

# Refractive Index of Water and Steam as Function of Wavelength, Temperature and Density

P. Schiebener and J. Straub

*Lehrstuhl A für Thermodynamik, Technische Universität München, Arcisstrasse 21, D-8000 München 2, Federal Republic of Germany*

J. M. H. Levelt Sengers and J. S. Gallagher

*Thermophysics Division, Center for Chemical Technology, National Institute of Standards and Technology, Gaithersburg, MD 20899*

Received September 1, 1989; revised manuscript received February 28, 1990

Based on a comprehensive collection of data previously obtained by Thormählen *et al.* on the experimental refractive index of water and steam from the 1870s to the present, a new formulation is presented for the range of 0.2 to 2.5  $\mu\text{m}$  in wavelength,  $-10$  to  $+500$   $^{\circ}\text{C}$  in temperature and 0 to 1045  $\text{kg m}^{-3}$  in density. The Lorentz-Lorenz function or molar refraction, a strong function of wavelength but only weakly dependent on density and temperature, is fitted to a selected set of accurate refractive index data. The NBS/NRC equation of state for water and steam, the new international standard, is used to convert the experimental pressures to density.

The deviations of all experimental data from the formulation are shown. A detailed assessment of the accuracy of the formulation is presented. Although the formulation does not represent within their accuracy the data from the best sets in the visible range for liquid water below the boiling point, we show that inconsistencies between data sets, and minor deficiencies of the equation of state, prevent further improvement of a formulation based on data over as wide a range as considered here. It is shown that the best refractive index data can be used to discriminate between the various formulations of the equation of state of water and steam.

It is demonstrated that several recent formulations of optical properties of liquid water over large ranges of wavelength need improvement in the range covered here.

The new formulation is used to generate tables of the refractive index of water and steam at six wavelengths in the visible, near-infrared and near-ultraviolet, from 0 to 500  $^{\circ}\text{C}$  and up to 100 MPa in pressure.

Key words: data collection; data evaluation; formulation; infrared; molar refraction; refractive index; refractivity virials; steam; tabulation; ultraviolet; visible; water.

## Contents

1. Introduction.....	679	7. Comparison with Other Literature Data ...	694
2. Approach.....	680	8. Estimate of Reliability of the Formulation..	703
3. Data Sources, Selection and Correction....	683	9. Tabulation of the Refractive Index.....	703
4. The Formulation.....	686	10. Summary and Conclusions.....	713
5. Comparison with the Selected Data Sets...	686	11. Nomenclature.....	714
6. Temperature Dependence of $n$ in Liquid Water, $-12$ to $100$ $^{\circ}\text{C}$ , in the Visible Range...	688	12. Acknowledgments.....	714
		13. References.....	714

Appendix. Optimum Formulation of the Refractive Index of Liquid Water below $60$ $^{\circ}\text{C}$ , in the Visible Range, at Atmospheric Pressure.....	715
--	-----

©1990 by the U.S. Secretary of Commerce on behalf of the United States. This copyright is assigned to the American Institute of Physics and the American Chemical Society.  
Reprints available from ACS; see Reprints List at back of issue.

## List of Tables

1. Propagation of error in refractive index .....	683	11. Departures of all high-quality experimental data in the visible in liquid water at atmospheric pressure, plotted against temperature. They include those of Saubade <sup>9</sup> below 0 °C, Tilton and Taylor, <sup>1,2</sup> Flatow, <sup>17</sup> Hall, <sup>23</sup> and Jasse <sup>24</sup> ....	693
2. Experimental data sources .....	684	12. Departures of all <i>n</i> data in supercooled water, plotted against temperature. Data are by Damien, <sup>34</sup> Hawkes, <sup>35</sup> Pulfrich, <sup>36</sup> and Saubade <sup>9</sup> ...	693
3. Refractive index data used in the formulation ..	685	13. Departures from the formulation of the high-quality <i>n</i> data in the visible and at temperatures close to ambient, of Brühl, <sup>37</sup> Conroy, <sup>38</sup> Duffet, <sup>39</sup> Lorenz, <sup>40</sup> Quincke, <sup>41</sup> Verschaffelt, <sup>42</sup> and van der Willigen, <sup>43</sup> plotted against wavelength .....	696
4. Coefficients of equation (7) for the full range ..	687	14. Departures from the formulation of the high-quality <i>n</i> data in the visible and in the temperature range 0–40 °C; the data are by Damien, <sup>34</sup> Grange, <sup>44</sup> Landolt, <sup>45</sup> Willner, <sup>46</sup> Wiedemann, <sup>47</sup> and Walter <sup>48</sup> .....	696
5. Sources of a few data points each .....	695	15. Departures from the formulation of high- and medium-quality <i>n</i> data in the visible and at temperatures near ambient, and plotted against wavelength. The data are by Bayen, <sup>49</sup> Boguth, <sup>50</sup> Ducleaux, <sup>51</sup> Gifford, <sup>52</sup> Gregg-Wilson, <sup>53</sup> Kruis, <sup>54</sup> Moreels, <sup>55</sup> and Schütt. <sup>56</sup> Two outliers by Bayen have been removed. ....	697
6. Estimated uncertainty of the refractive index formulation .....	703	16. Departures from the formulation of medium- and high-quality <i>n</i> data in the visible and in the temperature range of 0 to 100 °C. The data are by Bender, <sup>57</sup> Damien, <sup>34</sup> Hall, <sup>23</sup> Hawkes, <sup>35</sup> Jasse, <sup>24</sup> and Ketteler <sup>57</sup> .....	697
7. Refractive index of water .....	704	17. Departures from the formulation of low-quality <i>n</i> data in the visible as a function of temperature. The data are those of Dale, <sup>59</sup> Fouqué, <sup>60</sup> Osborn, <sup>61</sup> and Rühlmann. <sup>62</sup> An outlier of Rühlmann at 15 °C has been removed .....	698
8. Refractive indices of water and steam at state of saturation .....	711	18. Departures from the formulation for <i>n</i> data in pressurized water. The data are those of Waxler <i>et al.</i> , <sup>3,4</sup> Rosen, <sup>25</sup> and Stanley <sup>26</sup> and are plotted versus density. An outlier has been removed from the Rosen data .....	698
9. Refractivity virial values; visible range, ambient temperature .....	713	19. Departures from the formulation of the low-quality Poindexter data <sup>63</sup> in pressurized water, plotted versus density .....	699
A.1. Coefficients of equation (7) for atmospheric liquid water .....	716	20. Departures from the formulation of the <i>n</i> data of Bayen <sup>49</sup> in the ultraviolet plotted versus wavelength .....	699
		21. Departures from the formulation of <i>n</i> data in the ultraviolet plotted versus wavelength. The data are by Boguth, <sup>50</sup> Ducleaux, <sup>51</sup> Flatow, <sup>17</sup> Gifford, <sup>52</sup> and Kruis <sup>54</sup> .....	700
		22. Departures from the formulation of the <i>n</i> data in the ultraviolet plotted versus wavelength. The data are by Roberts, <sup>64</sup> Simon, <sup>65</sup> and van der Willigen. <sup>43</sup> Three points by Simon below .25 μm in wavelength, with negative deviations down to -0.01 at λ = 0.22 μm, have been omitted .....	700
		23. Departures from the formulation of the refrac-	

