the OH stretching band of water”. Here “water” means water with purity ranging from that of Edmonton drinking water to that of water triply distilled from permanganate or deionized water from a Millipore Super-Q system.⁸

Since that time, several developments in this laboratory have made it desirable to report additional findings about the optical constants and the integrated area under the OH stretching band of liquid water. First, the experimental methods have been improved. Second, the accuracy of the computation of optical constants from ATR spectra has been improved.⁹ Third, several good sets of measurements by different workers now exist in this laboratory, because water is the natural sample to use while learning the technique. Fourth, as part of a study of acetonitrile–water mixtures last year, the current authors measured k values for the OH stretching band that were 5% lower than those measured as part of a study of methanol–water mixtures three years ago. It was clearly necessary to resolve the difficulty, and this has been achieved. The results obtained, and the best current values of the optical constants of the OH stretching band of water, are reported in this paper.

There have been four other significant studies of the optical constants of water since 1990. Marechal¹⁰ has determined the dielectric constant spectra of liquid H₂O, D₂O, and their mixtures, at temperatures between -5 and $+80$ °C from ATR spectra between 5000 and 750 cm⁻¹.

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Marechal presented an extensive analysis of his spectra, but reported no numerical optical or dielectric constants.

Kou et al.¹¹ have determined the optical constants of H₂O at 22 °C from transmission measurements between 4000 and 15,000 cm⁻¹ at 16-cm⁻¹ resolution. They also reported values for water at -8 °C and ice at -25 °C, which will not be discussed further. They used long-path transmission cells, because the absorption is very weak in this region, and compared their results with those reported previously by Palmer and Williams,¹² Downing and Williams,⁶ and Hale and Query.¹³ Good agreement was reported with the results of Palmer and Williams,¹² who also used transmission measurements with long-path cells. It should be noted that Downing and Williams⁶ reported the values of Palmer and Williams¹² above ~3850 cm⁻¹ and those of Robertson and Williams¹⁴ for those regions between 3850 and 1700 cm⁻¹ where the absorption is weak.

Marley et al.¹⁵ used a combination of calibrated ATR measurements and transmission measurements to re-examine the weak absorption between 3300 and 934 cm⁻¹. They reported the Lambert absorption coefficients, from which the k values can be obtained. It is of particular note that these workers have found much smaller values of k near 2500 cm⁻¹ than any previous worker—in particular, much smaller than those of Robertson and Williams,¹⁴ who also used transmission cells with long path-lengths.

Zelmann¹⁶ measured the transmission spectrum of H₂O(l) at temperatures between -5.6 and +81.4 °C over the wavenumber range 450–25 cm⁻¹. He used a cell with thick silicon windows and used ~2-cm⁻¹ resolution, which is sufficiently low to average over the interference fringes from multiple reflections within the windows. As is done in this laboratory,¹⁷ Zelmann used the methods of Jones et al.¹⁸ to compute the optical constants from the transmission spectra. In order to compute the real refractive index by Kramers–Kronig (KK) transformation, and to fit his k spectrum with four Gaussian bands, he added values reported by Afsar and Hasted¹⁹ to the low-wavenumber end of his measurements and those of Draegert et al.²⁰ to extend the high-wavenumber end to ~987 cm⁻¹. Zelmann tabulated values of k and n between 20 and 600 cm⁻¹. Unfortunately, the tabulated k values are the fitted values, not the experimental ones.

Water is such a fundamentally important liquid that it is desirable to present the best results obtained in this laboratory over a period of ten years. This importance is illustrated by the fact that much of the recent interest in its infrared optical constants has been stimulated by the need for accurate calculation of radiative energy balances through the atmosphere. Accordingly, this paper contains a brief account of our recent ATR measurements and conclusions with respect to the OH stretching band. It also contains an evaluation of the literature values of the real and imaginary refractive indices of water between 15,000 and 1 cm⁻¹, and presents the values that are believed to be currently the most reliable. As part of the evaluation process, we have used transmission methods to re-measure the weak absorption between 4000 and 3700 cm⁻¹, as well as that between 3300 and 1700 cm⁻¹, where we sought to test the very small k values reported by Marley et al.¹⁵

METHODS AND RESULTS

The experimental and computational methods have been described in detail.^{1,4,7,9,21}

Experimental and Computational Improvements.

The most important improvement in the experimental method over that used previously for water^{1,8} is that a shorter sample holder was used. The ~6-mm sample holder used previously yields a pATR value close to 2 at the peak of the OH stretching band. Peak pATR values near 1 are less sensitive to noise and instability, and are now obtained in a 3-mm sample holder.

The most important improvement in the computational methods⁹ over those⁷ used in the previous work on water^{1,8} lies in the calculation of the optical constants from the ATR spectrum by an iterative procedure. Part of this procedure^{7,9,21} is to calculate an estimate of the k spectrum from the ATR spectrum and then to Kramers–Kronig transform the k spectrum to obtain the n spectrum. Ideally, the KK transform requires the k spectrum from 0 to infinite wavenumber. This is never available, and, more practically, the KK transform yields an erroneous n spectrum if strong absorption is omitted to low wavenumber of the k spectrum that is available from the ATR spectrum. This is always the case when H₂O(l) is measured with a ZnSe ATR rod, because the latter yields a spectrum only above 700 cm⁻¹ and the intense band due to rotational vibrations in water lies largely below 700 cm⁻¹. To overcome this difficulty it is now possible to extend the k spectrum from ATR, solely for the purpose of the KK transform, by adding the known k spectrum of water below 700 cm⁻¹. Even if the accuracy of this added k spectrum is uncertain, its addition reduces the error in the n spectrum considerably, and this leads to reduced error in the final k spectrum. During the calculation of the optical constant spectra from ATR spectra in the present work, the k spectrum was always extended for the KK transform by adding the k spectrum of Downing and Williams⁶ between 700 and 10 cm⁻¹.

A second significant improvement over the computational methods used previously is that the value of n at the high-wavenumber limit of the data is no longer taken to be constant. When, as in the present work, the KK integral includes all the strong infrared absorption, the value required for the calculation of n at wavenumber $\tilde{\nu}_a$ is the value the real refractive index would have at $\tilde{\nu}_a$ if it were due solely to electronic polarization.²² A simple dispersion equation that provides this value has been determined for water,²² and the appropriate value was used.

Exploration of the Nonreproducibility of the OH Stretching Band. To explore the nonreproducibility of the OH stretching band of water in our experiments, we studied two factors: first, the sample temperature and, second, the reproducibility with which the cell was filled with water.

The temperature of the water samples was previously reported as 22 °C. In fact, the temperature of the samples when equilibrated with the sample compartment of our Bruker IFS 113V spectrometer is 24.5 ± 1 °C, and we now give 25 °C as the sample temperature. The temperature of the sample before it is injected into the cell, which is kept under vacuum *in situ* in the sample compartment, is room temperature, 21 to 22 °C. It was

thought that the sample temperature might not reliably reach 25 °C before the spectra were recorded. This possibility was thought to be a potentially more serious error for water than for other liquids, because the hydrogen bonding is temperature-dependent.

To explore this issue, we held samples at 4, 24.5, or 38 °C before use. The initial sample temperature was measured, and the sample was immediately injected into the Circle®† cell (through a 15-cm length of 1.5-mm diameter Teflon® tubing, 13 cm of which passes through a vacuum). The interferogram collection was started right after the cell was filled, and collection of 64 scans at 4-cm⁻¹ resolution took 1 min. The resulting *k* spectra and their areas are not reported in detail, because the sample temperature is not well known, but the *k* values at the peak of the OH stretching band and the area under the *k* band between 4000 and 2660 cm⁻¹ were always within 1.9% and 1.5%, respectively, of those for the sample held at 24.5 °C. Thus, an initial sample temperature between 20 and 25 °C cannot influence the peak height and area by more than 1% and cannot be responsible for nonreproducibility of the magnitude observed. This conclusion was confirmed for samples with an initial temperature of 22 °C, and is consistent with the measured²³ temperature variation of *k*. It can be noted that the effect on the molar absorption coefficients and imaginary molar polarizabilities²⁴, is even smaller, because the increase in the molar volume offsets the decrease in the *k* values with increasing temperature.

The reproducibility with which the Circle® cell was filled with water was explored. The inside diameter of the liquid holder is only 1.5 mm larger than the outside diameter of the rod, and air bubbles frequently form when the cell is filled with water if the liquid holder is significantly off-center. The remedy, when an air bubble forms regularly in the cell, is to dismantle the cell, clean the rod, and polish it with jeweler's rouge and alcohol, and then reassemble the cell, taking particular care to ensure that the ATR rod and the cylindrical glass liquid holder are coaxial. Once the cell has been assembled correctly, it can be repeatedly refilled with water without bubble formation, provided that it is dried with alcohol and benzene before it is refilled. When no bubbles were visible, the *k* values and the area under the OH stretching band were reproducible to ~1%. Heise and Bittner²⁵ have also identified the formation of bubbles in the cell as an important limitation on the reproducibility of ATR spectra of aqueous solutions.

Recent Spectra with Improved Methods. The improved experimental and computational methods have been used to determine *k* and *n* spectra of water at 25 °C that are independent of those reported previously.¹ Five sets of pATR spectra of water in the short cell, obtained in different years by four different workers, were converted to optical constant spectra. In some cases the set was a single pATR spectrum that was the average of several pATR spectra. The average pATR spectrum was transformed in this work to a single pair of *n* and *k* spectra. In other cases, the set consisted of several pATR spectra, each of which was converted to a pair of *n* and *k* spectra, and the *k* spectra were then averaged. Five *k*

spectra resulted from the five sets of pATR spectra, and they were compared to determine the precision of the *k* values obtained by the ATR method in this laboratory. The agreement was very good, and the five *k* spectra were averaged, unweighted, to give a single final *k* spectrum.

The agreement between the *k* spectra is illustrated by the 95% confidence limits of *k*_{max}, the *k* value at the peak of the OH stretching band, and of the area under the OH stretching band. *k*_{max} was 0.312 with a 95% confidence limit of 0.003, and the area under the *k* spectrum and above the zero ordinate between 4000 and 2660 cm⁻¹ was 123.7 cm⁻¹ with a 95% confidence limit of 0.4 cm⁻¹. For the OH stretching band, the precision of the imaginary refractive index is, thus, 1%, and that of the area is 0.33%.

The precision of the other pronounced band, due to $\tilde{\nu}_2$, the HOH bending vibration at 1640 cm⁻¹, was of the same order, 1.7% for the peak height and 0.9% for the area. For the weaker absorption between 2660 and 1890 cm⁻¹, the precision is about 6% of the *k* value. This result is significantly worse than the value that was estimated for the spectra previously reported,¹ probably in part because of the use of the short cell but mainly because the absorption in this region is too weak to be defined very well by ATR measurements, even with the long cell. Transmission measurements through long-path cells should be much superior in this region.

Comparison with Our Previous Spectra. The imaginary refractive index spectrum of water determined with the short ATR cell in this work is plotted in Fig. 1 together with the spectra determined with the long cell and reported in 1989.^{1,8} The agreement is generally very good. It is ~2% at the peaks of the three bands above 1200 cm⁻¹, but is only ~20% near 2600 cm⁻¹, where *k* is only 0.003.

The new *k* spectrum is about 2% higher at the OH stretching peak. This observation is barely significant, but the new spectrum should be the most reliable in that the measurements near the peak were less sensitive to noise and instability because the pATR values were near 1 instead of 2.

For the OH stretching band, the peak heights and areas in the imaginary refractive index and molar absorption coefficient, *E*_m, spectra are given in Table I, with the peak height in the imaginary molar polarizability,^{4,24} α''_m , spectrum, and the area *C_j* under the $\tilde{\nu}\alpha''_m$ spectrum.

It should be noted that the integrated intensity of the OH stretching band was previously given as the area under the molar conductivity spectrum, $V_m \int \tilde{\nu}\epsilon'' d\tilde{\nu}$, which was 194 ± 4 km mol⁻¹ between 4000 and 2500 cm⁻¹. In order to relate this quantity to the molecular dipole transition moment, one has to use^{1,24} the hypothetical value of the real refractive index that would exist in the region of the band if the band were not present. This value cannot be determined with accuracy,²⁴ and for this and other reasons²⁴ the integrated intensity that is the most useful, and is now used in this laboratory, is $C_j = \int \tilde{\nu}\alpha''_m d\tilde{\nu}$, where the integration is over band *j*. The value of *C_j* calculated from the previously reported¹ spectra over the currently used integration range, 4000 to 2660 cm⁻¹, is 10.2 ± 0.2 km mol⁻¹. The value found in this work is the same, with slightly higher precision, 10.20 ± 0.03 km mol⁻¹ (Table I).

† Trademark of Spectra-Tech Inc.

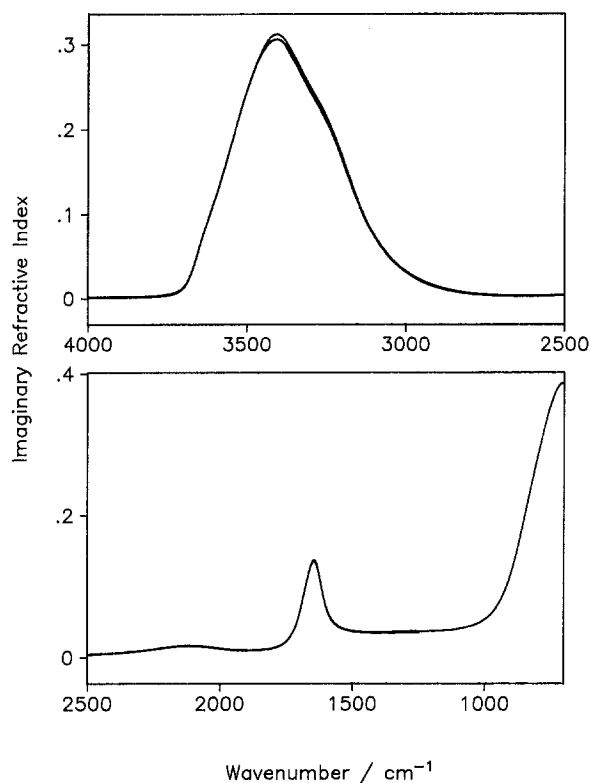


FIG. 1. Imaginary refractive index spectra of $\text{H}_2\text{O}(\text{l})$ at $25 \pm 1^\circ\text{C}$ determined in this laboratory by calibrated multiple attenuated total reflection spectroscopy. Three spectra are shown. Two extend from 4000 to 1250 cm^{-1} and almost coincide. They were reported previously^{1,8} from measurements with the long (6-cm) cell. The spectrum determined in this work with the short (3-cm) cell extends from 4000 to 700 cm^{-1} and is the highest curve at the peak of the OH stretching band.

The intensity of the OH stretching band is not very sensitive to the integration limits used. The value 10.20 km mol^{-1} for the range 4000 to 2660 cm^{-1} is increased by only 0.3% for the range 4000 to 2500 cm^{-1} and is decreased by only 0.4% for the range 3800 to 2700 cm^{-1} .

On the basis of considerations of the temperature control, precision of calibration, and reproducibility of intensity measurements made with different instruments,^{17,26} the uncertainty in the 10.2 km mol^{-1} integrated intensity of the OH stretching band of water is estimated to be $\sim 2\%$.

Dipole Moment Derivatives of $\text{H}_2\text{O}(\text{l})$. The integrated intensity C_j in km mol^{-1} is multiplied by 1.8686 to convert it^{4,24} to $|\delta\mu/\delta Q_j|^2 = 19.06 (\text{D}\text{\AA}^{-1} \text{amu}^{-1/2})^2$, 1.5% smaller than reported previously. From the previous analysis, this yields $|\delta\mu/\delta R| = 3.00 \text{ D}\text{\AA}^{-1}$, the same as the value 3.02 ± 0.03 reported previously.¹ Here $\delta\mu/\delta Q_j$ is the derivative of the molecular dipole moment with respect to the normal coordinate, and $|\delta\mu/\delta R|$ is the derivative of the bond dipole moment with respect to the OH stretching internal coordinate and is assumed to point along the bond.

Thus, the previous discussion¹ of the dipole moment derivative with respect to OH bond displacement requires no change. It is clear from Fig. 1 that the previous discussion¹ for the HOH bending vibration also remains valid.

It should be noted, however, that Luck et al.²⁷ have

TABLE I. Peak height and integrated intensity of the OH stretching band of $\text{H}_2\text{O}(\text{l})$ at 25°C .

	Peak height ^a	Area ^{a,b}
Imaginary refractive index, k	0.312 (3)	123.7 (4)
Molar absorption coefficient, E_m	104.9 (8) ^c	410 (1)
Imaginary molar polarizability, α_m''	0.787 (5) ^c	
$C_j = \int \tilde{\nu} \alpha_m'' d\tilde{\nu}$		10.20 (3)

^a The number in parentheses is the 95% confidence limit in the last digit.

^b The integration limits are 4000 to 2660 cm^{-1} . The unit is cm^{-1} for the area under the k spectrum and km mol^{-1} for the other two areas. The area under E_m is equivalent to $410 \times 10^2 \text{ L mole}^{-1} \text{ cm}^{-2}$.