## List of Figures

1. Wavelength-dependence of the Lorentz-Lorenz function of liquid water at 25 °C and ambient pressure .....	680
2. Density-dependence of the Lorentz-Lorenz function of steam at low densities, according to Achtermann and Rögener <sup>6</sup> at 225 °C .....	681
3. Density-dependence of the Lorentz-Lorenz function of pressurized water at 54.3 °C, according to Waxler <i>et al.</i> <sup>3,4</sup> .....	681
4. Departures from the formulation of the fitted experimental <i>n</i> data of Tilton and Taylor, <sup>1,2</sup> plotted against wavelength .....	687
5. Departures from the formulation of the fitted experimental <i>n</i> data of Achtermann and Rögener, <sup>6</sup> plotted against density .....	689
6. (a). Departures from the formulation of the fitted experimental <i>n</i> data of Waxler <i>et al.</i> , <sup>3,4</sup> plotted against temperature. A few outliers have been removed .....	690
6. (b). Departures from the formulation of the fitted experimental <i>n</i> data of Waxler <i>et al.</i> , <sup>3,4</sup> plotted against density. A few outliers have been removed .....	690
7. Departures from the formulation, plotted against density, of the partially fitted experimental <i>n</i> data of Stanley <sup>26</sup> in pressurized water .....	691
8. Departures from the formulation of the fitted experimental <i>n</i> data of Flatow <sup>17</sup> in the ultraviolet, plotted against wavelength .....	691
9. Departures from the formulation of the fitted experimental <i>n</i> data in the infrared, those of Rubens, <sup>27</sup> Ingersol, <sup>28</sup> and Vincent-Geisse, <sup>29</sup> plotted against wavelength .....	692
10. Departures from the formulation of the fitted <i>n</i> data that Pontier <sup>30</sup> derived from reflectance measurements in the infrared; data are plotted against wavelength .....	692

- tive index data of Schulz<sup>18</sup> plotted against wavelength. The data are a composite, prepared by Schulz, of his own data in the ultraviolet in the range of 0–100 °C, and by others in the visible ..... 701
24. Departures from the formulation of  $n$  data derived from reflectance and absorbance data in the infrared plotted versus wavelength. The plot is cut off at 2.6  $\mu\text{m}$ , beyond which the deviations become very large. The data are those of Centeno<sup>66</sup> ..... 701
25. Departures from the formulation of the refractive index data calculated from reflectance and absorbance over large ranges of wavelength. The predictions are due to Hale,<sup>67</sup> Palmer,<sup>68</sup> and Rusk<sup>69</sup> ..... 702
26. Departures of the Zolotarev's<sup>71,72</sup> refractive index data, both measured and predicted from reflectance and absorbance over large ranges of wavelength ..... 702
- A1. Departures of the data of Tilton and Taylor<sup>1,2</sup> and of Saubade<sup>9</sup> in liquid water at atmospheric pressure from an alternative formulation based on Sato's equation for the density of water ..... 717

## 1. Introduction

The refractive index of water has been measured with care by many researchers for well over a century. The reasons are many: water is the most prevalent liquid on earth; its properties are anomalous, and so is its refractive index; propagation, reflection and absorption of light in water all pose challenging scientific and practical problems, that require knowledge of the refractive index in order to be resolved. Water also is an excellent reference for relative refractive index measurements in other liquids. Finally, the refractive index itself is increasingly used as a local probe of properties, such as the density, that cannot readily be measured *in situ*. Given the amount of information accumulated over the years on the wavelength, temperature and pressure dependence of the refractive index of water, it appeared desirable to accumulate the data, assess their accuracy and devise a comprehensive formulation for this important property.

Traditionally, the experimental emphasis has been on liquid water below the boiling point. Many studies, and particularly that of Tilton and Taylor<sup>1,2</sup>, a classical example of careful experimentation, concentrate on wavelength dependence in the visible range at temperatures near ambient; fewer on wavelength dependence in the infrared and ultraviolet. In other studies, the emphasis is on the temperature dependence of the refractive index along the saturation curve up to the boiling point. Only a handful of publications deal with the pressure dependence of the refractive index in liquid water, but at least one of these studies, that of Waxler and coworkers<sup>3,4</sup>, is extensive, covering several wavelengths and a substan-

tial range of pressure while maintaining good accuracy. There are no measurements on liquid water that extend beyond 100 °C. Measurements of the refractive index of water vapor are virtually nonexistent, with one exception, the work of Achtermann and Rögner<sup>5,6</sup>, in which the range from 100 to 225 °C was covered with exemplary accuracy.