^c The unit of E_m is $\text{L mole}^{-1} \text{ cm}^{-1}$. The unit of α_m'' is $\text{cm}^3 \text{ mole}^{-1}$.

found that only 87% of the OH bonds in water form OH–O bonds, with the remaining 13% being “free”. The intrinsic intensity of the stretching vibrations of “free” OH bonds is about 7% of that of OH–O bonds,¹ so free bonds contribute less than 1% to the total intensity. Given the result of Luck et al., the $|\delta\mu/\delta Q|^2$ value of the OH–O bonds becomes $19.06 \div 0.87 = 21.91 (\text{D}\text{\AA}^{-1} \text{amu}^{-1/2})^2$, and the $|\delta\mu/\delta R|$ value becomes $3.22 \text{ D}\text{\AA}^{-1}$.

THE BEST CURRENT REFRACTIVE INDEX SPECTRA OF WATER AT 25°C

The imaginary refractive index values of $\text{H}_2\text{O}(\text{l})$ at 25°C reported in the literature are evaluated region by re-

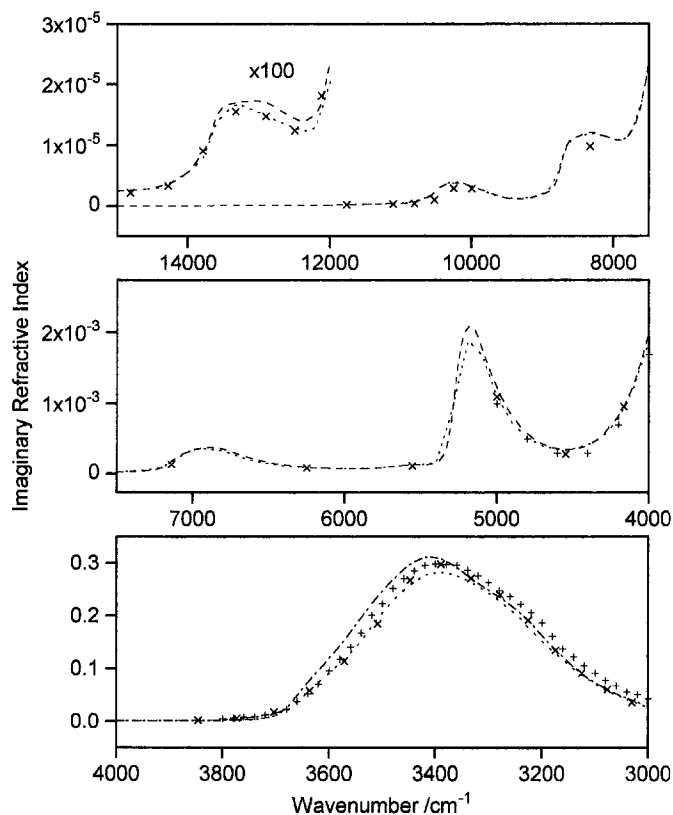


FIG. 2. Imaginary refractive index spectra of $\text{H}_2\text{O}(\text{l})$ between 15,000 and 3000 cm^{-1} determined by different workers. Top two boxes: (dashed line) Kou et al.¹¹ (22°C); (dotted line) Palmer and Williams¹² (27°C); (crosses), Hale and Querry¹³ (25°C); (plus sign) Zolotarev and Demin³ (25°C). Bottom box: As in the other boxes except without the spectrum of Kou et al. and with (dotted line) Downing and Williams⁶ (27°C) instead of Palmer and Williams;¹² (dash-dotted line) this work by ATR (25°C).

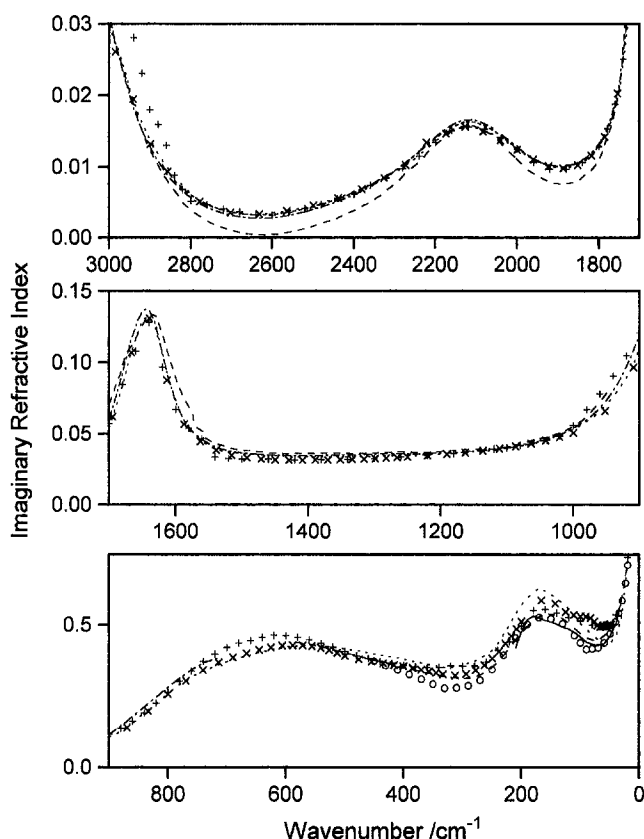


FIG. 3. Imaginary refractive index spectra of $\text{H}_2\text{O}(\text{l})$ between 3000 and 0 cm^{-1} determined by different workers. Top box: (dotted line) Downing and Williams⁶ (27 °C); (crosses) Hale and Querry¹³ (25 °C); (plus sign) Zolotarev and Demin³ (25 °C); (dash-dotted line) this work by ATR (25 °C); (upper dashed line) this work by transmission (25 °C); (lower dashed line) Marley et al.¹⁵ (no temperature given). Middle box: As top box except without this work by transmission. Bottom box: As in middle box except without Marley et al. and with (dashed line) Zelsmann¹⁶ (25 °C); (open circle) Afsar and Hasted¹⁹ (19 °C); (solid line) Afsar and Hasted²⁹ (25 °C).

gion in this section. The values believed to be the most reliable have been assembled into a single k spectrum that is recommended for use. The likely errors in the values reported in the following sections are intentionally conservative. They indicate the probable maximum percent differences between the values recommended and the correct values. They are, of course, considerably larger than the reproducibility with which the values can be measured in one laboratory.

The Region 15,000 to 4000 cm^{-1} . The k values of Kou et al.¹¹ are recommended for this region. The error in the values is unlikely to exceed 4% below 13,500 cm^{-1} or 20% above 13,500 cm^{-1} .

Numerical data have been tabulated for this region by Hale and Querry¹³ for 25 °C; Palmer and Williams¹² for 27 °C; and Kou et al.¹¹ for 22 °C. Below 5000 cm^{-1} , Downing and Williams⁶ also tabulated Palmer and Williams' values, and values interpolated between them. The tabulated values are compared in the top two boxes of Fig. 2.

Hale and Querry¹³ analyzed the literature to the early 1970s and tabulated the optical constants at large wavelength intervals, as shown by the crosses (x) in Fig. 2. Palmer and Williams¹² measured the spectrum by trans-

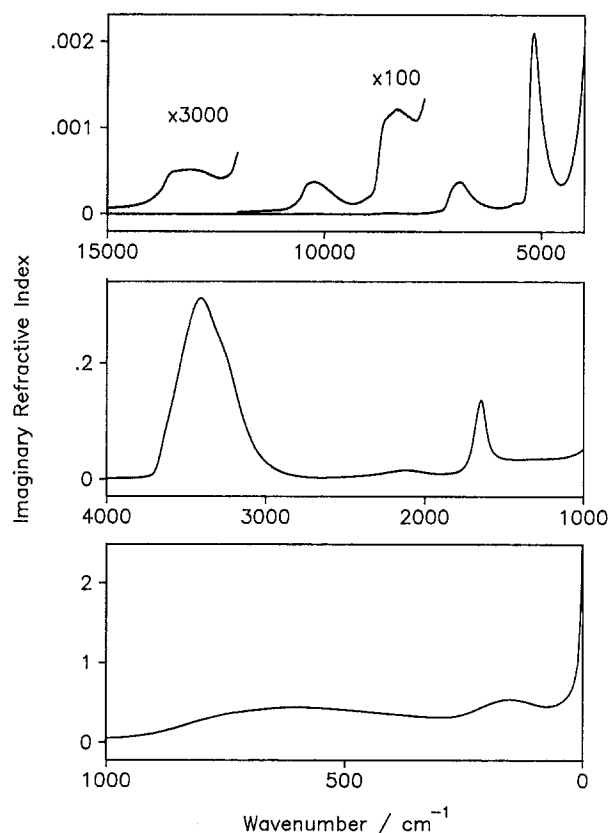


FIG. 4. The recommended imaginary refractive index spectrum of $\text{H}_2\text{O}(\text{l})$ between 15,000 and 1 cm^{-1} . For the upper two curves in the top box, the ordinate labels must be divided by 100 or 3000, as shown.

mission through long-path cells and tabulated values at 100- cm^{-1} intervals. Their spectrum is shown by the dotted line in Fig. 2. Their values agree fairly well with those of Hale and Querry, although distinct differences exist. Kou et al.¹¹ have summarized this earlier literature in their paper,¹¹ which presents the most recent study. Kou et al. used a Fourier transform spectrometer. For the weakest absorption they used cells with pathlengths up to 20 cm, significantly longer than the $\leq 5\text{-cm}$ paths used by Palmer and Williams in their study with a dispersive spectrometer. Both Palmer and Williams and Kou et al. removed the loss of light due to reflection at the window surfaces appropriately. Neither group considered the multiple reflection in the liquid layer between the windows, but this consideration can be safely ignored in cells with long pathlengths. The use by Kou et al. of a Fourier transform spectrometer enhances the value of their work, because well-aligned FT spectrometers have been shown to be reproducible between laboratories and manufacturers to about 3% with a liquid cell in the beam.^{17,26} The k values of Kou et al. agree with those of Palmer and Williams to better than 5% between 4000 and 14,500 cm^{-1} , except in two regions; their values are $\sim 10\%$ higher near the 5200- cm^{-1} peak and near 12,750 cm^{-1} . In the latter region, the longer paths used by Kou et al. were an improvement, and their k values are considered the most reliable. Kou et al. reported the percent error of their measurements on the basis of the uncertainty in the pathlengths and the standard deviation of their data.¹¹ The maximum probable

TABLE II. Imaginary refractive indices between 4154.88 and 1 cm⁻¹ of liquid water at 25 °C.^{a,b}

cm ⁻¹	XE	YE	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
4154.88	5	-6	1006	1149	1311	1539	1776	1955	2053	2116	2150	2230	2439						
3842.47	2	-6	2474	2515	2559	2605	2659	2709	2769	2830	2897	2965	3039	3119	3205	3289	3386	3486	3589
3776.90	2	-6	3699	3819	3948	4090	4236	4397	4570	4768	4979	5220	5489	5797	6144	6551	7016	7481	7946
3711.33	2	-5	882	985	1109	1253	1426	1627	1864	2135	2450	2803	3195	3623					
3661.19	3	-4	456	555	653	749	839	926	1012	1098	1186	1277	1370	1466	1565	1667	1770	1873	1977
3530.06	3	-4	2079	2179	2277	2371	2463	2551	2635	2714	2790	2861	2925	2983	3031	3071	3098	3115	3120
3398.92	3	-4	3111	3092	3063	3023	2978	2927	2872	2816	2758	2702	2645	2591	2538	2487	2437	2386	2335
3267.79	3	-4	2283	2228	2168	2106	2038	1966	1890	1810	1729	1645	1561	1477	1396	1317	1239	1166	1095
3136.65	3	-4	1028	964	903	846	792	742	694	649	607	567	530	495	463	433	404	377	352
3005.51	3	-5	3289	3072	2867	2678	2529	2388	2221	2083	1945	1816	1694	1588	1489	1395	1309	1230	1151
2874.38	3	-5	1081	1020	953	894	845	795	750	701	665	636	606	577	546	518	493	470	451
2743.24	3	-6	4315	4156	4016	3890	3785	3694	3601	3542	3486	3426	3376	3348	3358	3354	3365	3394	3400
2612.11	3	-6	3461	3507	3546	3639	3695	3745	3821	3911	3990	4066	4160	4253	4330	4463	4594	4706	4804
2480.97	3	-6	4924	5063	5196	5347	5490	5642	5770	5922	6103	6264	6444	6611	6773	6935	7140	7353	7548
2349.83	3	-5	779	801	822	842	868	897	930	961	994	1029	1063	1099	1136	1173	1211	1250	1287
2218.70	3	-5	1326	1366	1403	1442	1479	1512	1545	1573	1600	1622	1639	1652	1660	1663	1662	1656	1645
2087.56	3	-5	1629	1609	1588	1562	1533	1502	1469	1433	1399	1363	1327	1291	1255	1221	1190	1160	1132
1956.43	3	-5	1105	1083	1064	1047	1034	1023	1016	1012	1011	1013	1018	1026	1038	1052	1073	1096	1125
1825.29	3	-5	1160	1200	1249	1307	1377	1462	1567	1692	1846	2035	2273	2574	2960	3455	4079	4862	5821
1694.16	3	-4	696	823	958	1091	1213	1310	1368	1366	1295	1165	1013	871	753	662	593	541	501
1563.02	3	-5	4711	4473	4278	4120	3999	3901	3817	3752	3703	3664	3624	3600	3573	3554	3544	3535	3527
1431.88	3	-5	3518	3514	3509	3506	3508	3511	3516	3520	3527	3534	3543	3553	3562	3574	3584	3596	3604
1300.75	3	-5	3614	3622	3635	3644	3650	3650	3642	3632	3624	3632	3637	3657	3683	3696	3693	3704	3724
1169.61	3	-5	3743	3763	3797	3849	3853	3848	3863	3918	3972	4027	4085	4145	4210	4278	4356	4441	4535
1038.48	3	-4	464	476	490	504	521	540	561	585	612	643	678	720	766	819	880	948	1024
907.34	3	-4	1108	1201	1302	1411	1527	1650	1778	1910	2045	2181	2317	2452	2584	2714	2839	2961	3077
776.21	3	-4	3196	3310	3419	3521	3608	3691	3756	3812	3868	3923	3980	4034	4085	4130	4172	4214	4259
645.07	3	-4	4301	4335	4362	4389	4407	4419	4425	4425	4408	4376	4354	4328	4299	4266	4232	4195	4157
513.93	3	-4	4118	4078	4038	3997	3956	3916	3876	3836	3796	3757	3717	3678	3638	3598	3558	3518	3477
382.80	3	-4	3437	3398	3358	3320	3283	3248	3217	3188	3164	3146	3134	3133	3143	3170	3215	3284	3378
251.66	3	-4	3498	3644	3813	4000	4199	4403	4605	4798	4974	5127	5250	5339	5389	5398	5368	5300	5201
120.53	3	-4	5076	4937	4794	4663	4556	4491	4478	4531	4651	4845							
47.25	2	-3	497	512	530	552	580	612	657	717	802	922	1180	1628	2819				

Note: Footnotes follow Table IV.

error reported above is approximately twice the reported percent error of their measurements.

The existing data give no useful information about the effect of temperature differences between 15 and 35 °C on the absorption intensities of H₂O(l).

The Region 4000 to 3715 cm⁻¹. The k values obtained by transmission spectroscopy in this work are recommended for this region of weak absorption. The error in the values is unlikely to exceed 5% above 3850 cm⁻¹ and 30% between 3850 and 3720 cm⁻¹.

In the first report on H₂O(l) from this laboratory,¹ the imaginary refractive indices reported by Downing and Williams⁶ for 27 °C and by Zolotarev and Demin³ for 25 °C were considered to be the best in the literature. Those reported by Williams and his co-workers were much preferred because they were more consistent over time than those from Zolotarev and his colleague.³ The values reported by Downing and Williams are those of Palmer and Williams¹² above 3800 cm⁻¹ and those of Robertson and Williams¹⁴ below 3800 cm⁻¹, both obtained from transmission measurements through thick films and both interpolated to 10-cm⁻¹ intervals. These spectra are shown in the bottom box of Fig. 2, with those obtained from the current ATR study in this laboratory. Hale and Querry's values¹³ (25 °C) are included in the figure. It can be seen that below ~3800 cm⁻¹ the earlier workers^{6,3,13} all obtained values about twice as large as those from our ATR work. Downing and Williams saw a plateau or shoulder between ~3850 and 3720 cm⁻¹.

The absorption in this region is weak, and the best

intensities should come from transmission measurements through fairly thick liquid films. Transmission measurements were therefore made in this laboratory in order to explore the differences between Downing and Williams's values and our values from ATR.

The transmission methods have been described.¹⁷ Cells with CaF₂ windows were used with pathlengths of 150, 125, 115, 100, and 85 μm. The anchor points¹⁷ are at 4501 and 3727.7 cm⁻¹, where the linear absorption coefficients are 9.29 ± 0.3 cm⁻¹ and 130.9 ± 0.7 cm⁻¹, respectively. The k values obtained agree with our values from ATR near 3715 cm⁻¹, where Downing and Williams' values are about 70% larger, and agree with Downing and Williams' values within 3% above 3850 cm⁻¹ and within 1% above 3900 cm⁻¹, where our values from ATR are about 30% lower. The difference between our transmission results and our ATR results is unusually large, much better agreement having been obtained for, *inter alia*, the isotopomers of methanol.^{4,28}

Accordingly, the k values from our transmission measurements are recommended. They connect extremely well at 4000 cm⁻¹ to the spectrum of Kou et al.¹¹ The large possible error cited above for the lower part of the range reflects the large disagreement with both the values from our ATR spectra and the values of Downing and Williams.