Given the patchy data situation, to devise a comprehensive formulation over a substantial range of wavelengths, temperature and pressure could be a hazardous undertaking, were it not that in the process of sifting out the reliable data sources a discovery was made that greatly simplified all further work. In the earlier formulation, Thormählen *et al.*<sup>7</sup> made use of the fact that the Lorentz-Lorenz function  $LL = (n^2 - 1) / \{(n^2 + 2) \rho\}$ , although depending strongly on the wavelength, has a simpler dependence on density and temperature than the refractive index itself. Here  $n$  is the refractive index with respect to vacuum and  $\rho$  is the density. Nevertheless, in certain ranges of their formulation,  $LL$  still varied by 50% at fixed wavelength, due mainly to the effects of data of uncertain accuracy. By comparing, at fixed wavelength, the three highly reliable data sources mentioned (one in the vapor above 100 °C and two in the liquid below 100 °C), we noted that, for given wavelength, the Lorentz-Lorenz function did not vary more than 2 percent in temperature and in density over the entire experimental range. Thus, the molar refractivity of water at fixed wavelength behaves no different than that of simpler fluids, for which similar behavior has been found and theoretically explained.

Our work thus simplified to first finding the correct wavelength-dependence for the Lorentz-Lorenz function of liquid water in a modest temperature range, by fitting the Tilton and Taylor data augmented by the limited reliable refractive index measurements obtained in the infrared and ultraviolet. A minimum of temperature- and density-dependent terms were then added so as to fit the pressurized-liquid and high-temperature vapor data.

All conversions from experimental pressures to densities were carried out by means of the NBS/NRC equation of Haar, Gallagher and Kell (HGK), which is the internationally accepted standard for water and steam<sup>8</sup>. This procedure limits the accuracy of the Lorentz-Lorenz function to that of the NBS/NRC equation. In several instances of high-quality data, this latter uncertainty dominates.

Weights have been assigned in accordance not only with the known or estimated experimental uncertainty in  $n$ , but also with other factors to be discussed below (Sec. 3). Only linear regression techniques have been used, so as to avoid the pitfalls associated with nonlinear regression for multiparameter fits. Two parameters occurring nonlinearly in the wavelength-dependence of the Lorentz-Lorenz function were determined by stepwise variation until an optimum fit was obtained.

The formulation has been compared with all data published since the middle of last century. It is demonstrated that most of the basic data sets are fitted to within an

order of magnitude of their claimed experimental accuracy.

We report a number of inconsistencies between data sets. In the few cases where ppm-level data are available, some deficiencies of our model have to be ascribed to the equation of state. In fact, we will demonstrate that the very-high-quality refractive index data can be used to discriminate between several equations of state proposed for water and steam. In the regions where accurate data are available for comparison, the present formulation has an order of magnitude more accuracy than that of Thormählen *et al.*<sup>7</sup>, whereas only ten adjustable parameters are used instead of fourteen in the preceding formulation.

The formulation has been used to generate tables of the refractive index of water and steam for six wavelengths from the near ultraviolet, through the visible, to the near infrared, for the range 0–500 °C and up to 100 MPa.

The paper is arranged as follows. The philosophy of our approach is explained in Sec. 2. The data sources, and the selected set we choose to fit, are the topic of Sec. 3. Section 4 gives the form of the representation, and the optimum values of the coefficients. Section 5 gives a mostly pictorial comparison with the basic data sets used in the fit. Section 6 is concerned with the data emphasizing the temperature dependence of the refractive index in liquid water. Section 7 compares with all remaining literature data. Section 8 assesses the reliability of the formulation. In Sec. 9, we present tables of the refractive index of water and steam as function of pressure and temperature for six different wavelengths. Section 10 presents a summary and conclusions. The Appendix contains the best formulation of the Tilton and Taylor<sup>1,2</sup> and Saubade<sup>9</sup> data in the visible, in the range of –12 to 60 °C in liquid water at ambient pressure.

## 2. Approach

The molar refraction or Lorentz-Lorenz function of liquid water, defined as

$$LL = \frac{n^2 - 1}{(n^2 + 2)\rho} \quad (1)$$

with  $n$  the refractive index,  $\rho$  the density of the fluid (in units to be specified shortly), is in some respects a very simple, but in others<sup>7</sup> a very complex property. It has a complicated wavelength dependence, as is evident from Fig. 1. Two resonances, one at about 0.18  $\mu\text{m}$ , the other at about 2.7  $\mu\text{m}$ , are responsible in great measure for the variation of the molar refraction in the visible and in the near ultraviolet and infrared, the object of our study. The molar refraction depends, however, only weakly on density and temperature; this is evident from Fig. 2, which displays the density dependence of  $LL$  in the high-temperature vapor according to Achtermann and Rögener<sup>5,6</sup>, and from Fig. 3, where the same is shown for pressurized liquid water below the boiling point, accord-

ing to Waxler and coworkers<sup>3,4</sup>. The combined variation with temperature and density does not exceed a few percent of the value of the Lorentz-Lorenz function. The molar refraction is slightly lower in the liquid than in the vapor, just as has been found for fluids of lesser complexity than water and steam, such as carbon dioxide<sup>10</sup> and argon<sup>11</sup>.