The Region 3715 to 2982 cm⁻¹. The k values determined by ATR measurements of H₂O(l) at 25 °C in this work are recommended for this region. The error in these values is unlikely to exceed 4%.

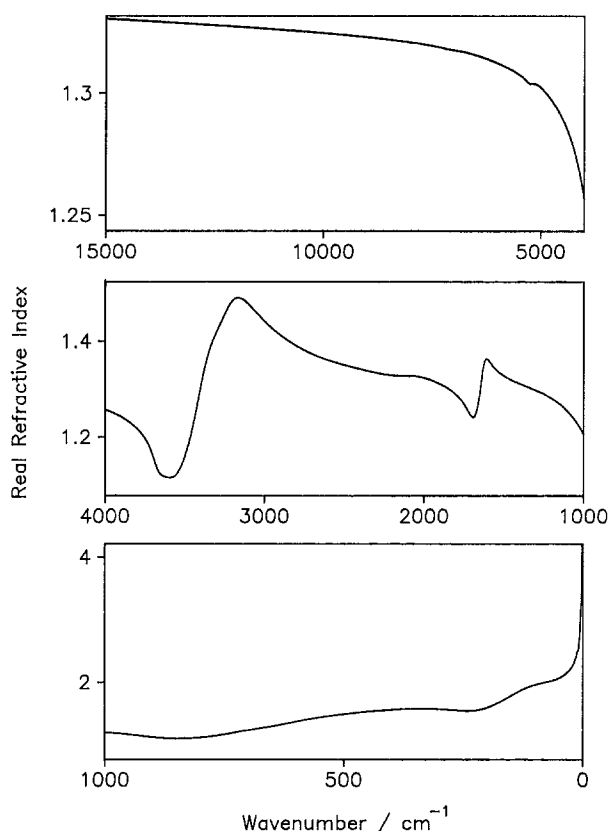


FIG. 5. The recommended real refractive index spectrum of $\text{H}_2\text{O}(\text{l})$ between 15,000 and 1 cm^{-1} .

The region is shown in the bottom box of Fig. 2. For reasons discussed previously,¹ the values obtained from calibrated ATR measurements in this laboratory are preferred to the values in the literature. Our 1989^{1,8} and 1995 spectra are compared in Fig. 1 and have been discussed above. Our 1995 spectrum is included in the bottom box of Fig. 2 and is the preferred spectrum in this region.

Two features are evident in the figure and deserve comment. As noted previously,¹ Zolotarev and Demin's spectrum³ agrees quite well with ours in intensity, to about 5% with our new spectrum, but is shifted markedly to low wavenumber. The spectrum of Downing and Williams⁶ is significantly less intense than ours, and has a different shape. Thus, while the low-wavenumber end of their band coincides with ours, their peak is at a lower wavenumber, and the high-wavenumber side of their band is at a lower wavenumber than even that of Zolotarev and Demin. These differences are undoubtedly due to the instrumental and computational limitations of the early 1970s. Thus, the OH stretching band reported by Downing and Williams is strongly influenced by that of Rusk et al.,² which was calculated from a normal incidence reflection spectrum. The percent reflection is less than 5% throughout, and was very difficult to measure well with the dispersive instruments available in the early 1970s. Thus, their reflection spectrum was noisy and gave a noisy real refractive index spectrum as the primary result. Their k spectrum was calculated from the noisy n spectrum by Kramers–Kronig transformation. The accuracy claimed was on the order of 10%, which is roughly

consistent with the agreement with our new spectrum. The agreement that is observed is a tribute to the work of Williams and his colleagues.

The Region 2982 to 2800 cm^{-1} . The average of the k spectra from Downing and Williams⁶ and from the ATR measurements of this work is recommended for this region. The error in the values is unlikely to exceed 10%.

This short region is shown in the top box of Fig. 3. The absorption intensity is moderate, so both transmission and ATR methods can give good results. All spectra agree well, except those of Zolotarev and Demin³ and of Marley et al.¹⁵ Our transmission measurements between 2867 and 2800 cm^{-1} gave k values 6% below those of Downing and Williams⁶ and 4% above those from our ATR measurements. Thus the average of the latter two spectra is used.

The Region 2800 to 2320 cm^{-1} . The k values of Downing and Williams⁶ are recommended for this region. The error in the values is unlikely to exceed 6%.

The region contains only weak absorption, as shown in the top box of Fig. 3. Marley et al.¹⁵ (lower dashed curve) have recently reported k values about a factor of ten lower than those of all previous workers (Fig. 3, top box). Transmission measurements were undertaken in this laboratory to see whether Marley et al. are correct. Cells with CaF_2 windows were used with pathlengths of 125, 115, 100, and 85 μm . The anchor points are at 2630 and 1885 cm^{-1} , where the linear absorption coefficients are $48.6 \pm 0.3\text{ cm}^{-1}$ and $103.8 \pm 0.4\text{ cm}^{-1}$, respectively. The anchor point measurements used pathlengths up to 325 μm . Our results agree with those of the previous workers, not with those of Marley et al. In fact, our transmission measurements agree with those of Downing and Williams⁶ to within 4% in this region.

The Region 2320 to 713 cm^{-1} . The k values from our new ATR measurements are recommended in this region. The error in their values is unlikely to exceed 5% above, and 10% below, 1000 cm^{-1} .

This region is shown in Fig. 3. Again, the absorption is moderate, and both ATR and transmission measurements should be reliable. The k values from the ATR measurements in this work agree with those of Downing and Williams⁶ within 2% for most of this region, except near the 1640-cm^{-1} peak, where our measurements should be better. Accordingly, the k values from these ATR measurements are used throughout the region. Our spectrum is higher than that of all workers except Zolotarev and Demin³ below $\sim 1000\text{ cm}^{-1}$, but was reproducible and is considered reliable. As an illustration, the greatest difference occurs near 812 cm^{-1} , where our many ATR spectra gave $k = 0.262$ with a maximum deviation of 3%, while the values of Downing and Williams and Zolotarev and Demin are 10% smaller, 0.237 and 0.240, respectively. A final test of our k values from ATR was made at the end of this study. The calculation of the k spectrum from the pATR spectrum was redone by extending the k spectrum for the KK transform by adding the final recommended k spectrum below 700 cm^{-1} instead of adding Downing and Williams' k spectrum (*vide infra*). The resulting k value at 700 cm^{-1} was higher by 2%, but the difference decreased rapidly with increasing wavenumber and was already virtually zero at 710 cm^{-1} .

TABLE III. Real refractive indices between 15,000 and 1 cm⁻¹ of liquid water at 25 °C.^{a,b}