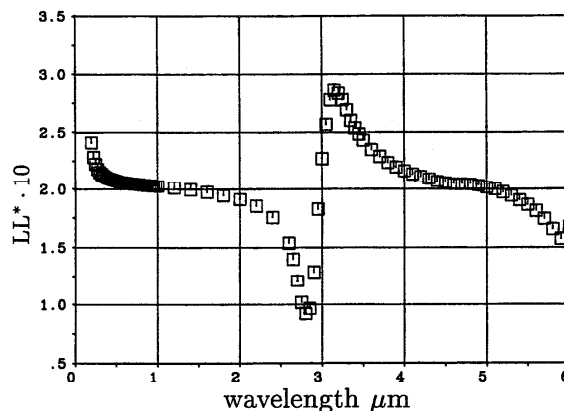


FIG. 1. Wavelength-dependence of the Lorentz-Lorenz function of liquid water at 25 °C and ambient pressure.

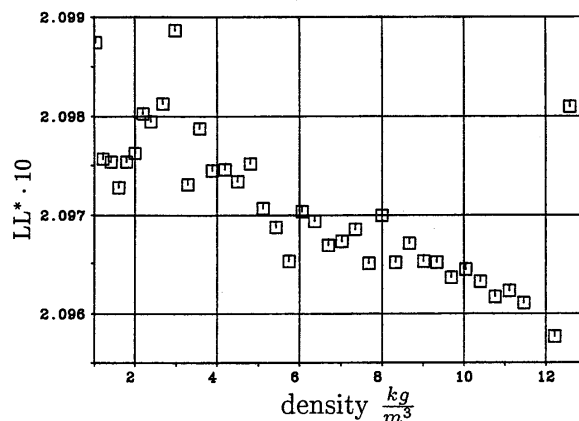


FIG. 2. Density-dependence of the Lorentz-Lorenz function of steam at low densities, according to Achtermann and Rögener<sup>6</sup> at 225 °C.

In principle, it should be expected that the molar refraction depends on the state of the fluid; the temperature dependence is expected to be mostly implicit, namely by shifting the resonance frequencies. The density dependence of the molar refraction is expected to be of the form of a virial series<sup>12</sup>.

Experimental studies of the temperature dependence of the molar refraction of water and steam have been few and of limited accuracy. The most accurate data,

those in the visible, are too far from the nearest resonances for effects of resonance shifts due to temperature to be detectable. We have found the two reports on temperature dependence of the molar refractivity near the ultraviolet resonance mutually conflicting and not consistent with the data in the visible. The density dependence of the molar refraction of H<sub>2</sub>O has never been explicitly studied, and is therefore intertwined with the nonideality of the gas. We will show that the procedures we have followed allow a plausible separation of the refractivity virials and gas nonideality effects.

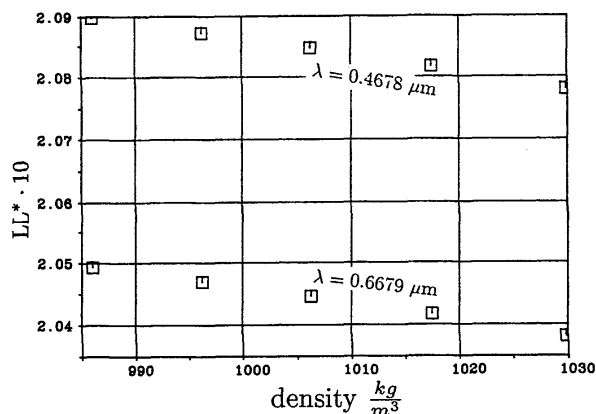


FIG. 3. Density-dependence of the Lorentz-Lorenz function of pressurized water at 54.3 °C, according to Waxler *et al.*<sup>3,4</sup>

In developing the new formulation, the following principles have been our guidelines: (a) incorporate what is known about the physics of the problem; (b) base the formulation solely on high-quality, mutually consistent data; (c) to the extent possible, determine separately the dependencies on each of the three independent variables; (d) assign weights carefully and avoid overfitting; (e) avoid nonlinear regression.

As to point (a), the elements we have incorporated are: some of the known resonance features, proper low-density behavior and the expectation that, at constant wavelength, the molar refraction should assume a value close to constant. The Lorentz-Lorenz<sup>13,14</sup> equation relates the refractive index to the molecular polarizability  $\alpha$  (at optical frequencies) by means of:

$$\frac{n^2 - 1}{(n^2 + 2)\rho_m} = \frac{N_A \alpha}{3\epsilon_0} \quad (2)$$

where  $N_A$  is Avogadro's number,  $\rho_m$  the density in moles per unit volume and  $\epsilon_0$  the vacuum permittivity. The left-hand side of (1), the molar refraction, depends on the wavelength according to the dispersion relation<sup>15</sup>

$$\frac{n^2 - 1}{(n^2 + 2)\rho_m} = a_0 + \sum_i \frac{a_i}{\lambda^2 - \lambda_i^2} \quad (3)$$

where  $\lambda_i$  is the wavelength corresponding to the  $i^{\text{th}}$  resonance and the  $a_i$  are constants related to the strengths of the resonances. Although Eq.(2), in principle, sums over all resonances, the two nearest to the visible in the infrared and ultraviolet have an overriding effect on the refractive index in the range of interest here. Thus, we have included only those two in our formulation. The values of the two resonance wavelengths,  $\lambda_{UV}$  and  $\lambda_{IR}$ , may be considered effective resonances into which some effects of further resonances have been lumped. Thus we have

$$\frac{n^2 - 1}{(n^2 + 2)\rho_m} = a_0 + \frac{a_{UV}}{\lambda^2 - \lambda_{UV}^2} + \frac{a_{IR}}{\lambda^2 - \lambda_{IR}^2} \quad (4)$$

With appropriate choices of  $\lambda_{UV}$ ,  $\lambda_{IR}$  and with least-squares adjustment of  $a_0$ ,  $a_{UV}$  and  $a_{IR}$ , Eq. (4) describes the wavelength dependence of the highly accurate refractive index data of Tilton and Taylor<sup>1,2</sup> in the visible to a few parts in 10<sup>4</sup>, which is a good beginning. In practice, we added two small wavelength-dependent terms, one of which is proportional to  $\lambda^2$ , the other to  $1/\lambda^2$ . These terms improve the agreement with the modest number of reliable data in the ultraviolet and the infrared, in liquid water at atmospheric pressure.

In addition to incorporating the nearest resonances in a practical way, the formulation should display correct low-density behavior. The molar refraction can be expressed in a power series in the molar density<sup>12</sup>:

$$\frac{n^2 - 1}{(n^2 + 2)\rho_m} = A_R + B_R \rho_m + C_R \rho_m^2 + \dots \quad (5)$$

with  $A_R$ ,  $B_R$ , etc., the first, second, etc. refractivity virials, and  $A_R$  equal to  $N_A \alpha / 3\epsilon_0$  by virtue of Eq. (2).

Eq. (5) implies that the refractive index should vary linearly with density at low density. The preceding formulation of the molar refraction of steam<sup>7</sup> contained a pole at zero density; Eq. (5), however, ensures that all density-dependent terms approach zero or constant values as the density approaches zero.

As to (b), the preselection of the data sets, we have found this point of overriding importance in arriving at our present results. The accuracy of the available data sources varies by more than four orders of magnitude. In a region where an extensive set of high-quality data is available, no data of lesser quality or consistency have been included in the fit. Low-accuracy data have only been used when no other information was available in the region of interest. The exclusion from the fit of one inconsistent data set<sup>16</sup> in the supercritical region made all other high-quality data fall into place, and came a long way towards eliminating the large variations of the constant-wavelength molar refraction that Thormählen *et al.*<sup>7</sup> experienced in the previous formulation.

As to (c), separating the dependencies on the individual independent variables, once the wavelength-dependence of the molar refraction was incorporated accurately for liquid water, the temperature and density dependencies had to be dealt with. It is very well known, from a massive amount of experimental data, that the refractive index of liquid water at ambient pressure varies considerably with temperature. It is not always appreciated, however, that under these conditions the density varies as well as the temperature. In correlating the refractive index with temperature only, one is, in effect, formulating an equation of state for liquid water at atmospheric pressure. Since an accurate equation of state is available for water and steam under all conditions<sup>8</sup>, this is not a useful thing to do, except perhaps in the few cases where the refractive index is more accurately known than the equation of state.

Thormählen *et al.*<sup>7</sup> demonstrated that, in contrast to the refractive index, the molar refraction of liquid water at atmospheric pressure varies by less than 1 part in 10<sup>3</sup> between 0 and 100 °C. Thus, in formulating the molar refraction, a function results that is only very weakly dependent on temperature. As mentioned before, it is to be expected that most of this dependence is implicit, through temperature dependence of the resonance frequencies. Two experimental papers, by Flatow<sup>17</sup> and by Schulz<sup>18</sup>, have reported temperature dependence of the molar refraction of liquid water near the ultraviolet resonance. As will be discussed in Sec. 5, we have not been able to incorporate a temperature-dependent ultraviolet resonance wavelength that improves the fit to these data sets without affecting adversely the fit to the Tilton and Taylor data in the visible.

The dependence of the molar refraction on density needs to be considered next, Eq. (5). For the second refractivity virial,  $B_R$ , a first-principles relation between the virial and the molecular potential has been derived<sup>12,19</sup>, and has been evaluated for intermolecular potentials simpler than that of water<sup>19-22</sup>. In several instances, the second, and in some, higher virials have been measured for simple gases<sup>19-22</sup>. It has been found that both the second and third virial are required to represent experimental data of compressed gases, and indications have been found that a fourth may be needed<sup>22</sup>. It is expected that these virials have little temperature<sup>20,22</sup> or wavelength dependence<sup>19</sup>.

We have followed the practical approach of finding out how many virial terms were needed to represent the best data over the entire density range. The data for molar refraction in pressurized liquid water according to Waxler *et al.*<sup>3,4</sup> (Fig. 3) show a slight decrease with density. Also, the 225 °C vapor data of Achtermann and Rögner<sup>5,6</sup> show signs of a decline with density (Fig. 2). By adding a term linear in density to the expression (3) for the molar refraction, and optimizing the fit to the liquid data, it is found that the vapor data are overshoot by as much as 10%. This is not surprising since in several other fluids<sup>10,11</sup> it has likewise been observed that the decrease of the molar refraction occurs mainly at liquid-

like densities. A term of the form  $C_{RP} \rho^2$  was found to be effective in reconciling high-quality vapor and liquid data. The value of the second refraction virial thus obtained had a reasonable magnitude, compared to what is known for other gases. We have found that the use of a term cubic in density gives further marginal improvement in the fit to the data in pressurized water and in water at temperatures approaching the boiling point; we have decided against the inclusion of such a term because it had an undesirable effect on the magnitude of the second refraction virial and might conceivably lead to spurious behavior in ranges where no data were available.

Slight residual offsets between the accurate high- and low-temperature data in the visible could be eliminated by a small term linear in temperature. By trial and error we found that a term of the form  $T\lambda^2$  was more effective than a term proportional to  $\lambda^2$  alone.

(d) The estimation of the accuracy of the refractive index and the molar refraction presents some interesting problems because of the large ranges of variables spanned by the data; in particular, the density varies over three orders of magnitude, so that ppm-level inaccuracy in refractive index may result in inaccuracies in the molar refraction ranging from parts in 10<sup>5</sup> in the liquid to percents in the vapor. Furthermore, the uncertainties of the individual refractive index data sources vary over five orders of magnitude, from percents to parts in 10<sup>7</sup>.