cm ⁻¹	λ , μ	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
15000.6	5	13304	13303	13303	13303	13302	13302	13302	13301	13301	13301	13300	13300	13300	13299	13299	13299	13298
14476.0	5	13298	13298	13297	13297	13297	13296	13296	13296	13295	13295	13295	13295	13294	13294	13294	13293	13293
13951.5	5	13293	13292	13292	13292	13291	13291	13291	13290	13290	13290	13289	13289	13289	13288	13288	13288	13287
13427.0	5	13287	13287	13286	13286	13286	13285	13285	13285	13284	13284	13284	13283	13283	13283	13282	13282	13282
12902.4	5	13281	13281	13281	13280	13280	13280	13279	13279	13279	13278	13278	13278	13277	13277	13277	13276	13276
12377.9	5	13276	13275	13275	13275	13274	13274	13274	13273	13273	13272	13272	13272	13271	13271	13271	13270	13270
11853.3	5	13270	13269	13269	13269	13268	13268	13267	13267	13267	13266	13266	13266	13265	13265	13264	13264	13264
11328.8	5	13263	13263	13263	13262	13262	13261	13261	13261	13260	13260	13260	13259	13259	13258	13258	13258	13257
10804.2	5	13257	13256	13256	13255	13255	13255	13254	13254	13253	13253	13253	13252	13252	13251	13251	13250	13250
10279.7	5	13250	13249	13249	13248	13248	13247	13247	13246	13246	13245	13245	13244	13244	13244	13243	13243	13242
9755.15	5	13242	13241	13241	13240	13240	13239	13239	13238	13238	13237	13237	13236	13236	13235	13235	13234	13234
9230.61	5	13233	13233	13232	13231	13231	13230	13230	13229	13229	13228	13227	13227	13226	13226	13225	13224	13224
8706.06	5	13223	13222	13222	13221	13221	13220	13219	13219	13218	13217	13217	13216	13215	13214	13214	13213	13212
8181.52	5	13211	13211	13210	13209	13208	13207	13207	13206	13205	13204	13203	13202	13202	13201	13200	13199	13198
7656.98	5	13197	13196	13195	13194	13193	13192	13191	13190	13189	13188	13187	13186	13185	13183	13182	13181	13179
7132.43	5	13178	13177	13176	13176	13175	13174	13173	13172	13171	13170	13169	13168	13167	13166	13165	13163	13162
6607.89	5	13160	13159	13157	13156	13154	13152	13151	13149	13147	13145	13144	13142	13140	13138	13136	13134	13132
6083.35	5	13130	13127	13125	13123	13120	13118	13116	13113	13110	13108	13105	13102	13099	13096	13093		
5635.94	4	13092	13090	13089	13087	13085	13084	13082	13080	13078	13077	13075	13073	13071	13068	13066	13064	13061
5373.67	4	13059	13056	13053	13050	13046	13043	13041	13039	13039	13039							
5203.97	5	13039	13039	13038	13037	13034	13030	13026	13021	13015	13010	13003	12997	12990	12983	12976	12968	12960
4679.42	5	12952	12943	12934	12924	12914	12903	12892	12880	12867	12854	12840	12825	12809	12792	12774	12755	12734
4154.88	5	12714	12690	12664	12635	12604	12571	12534	12491	12441	12382	12313						
3842.47	2	12303	12294	12284	12273	12263	12252	12241	12230	12218	12206	12194	12181	12168	12155	12141	12127	12113
3776.90	2	12098	12082	12066	12050	12032	12015	11996	11977	11956	11935	11913	11890	11866	11841	11814	11786	11756
3711.33	2	11722	11689	11654	11617	11580	11541	11502	11462	11423	11386	11350	11317					
3661.19	3	11261	11221	11194	11177	11166	11158	11151	11145	11142	11141	11144	11150	11162	11181	11206	11238	11279
3530.06	3	11326	11381	11443	11511	11586	11666	11753	11845	11944	12049	12161	12279	12404	12531	12665	12802	12936
3398.92	3	13071	13201	13325	13442	13551	13652	13746	13831	13908	13979	14045	14107	14167	14224	14280	14338	14394
3267.79	3	14450	14508	14565	14620	14673	14723	14767	14807	14840	14867	14887	14900	14907	14909	14906	14898	14887
3136.65	3	14873	14855	14836	14814	14791	14766	14740	14714	14687	14660	14632	14604	14577	14549	14521	14494	14467
3005.51	3	14440	14413	14387	14361	14333	14311	14289	14265	14243	14221	14199	14177	14156	14136	14115	14096	14077
2874.38	3	14059	14041	14023	14006	13989	13973	13957	13941	13925	13910	13895	13881	13868	13854	13841	13828	13815
2743.24	3	13802	13790	13778	13766	13754	13743	13732	13721	13710	13700	13690	13679	13669	13660	13650	13641	13631
2612.11	3	13622	13614	13605	13596	13588	13580	13572	13564	13556	13548	13540	13533	13525	13518	13511	13504	13497
2480.97	3	13490	13483	13476	13469	13463	13456	13450	13443	13437	13431	13424	13418	13412	13406	13400	13394	13388
2349.83	3	13382	13376	13370	13364	13358	13352	13347	13341	13336	13331	13326	13321	13317	13313	13308	13305	13301
2218.70	3	13298	13295	13292	13290	13288	13286	13285	13284	13283	13282	13282	13281	13281	13281	13280	13280	13279
2087.56	3	13278	13277	13275	13273	13271	13267	13264	13260	13255	13250	13245	13239	13232	13225	13217	13208	13200
1956.43	3	13190	13181	13171	13160	13149	13138	13126	13114	13101	13088	13075	13060	13046	13030	13014	12998	12980
1825.29	3	12961	12941	12920	12898	12874	12848	12820	12790	12757	12722	12683	12642	12597	12552	12507	12466	12435
1694.16	3	12420	12429	12470	12545	12657	12807	12990	13193	13385	13531	13613	13638	13629	13601	13567	13530	13496
1563.02	3	13464	13434	13408	13382	13359	13338	13318	13299	13282	13266	13250	13236	13222	13209	13196	13184	13173
1431.88	3	13161	13150	13139	13128	13117	13107	13096	13086	13075	13065	13054	13044	13033	13023	13013	13003	12992
1300.75	3	12981	12971	12960	12949	12938	12927	12916	12902	12888	12873	12857	12842	12826	12813	12796	12778	12760
1169.61	3	12741	12722	12701	12683	12665	12643	12616	12590	12565	12539	12512	12484	12455	12424	12392	12359	12324
1038.48	3	12286	12247	12207	12164	12119	12072	12023	11971	11916	11859	11799	11737	11674	11609	11543	11478	11414
907.34	3	11351	11292	11239	11191	11150	11117	11094	11080	11076	11084	11102	11129	11163	11210	11263	11322	11385
776.21	3	11454	11535	11626	11724	11829	11928	12040	12141	12235	12328	12421	12520	12619	12720	12819	12916	13016
645.07	3	13125	13238	13350	13464	13584	13702	13823	13952	14066	14173	14275	14374	14470	14562	14650	14734	14814
513.93	3	14890	14962	15032	15097	15159	15219	15276	15331	15384	15434	15483	15529	15573	15615	15654	15691	15725
382.80	3	15755	15782	15804	15822	15836	15845	15847	15845	15836	15820	15796	15766	15727	15683	15634	15584	15540
251.66	3	15506	15491	15500	15539	15614	15726	15876	16066	16292	16551	16840	17152	17479	17813	18145	18467	18769
120.53	3	19045	19290	19501	19678	19827	19956	20082	20224	20406	20649							
47.25	2	20801	20976	21168	21396	21670	21986	22374	22879	23606	24609	25871	31053	48755				

Note: Footnotes follow Table IV.

The Region 713 to 590 cm⁻¹. The average of the k values reported by Downing and Williams⁶ and by Zolotarev and Demin³ is recommended in this region. These are the most recent sets of measurements in this region, and there is no way to judge between them. The maximum deviation from the average is $\sim 7\%$, and the error in the k values is unlikely to exceed this.

The Region 590 to 30 cm⁻¹. A k spectrum based on those reported by Zelsmann¹⁶ is recommended in this region. He reported k spectra at 20.2 and 38.7 °C from which a spectrum at 25 °C was calculated as described

below. The error in the k values is unlikely to exceed 12%.

The several spectra reported for this region are shown in the bottom box of Fig. 3. They require some explanation.

Zelsmann¹⁶ tabulated his fitted values (see Introduction) at, *inter alia*, 20.2 and 38.7 °C. A k spectrum for 25 °C was calculated under the assumption that the k values vary linearly with temperature. This spectrum is referred to below as Zelsmann's 25 °C spectrum.

Hasted and his colleagues have published three papers

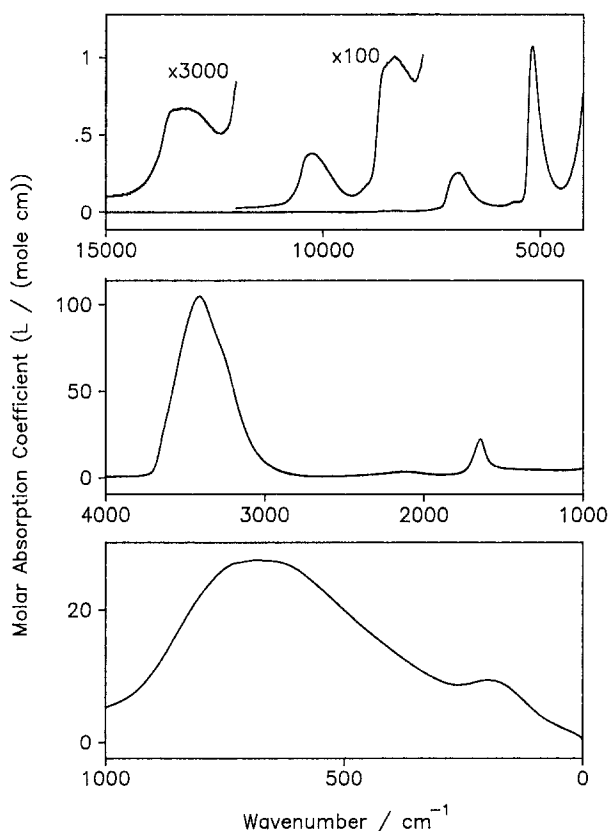


FIG. 6. The recommended molar absorption coefficient spectrum of $\text{H}_2\text{O}(\text{l})$ between 15,000 and 1 cm^{-1} . For the upper two curves in the top box, the ordinate labels must be divided by 100 or 3000, as shown.

relevant to this region.^{19,29,30} In 1985 Hasted et al.³⁰ reported optical constants of $\text{H}_2\text{O}(\text{l})$ at 20°C between 4 and 40 cm^{-1} . Although they reported³⁰ only the 20°C values, they said they had obtained values between 4 and 44°C with a new polarizing interferometer for dispersive FTS studies, and that the results above 15 cm^{-1} agreed with those of Afsar and Hasted.¹⁹

Afsar and Hasted¹⁹ tabulated optical constants of water at 19°C between 6 and 450 cm^{-1} . This is referred to below as A&H's 19°C spectrum.