It is very important to properly account for the large variations in accuracy of the molar refraction, in order to prevent overfitting, or fitting to poor data at the expense of the better ones. Table 1 gives an impression of how error in the refractive index propagates into the Lorentz-Lorenz function for some typical cases: visible, ultraviolet and infrared, liquid and vapor. The examples chosen are typical for the data sets that form the basis for this work.

In the present formulation, we have assigned the weights of the molar refraction data by propagation of the error in the original refractive index data into the molar refraction. These weights vary over many orders of magnitude, so that the low-accuracy data in the infrared and ultraviolet do not unduly influence the fit to the high-quality data in the visible. Apart from the uncertainty in the refractive index, that in the density enters into the value of the molar refraction. In all cases where pressure and temperature were given, we used the HGK equation<sup>8</sup> to calculate the density. In liquid water, the equation is accurate to a few parts in 10<sup>5</sup>, except near 0 °C, and in the vapor to a few parts in 10<sup>4</sup>. The uncertainty of the Lorentz-Lorenz function propagates into the refractive index in a way that depends mostly on the state of the fluid. For liquid water, the absolute uncertainty in  $n$  is roughly 1/3 of the relative uncertainty in the molar refraction, and in (dense) water vapor of 10 kg m<sup>-3</sup> density it is only 1/300 of the relative uncertainty in the molar refraction (Table 1). This implies that the uncertainty of the equation of state, which enters directly into the molar refraction, limits the accuracy of

TABLE 1. Propagation of error in refractive index

$\lambda$ , $\mu\text{m}$	0.6	0.6	0.6	2.7	0.22
$\rho$ , $\text{kg m}^{-3}$	1000	100	10	1000	1000
$n$	1.330	1.031	1.004	1.151	1.40
$\delta n/n$	$0.75 \delta n$	$0.97 \delta n$	$0.87 \delta n$	$0.71 \delta n$	
$LL$	0.204	0.204	0.204	0.097	0.242
$\delta LL$	$0.56 \delta n$	$6.6 \delta n$	$67 \delta n$	$0.63 \delta n$	$0.53 \delta n$
$\delta LL/LL$	$2.8 \delta n$	$32 \delta n$	$327 \delta n$	$6.4 \delta n$	$2.2 \delta n$
Typical for	Liquid below 100 °C, visible	Near-critical visible	Vapor visible	Liquid infrared	Liquid ultraviolet
Code	[TT 1938]	[S 1981]	[AR 1986]	[PSW 1977]	[F1903]
Reference	1,2	16	5,6	70	17
$\delta n$	$3 \cdot 10^{-7}$	$>10^{-3}$	$2 \cdot 10^{-7}$	0.01	$5 \cdot 10^{-4}$
$\delta LL/LL$	$10^{-6}$	$>0.03$	$7 \cdot 10^{-5}$	0.06	$1 \cdot 10^{-3}$

$n$  to about  $1 \cdot 10^{-5}$  in the liquid,  $1 \cdot 10^{-6}$  in the vapor. With the exception of the few highly accurate data sets, the equation of state contributes little error.

If the uncertainty of a particular data set cannot be estimated for lack of information, an idea of the precision can usually be obtained from the scatter of the data. If two data sets do not agree to within combined scatter, a decision is made on which one to disregard. This decision is based on judgment that includes reputation of the investigator and the institution, or (dis)agreement with other reputable sources.

Overfitting is a temptation when excellent data are available in restricted regions. We have experimented extensively with the form of the terms, so as to minimize the number of adjustable parameters in the formulation, and have documented many such attempts in the course of this paper. Although we have obtained closer fits to the data of Tilton and Taylor by adding another term, we declined to do so because the added higher-order terms, though small within the range of the Tilton and Taylor data, might cause unwanted oscillations in ranges where their behavior might be uncontrolled because of absence of adequate data. We also found that once other data sets were added to the Tilton and Taylor data, the effect of the additional term was washed out.

(e) Finally, we have avoided nonlinear multiple parameter regression by varying in steps parameters occurring nonlinearly, while fitting only for the ones occurring linearly by standard linear regression. Since only the low-accuracy data near the resonances are sensitive to the choice of the nonlinear parameters, we have avoided considerable numerical complications by the procedure chosen.

The above considerations reduced what initially appeared to be a formidable nonlinear multiparameter regression of a massive but patchy data set of uneven quality and depending on three independent variables, to

a relatively simple and manageable linear least-squares fit to a rapidly converging expression free of uncontrolled oscillations in the entire span of the variable space. It must be borne in mind, however, that the underlying hypothesis of minimal variation of the Lorenz-Lorentz function has not been subjected to verification in large parts of the range of the correlation, because of the absence of reliable data.

### 3. Data Sources, Selection and Correction

The complete set of data sources of the refractive index of water and steam is listed in Table 2. For each source, ranges of temperature, pressure and wavelength are given. The data go back to over a century ago, and, in our experience, several of the older references are to be preferred over recent ones. The cut-off date of our refractive index data research is December 1987. The selected data sources on which we have based our formulation are summarized in Table 3. The absolute weights used in the fit are calculated from an assigned standard deviation in  $n$  that is listed in Table 3 under the heading s.d.n. For reasons to be stated below, this standard deviation does not necessarily reflect the precision or accuracy of the data.

The data of Tilton and Taylor<sup>1,2</sup> form the core of the correlation. These data were obtained relative to air at the same temperature in a hollow prism provided with a thermostated mantle. The data are of high precision, better than 1 ppm in the refractive index, cover the temperature range of 0–60 °C and thirteen wavelengths in the visible. By complementing them with the Saubade data in supercooled water, and with the data of Achtermann and Rögner, which were taken in the vapor and reach to 225 °C, a large part of the density and temperature range in the visible is covered.