One year later, Afsar and Hasted²⁹ tabulated optical constants of water at 4, 30, and 57°C in two ranges, namely, between 10 and 45 cm^{-1} (measured with an InSb Rollin detector) and between 30 to 220 cm^{-1} (measured with a Golay detector). To obtain data for 25°C , we have interpolated between the 4 and 30°C data, again under the assumption that the imaginary refractive index changes linearly with temperature. These interpolated 25°C spectra are referred to below as A&H's 25°C spectra, and they agree rather well with A&H's 19°C spectrum.¹⁹ This result is not surprising, because the assumption on which our interpolation was based is unlikely to be valid between 4 and 30°C , but it does mean that the 25°C (interpolated) spectra and the 19°C spectrum are the best that can be obtained from Afsar and Hasted for the present purpose.

Downing and Williams⁶ and Zolotarev and Demin³ have also tabulated optical constants in this region for $\text{H}_2\text{O}(\text{l})$ at 27°C and 25°C , respectively.

Zelmann's 25°C spectrum,¹⁶ Zolotarev and Demin's

spectrum,³ and A&H's 19°C and 25°C spectra^{19,29} agree within 6% at the peak near 165 cm^{-1} . Downing and Williams' spectrum⁶ is about 17% more intense and is not considered further. Downing and Williams estimated their errors to be up to 20%. Zelmann's spectrum is very nearly the average of the remaining four spectra, so it is convenient to recommend its use even though it is a fitted spectrum,¹⁶ not the experimental one. The $\leq 12\%$ probable error in the k values is slightly larger than the maximum deviation of the remaining spectra from the average.

The Region 30 to 10 cm^{-1} . The average of Zolotarev's spectrum,³ A&H's 19°C spectrum,¹⁹ and A&H's 25°C spectrum²⁹ is used in this region. On the basis of the agreement between them, the error in the k values is unlikely to exceed 6%.

The Region 10 to 6 cm^{-1} . In 1987, Hasted et al.³¹ published optical constants of $\text{H}_2\text{O}(\text{l})$ at 10, 20, 30, and 40°C between 6 and 14 cm^{-1} . They used their new polarizing interferometer and estimated the errors in their values to be no larger than 3%. We have taken the average of the 20 and 30°C values to correspond to 25°C and recommend these values for this region. The error in the values is unlikely to exceed 5%.

The Region 5 to 1 cm^{-1} . Kaatz and Uhlendorf³² have reported the dielectric properties of $\text{H}_2\text{O}(\text{l})$ at several temperatures including 25°C between 0.5 and 100 GHz, i.e., 0.016 to 3.3 cm^{-1} . They estimated the error in their values to be about 2%. Their data were well described by the Debye relaxation function, and the Debye parameters were reported for each temperature. The values of the imaginary refractive index recommended for this region are those calculated from the dielectric constants calculated from the Debye function for 25°C . The error in the k values is unlikely to exceed 5%.

The Recommended k and n Spectra. The recommended k spectrum was constructed by merging the spectra recommended for the different regions. There were no significant discontinuities to be smoothed. The recommended k spectrum is shown in Fig. 4 and is tabulated in Compact Table format³³ in Table II. The real refractive index spectrum was calculated by Kramers–Kronig transform of this recommended k spectrum. In the KK transform to calculate the real refractive index at wavenumber $\tilde{\nu}_a$, the value of n_∞ was replaced by $n_{\text{el}}(\tilde{\nu}_a)$ calculated from the equation²²

$$n_{\text{el}}(\tilde{\nu}_a) = 1.32663 + 2.439 \times 10^{-11} \tilde{\nu}_a^2 + 3.74 \times 10^{-21} \tilde{\nu}_a^4.$$

The recommended n spectrum is shown in Fig. 5 and is tabulated in the Compact Table III. The molar absorption coefficient, E_m , spectrum was calculated from the k spectrum as described previously^{4,24} and is shown in Fig. 6 and tabulated in the Compact Table IV.

THE EFFECT OF TEMPERATURE

For many purposes it is necessary to know the small effect on band positions, shapes, and intensities of small changes in temperature near ambient, specifically changes of one or two degrees at temperatures between 20 and 35°C . It has been noted above that the existing data above 4000 cm^{-1} give no useful information about such

TABLE IV. Molar absorption coefficient between 15,000 and 1 cm⁻¹ of liquid water at 25 °C.^{a,b,c}