TABLE 2. Experimental data sources

First Author	Code	Reference	Experimental Range		
			$T$ ( $^{\circ}\text{C}$ )	$P$ (MPa)	$\lambda$ ( $\mu\text{m}$ )
Achtermann	[AR 1986]	5,6	100–225	0.01–2.5	0.63
Baxter	[BBD 1911]	73	20–30	0.1	0.59
Bayen	[B 1942]	49	7–36	0.1	0.19–0.59
Bender	[B 1899]	57	9–43	0.1	0.41–0.65
Boguth	[B 1973]	50	23	0.1	0.40–0.59
Brühl	[B 1891]	37	20–27	0.1	0.41–0.77
Centeno	[C 1941]	66	20	0.1	0.18–18
Cohen	[CE 1965]	74	25	0.1	0.44–0.55
Conroy	[CJ 1895]	38	0–90.1	0.59	
Cuthbertson	[CC 1913]	79	vapor		0.48–0.67
Dale	[DG 1858]	59	0–80	0.1	0.40–0.76
Damien	[D 1881]	34	–8–(+8)	0.1	0.32–0.66
Ducleaux	[DJ 1921]	51	20	0.1	0.18–0.57
Dufet	[D 1885]	39	16–21	0.1	0.41–0.72
Flatow	[F 1903]	17	0–80	0.1	0.21–0.59
Fouqué	[F 1867]	60	0–93	0.1	0.43–0.66
Fraunhofer	[F 1817]	80	19	0.1	0.40–0.69
Gifford	[G 1907]	52	15	0.1	0.19–0.80
Gladstone	[G 1870]	76	20	0.1	0.32–0.40
Grange	[GSV 1976]	44	5–25	0.1	0.63
Gregg-Wilson	[GW 1931]	53	–5–(+10)	0.1	0.59
Hale	[HQ 1973]	67	25	0.1	0.2–200
Hall	[HP 1922]	23	16–98	0.1	0.59
Hawkes	[HA 1948]	35	–5–(+27)	0.1	0.59
Ingersoll	[I 1922]	28	23	0.1	0.60–1.25
Jasse	[J 1934]	24	0–93	0.1	0.44–0.58
Kanonnikoff	[K 1885]	75	20	0.1	0.49–0.66
Ketteler	[K 1887]	58	21–94	0.1	0.54–0.67
Kruis	[KG 1940]	54	25	0.1	0.21–0.67
Landolt	[L 1862]	45	15–30	0.1	0.43–0.65
Lorenz	[L 1880]	40	10–100	0.1	0.59–0.67
Moreels	[M 1984]	55	25	0.1	0.48–0.63
Müttrich	[M 1864]	81	1–65	0.1	0.26–0.59
Osborn	[O 1913]	61	3–38	0.1	0.55
Palmer	[PW 1974]	68	27	0.1	0.36–2.6
Pinkley	[PSW 1977]	70	1–50	0.1	0.41–25
Poindexter	[PR 1934]	63	25	0.1–182	0.41–0.58
Pontier	[PD 1966]	30	27	0.1	1–40
Pulfrich	[P 1888]	36	–10–(+10)	0.1	0.59
Quincke	[Q 1883]	41	18–20	0.1	0.43–0.66
Roberts	[R 1930]	64	20	0.1	0.24–0.71
Röntgen	[RZ 1891]	77	19	0.1	0.59
Rosen	[R 1947]	25	25	0.1–152	0.40–0.58
Rubens	[R 1892]	27	12	0.1	0.43–1.25
Rubens	[RL 1909]	27	18	0.1	1–18
Rühlmann	[R 1867]	62	0–77	0.1	0.54–0.67
Ruoss	[R 1893]	78	23	0.1	0.59
Rusk	[RW 1971]	69	25	0.1	2.0–30
Saubade	[S 1981]	9	–12–(+20)	0.1	0.59
Scheffler	[SSG 1981]	16	16–374	0.1–70	0.55
Schulz	[S 1955]	18	15–95	0.1	0.22–0.77
Schütt	[S 1890]	56	18	0.1	0.43–0.77
Simon	[S 1894]	65	22	0.1	0.22–0.77
Stanley	[S 1971]	26	1–60	0.1–140	0.63
Tilton	[T 1936]	1	0–60	0.1	0.40–0.71
Tilton	[TT 1938]	2	0–60	0.1	0.40–0.71
Verschaffelt	[V 1894]	42	18–30	0.1	0.59
Vincent-Geisse	[VVG 1964]	29	18	0.1	0.59–1.53
Walter	[W 1892]	48	0–30	0.1	0.59
Waxler	[WW 1963]	3	2–54	0.1–113	0.47–0.67
Waxler	[WWS 1964]	4	2–54	0.1–113	0.47–0.67
Wiedemann	[W 1876]	47	13–25	0.1	0.54–0.76
van der Willigen	[W 1864]	43	17–32	0.1	0.40–0.76
Wüllner	[W 1868]	46	12–37	0.1	0.43–0.66



TABLE 2. Experimental data sources — Continued

First Author	Code	Reference	Experimental Range		
			T (°C)	P(MPa)	$\lambda(\mu\text{m})$
Yadev	[Y 1973]	82	25	18–820	0.59
Zeldovich	[ZSKY 1961]	83	185–875	4000–15000	0.59
Zolotarev	[ZMAP 1969]	71	25	0.1	2.1–10 <sup>6</sup>
Zolotarev	[ZD 1977]	72	25	0.1	2.0–5·10 <sup>4</sup>