cm ⁻¹	<i>XE</i>	<i>YE</i>	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
15000.6	5	-7	359	358	356	356	355	355	381	380	379	378	378	377	376	402	401	401	399
14476.0	5	-7	426	424	450	449	474	500	498	523	548	573	599	623	647	672	722	746	796
13951.5	5	-7	871	920	995	1044	1118	1191	1264	1388	1510	1658	1779	1950	2020	2115	2159	2180	2200
13427.0	5	-7	2219	2215	2209	2229	2223	2242	2237	2232	2227	2245	2241	2235	2230	2201	2196	2190	2162
12902.4	5	-7	2156	2151	2123	2093	2066	2037	1985	1957	1929	1879	1851	1823	1795	1745	1740	1714	1709
12377.9	5	-7	1705	1701	1719	1737	1755	1795	1836	1899	2005	2156	2350	2587	2779	2904	3005	3063	3121
11853.3	5	-7	3179	3213	3270	3283	3318	3373	3429	3441	3517	3572	3626	3700	3775	3849	3943	4037	4152
11328.8	5	-7	4244	4358	4469	4581	4692	4802	4891	5000	5129	5257	5404	5570	5776	6040	6364	6805	7363
10804.2	5	-6	806	894	996	1108	1218	1375	1543	1729	1958	2262	2623	3027	3334	3542	3656	3728	3764
10279.7	5	-6	3800	3815	3806	3762	3708	3628	3535	3430	3318	3202	3075	2950	2806	2662	2534	2405	2254
9755.15	5	-6	2116	1984	1850	1734	1624	1525	1434	1342	1280	1220	1178	1138	1120	1105	1103	1114	1131
9230.61	5	-6	1171	1225	1280	1346	1435	1522	1613	1715	1820	1866	2011	2188	2475	2963	3731	4823	6041
8706.06	5	-5	725	830	889	924	938	948	965	966	976	985	994	1004	1002	995	986	977	967
8181.52	5	-5	951	939	929	913	905	889	874	863	859	849	848	864	879	912	938	984	1042
7656.98	5	-4	112	122	133	148	164	183	204	226	249	267	286	313	351	418	537	736	1054
7132.43	5	-4	1414	1734	2001	2173	2335	2443	2527	2555	2570	2559	2492	2375	2226	2072	1892	1746	1599
6607.89	5	-4	1453	1325	1220	1130	1022	942	869	804	748	705	664	625	594	569	545	525	506
6083.35	5	-5	4925	4801	4698	4626	4578	4579	4592	4637	4732	4892	5095	5382	5786	6185	6711		
5635.94	4	-5	6884	7034	7147	7207	7205	7182	7245	7236	7182	7217	7238	7320	7473	7682	7909	8505	9372
5373.67	4	-4	1066	1264	1613	2163	2960	4120	5597	7158	8499	9483							
5203.97	5	-3	1050	1071	1029	943	843	746	655	575	508	446	395	351	310	277	249	225	206
4679.42	5	-4	1904	1778	1693	1629	1588	1575	1584	1621	1683	1782	1920	2093	2315	2579	2936	3248	3652
4154.88	5	-4	4120	4672	5290	6166	7060	7713	8034	8216	8284	8526	9248						
3842.47	2	-3	937	952	968	984	1003	1021	1043	1065	1089	1113	1140	1168	1200	1230	1265	1301	1338
3776.90	2	-3	1377	1421	1467	1519	1571	1629	1691	1763	1839	1926	2023	2135	2260	2407	2575	2743	2911
3711.33	2	-2	323	360	405	457	520	592	678	776	889	1016	1157	1311					
3661.19	3	-2	1647	1999	2349	2685	3003	3308	3607	3907	4210	4521	4841	5170	5508	5852	6200	6549	6895
3530.06	3	-1	723	757	789	820	850	878	905	930	954	976	996	1013	1027	1039	1045	1049	1048
3398.92	3	-1	1043	1034	1022	1006	989	970	949	929	908	887	866	847	828	809	791	772	754
3267.79	3	-2	7355	7160	6953	6738	6505	6260	6005	5737	5465	5187	4911	4637	4370	4113	3861	3623	3395
3136.65	3	-2	3179	2973	2780	2598	2426	2265	2114	1972	1839	1715	1599	1491	1390	1295	1206	1123	1046
3005.51	3	-3	9748	9079	8453	7875	7418	6986	6482	6062	5646	5258	4892	4574	4276	3996	3740	3504	3271
2874.38	3	-3	3065	2883	2687	2514	2371	2224	2092	1949	1844	1758	1672	1586	1497	1417	1344	1279	1224
2743.24	3	-3	1167	1121	1080	1043	1012	985	958	939	922	903	887	878	878	874	874	879	878
2612.11	3	-3	891	900	908	929	940	950	967	986	1003	1019	1040	1060	1076	1105	1134	1158	1179
2480.97	3	-3	1205	1235	1263	1296	1326	1359	1385	1417	1456	1490	1527	1562	1595	1628	1670	1715	1755
2349.83	3	-3	1805	1849	1892	1931	1985	2045	2112	2176	2243	2313	2382	2455	2528	2601	2677	2753	2825
2218.70	3	-3	2900	2977	3048	3121	3191	3251	3309	3358	3403	3437	3461	3475	3480	3474	3459	3435	3398
2087.56	3	-3	3354	3300	3245	3180	3108	3035	2957	2874	2794	2712	2630	2549	2469	2393	2322	2255	2192
1956.43	3	-3	2132	2081	2036	1997	1962	1935	1913	1898	1889	1884	1886	1893	1908	1925	1955	1990	2033
1825.29	3	-3	2087	2151	2228	2322	2437	2575	2748	2955	3210	3523	3918	4417	5058	5876	6907	8195	9768
1694.16	3	-2	1162	1369	1586	1798	1989	2139	2223	2210	2084	1867	1615	1382	1190	1040	927	842	777
1563.02	3	-3	7260	6859	6529	6256	6041	5863	5709	5582	5482	5396	5309	5247	5181	5125	5085	5044	5007
1431.88	3	-3	4967	4934	4900	4870	4845	4824	4803	4783	4765	4748	4733	4719	4704	4693	4679	4666	4650
1300.75	3	-3	4635	4618	4606	4591	4570	4543	4505	4465	4428	4409	4388	4384	4388	4375	4343	4328	4323
1169.61	3	-3	4316	4311	4321	4351	4327	4292	4279	4310	4339	4369	4400	4433	4471	4510	4559	4615	4678
1038.48	3	-3	4751	4838	4939	5049	5176	5322	5486	5678	5897	6146	6428	6767	7149	7580	8071	8626	9235
907.34	3	-2	991	1065	1145	1230	1319	1414	1509	1607	1705	1802	1897	1988	2076	2160	2238	2311	2378
776.21	3	-2	2446	2508	2565	2614	2651	2684	2703	2714	2725	2734	2743	2750	2753	2753	2749	2744	2741
645.07	3	-2	2736	2724	2708	2692	2669	2642	2613	2579	2535	2484	2438	2391	2342	2291	2241	2190	2138
513.93	3	-2	2087	2035	1985	1934	1885	1835	1787	1739	1693	1646	1601	1556	1512	1468	1424	1381	1339
382.80	3	-2	1297	1257	1216	1177	1139	1103	1067	1034	1002	972	945	920	900	883	871	865	864
251.66	3	-3	8680	8765	8882	9013	9143	9250	9326	9351	9316	9212	9035	8781	8453	8057	7604	7105	6576
120.53	3	-3	6032	5492	4968	4478	4028	3629	3278	2972	2697	2441							
47.25	2	-3	2317	2190	2065	1942	1819	1687	1562	1432	1297	1139	1010	774	268				

^a The column headed cm⁻¹ contains the wavenumber of the first ordinate value in the row. The columns headed *XE* and *YE* contain the *X*-exponent and the *Y*-exponent, respectively, for the row. The columns headed 0, 1, 2, . . . 16, contain the ordinate values, and the headings give the indices of the ordinate values in the row. In a row which starts with $\tilde{\nu}(0)$, the wavenumber corresponding to the ordinate indexed *J* is $\tilde{\nu}(J) = \tilde{\nu}(0) - \frac{15798.002}{16384}J \cdot 2^{XE}$. In Tables II and IV, the $k(\tilde{\nu})$ and $E_m(\tilde{\nu})$ values in that row are the ordinate value shown times 10^{YE} . In Table III, the $n(\tilde{\nu})$ values are given directly, with the decimal point implicitly after the first digit. Thus the entry indexed 16 in the second row of Table II shows that, at

$\tilde{\nu} = 3842.47 - \frac{15798.002}{16384} \times 16 \times 2^2 = 3780.76 \text{ cm}^{-1}$, the k value is $3589 \times 10^{-6} = 3.589 \times 10^{-3}$; the entry indexed 16 in the second row of

Tables III and IV show that, at $\tilde{\nu} = 14476.0 - \frac{15798.002}{16384} \times 16 \times 2^5 = 13982.3 \text{ cm}^{-1}$, the ordinate values are $n = 1.3292$ and $E_m = 796 \times 10^{-7} = 7.96 \times 10^{-5} \text{ L mole}^{-1} \text{ cm}^{-1}$.

^b The 4-point spline interpolation program TRECOVER³³ interpolated the $k(\tilde{\nu})$ and $E_m(\tilde{\nu})$ values in the table to the original wavenumber spacing, 0.964234 cm⁻¹, and yielded the original values accurate to 1%. The original $n(\tilde{\nu})$ values were similarly recovered, accurate to 0.1%.

^c The unit of E_m is L mole⁻¹ cm⁻¹. Multiply the values by 1000 to change the unit to cm² mole⁻¹.

effects. The same is essentially true for the mid-infrared region, and for all except the extreme far-infrared. Only Williams and his co-workers^{23,34} have specifically studied the effect of temperature on the mid-infrared optical constants of H₂O(l), with the second paper²³ superseding the first.³⁴ In both cases the measurements were by near-normal reflection from an air/water interface, and the results are valuable guides. However, neither supplies reliable detailed information of the type noted above.

We recommended that this information be obtained by ATR or transmission, by using the analytical technique of eliminating as many sources of variation as possible in order to obtain spectra of very high precision. Such spectra are of questionable accuracy, because many variables are fixed, so that many systematic errors are likely to be fixed with them, but the spectra can be calibrated with a factor determined by scaling the data at 25 °C to the values reported in this paper. We believe that only in this way will data be obtained with sufficient precision to show clearly the small spectral changes caused by temperature changes of a few degrees near 25 °C. Heise and Bittner²⁵ have recently published a graph which shows such effects between 2000 and 800 cm⁻¹ for a 5° change in temperature.

CONCLUSION

It has been found that the previously reported nonreproducibility of the intensity of the OH stretching band of water can be eliminated in measurements with the Circle® multiple ATR cell by ensuring that the ATR rod is coaxial with the glass liquid holder. Normal laboratory temperature variations of a few degrees change the intensity by less than 1%. A new imaginary refractive index spectrum of water has been determined between 4000 and 700 cm⁻¹ as the average of spectra calculated from ATR spectra recorded by four workers in this laboratory over the past seven years. It was obtained under experimental and computational conditions superior to those used previously, but is only marginally different from the spectra reported in 1989.^{1,8} In particular, the integrated intensities of the fundamentals are not changed significantly from those reported previously.^{1,8}

The available imaginary refractive index, k , values between 15,000 and 1 cm⁻¹ have been compared. The values that appear to be the most reliable have been combined into a recommended k spectrum of H₂O(l) at 25 °C between 15,000 and 1 cm⁻¹, from which the real refractive index spectrum has been calculated by Kramers–Kronig analysis. The recommended values of the real and imaginary refractive indices and molar absorption coefficients of liquid water at 25 ± 1 °C are presented in graphs and tables. The real and imaginary dielectric constants in this wavenumber range can, of course, be calculated from the tabulated values. The probable absolute errors associated with the recommended values are conservative. The relative errors between regions are far smaller, and the rec-

ommended values should be of considerable value as (tentative) standard intensities of liquid water, which will facilitate lab-to-lab transfer of intensities.

The recommended real and imaginary refractive index spectra are available in digital form from J.E.B.

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