TABLE 3. Refractive index data used in the formulation

Authors	Code	Ref.	# data	s.d.n	Pressure MPa	Temperature °C	Wavelength $\mu\text{m}$
Tilton and Taylor	[TT 1938]	2	120	1.E-6	0.1	5–60	0.40–0.70
Tilton and Taylor	[TT 1938]	2	13	1.E-4	0.1	0	0.40–0.70
Jasse	[J 1934]	24	11	1.E-4	0.1	52–89	0.44–0.58
Jasse	[J 1934]	24	8	1.E-5	0.1	90–93.5	0.44–0.58
Hall and Payne	[HP 1922]	23	8	1.E-4	0.1	52–70	0.59
Hall and Payne	[HP 1922]	23	12	1.E-5	0.1	73–98	0.59
Achtermann	[AR 1986]	5,6	125	7.E-7	0.01–2.5	100–225	0.63
Waxler <i>et al.</i>	[WWS 1964]	4	112	4.E-5	0.1–113	7–54	0.47–0.67
Waxler and Weir	[WW 1963]	3	39	1.E-3	0.1–113	1.5	0.47–0.67
Stanley	[S 1971]	26	22	1.E-4	100–138	1–60	0.63
Flatow	[F 1903]	17	85	1.E-4	0.1	0–80	0.21–0.59
Rubens	[R 1892]	27	12	1.E-4	0.1	12	0.43–1.25
Ingersoll	[I 1922]	28	2	1.E-4	0.1	23	1.0, 1.25
Vincent-Geisse <i>et al.</i>	[VVG 1964]	29	5	1.E-4	0.1	18	0.59–1.53
Pontier	[PD 1966]	30	5	1.E-4	0.1	27	1.2–2.0
Pontier	[PD 1966]	30	3	5.E-4	0.1	27	2.0–2.6
Saubade	[S 1981]	9	33	1.E-4	0.1	–12–(+20)	0.59

Saubade<sup>9</sup> measured the index of refraction in super-cooled water, down to  $-12$  °C, for sodium light by means of a commercial immersion interferometer. He used the data of Tilton and Taylor above  $0$  °C for calibrating the instrument. This enabled him to boost the precision below  $0$  °C to a level of uncertainty of  $1 \cdot 10^{-6}$ .

Achtermann and Rögner<sup>5,6</sup> recently measured the absolute refractive index of water vapor from  $100$  °C to  $225$  °C in a double interferometer, one cell containing the water vapor, the other a reference gas maintained at the same pressure and temperature, and serving as a manometer. An accuracy of  $2 \cdot 10^{-7}$  in refractive index is claimed by the authors.

We included in the fit data of Flatow<sup>17</sup>, Hall<sup>23</sup> and Jasse<sup>24</sup> in liquid water above  $60$  °C. Flatow measured the refractive index of water in the visible and the ultraviolet around the turn of the century in a thermostated prism-shaped cell and at temperatures from  $0$  to  $80$  °C. In the visible, Tilton and Taylor reported good agreement, to about  $5 \cdot 10^{-5}$ , with their own data. This gave us reason to believe that Flatow would be a reliable source for the ultraviolet.

Hall and Payne<sup>23</sup>, also early in the century, measured the refractive index of water from  $16$  to  $100$  °C for

sodium light, in a brass prism with two plateglass windows. Hall believed his indices with respect to air have an uncertainty of  $2 \cdot 10^{-5}$  at the lower,  $3 \cdot 10^{-5}$  at the higher temperatures. These authors were, however, not certain of the way the correction for the index of refraction of air should be applied. They opted for the hypothesis that air should be considered at room temperature, but conceded that the air might be effectively at some intermediate temperature. At the highest temperature, the difference in refractive index of air between ambient and high temperature amounts to  $8 \cdot 10^{-5}$ , which then represents the maximum possible error due to uncertainty about the air temperature. We have corrected these data with respect to air at  $25$  °C and note that correcting with respect to air at higher temperatures would lower the values we have used in the fit.

Just prior to the work of Tilton and Taylor, Jasse<sup>24</sup> measured the refractive index of water with respect to air in a double interferometer, one filled with water, one with air at the same temperature and at four wavelengths in the temperature range from  $0$  to  $94$  °C. From Tilton and Taylor's comparison<sup>1,2</sup>, we know that her data agree with theirs on the level of a few parts in  $10^5$ , with a systematic decline to  $-1 \cdot 10^{-4}$  at temperatures from  $40$  to

60 °C. We have included in the fit the three older and somewhat less accurate data sets of Flatow, Hall and Jasse because they contain valuable information about the refractive index in the range of 60 to 100 °C.

The data sets of Waxler *et al.*<sup>3,4</sup>, and those of Rosen<sup>25</sup> and of Stanley<sup>26</sup>, reach to high pressures. Waxler *et al.* measured interferometrically the absolute refractive index of pressurized water up to 1100 bar, overlapping with Tilton and Taylor both in temperature and wavelength at atmospheric pressure, and using the latter data as a reference. Waxler *et al.* estimate their uncertainty as  $1 \cdot 10^{-4}$ . The Rosen set, which, for pure water, contains only four data points at one wavelength, was not used in the fit, but was found to be consistent with the data of Waxler *et al.* The Stanley data, obtained in a high-pressure Fabry-Perot interferometer, range from 0 to 60 °C at pressures up to 1400 bar, are referenced to the Tilton and Taylor data, and claim an uncertainty of  $6 \cdot 10^{-5}$ . Our formulation reveals, however, that they are not fully consistent with the data of Waxler *et al.* Since the latter data are consistent with those of Tilton and Taylor and of Rosen to within mutual uncertainty, we have included Stanley's data with low weight, except for pressures exceeding those of Waxler.

The rest of the data sets in Table 3, some of them really very old, serve to define the formulation in the infrared and in the ultraviolet. Flatow's data, as mentioned, stretch into the ultraviolet and agree well with Tilton and Taylor's data in the visible.

Rubens<sup>27</sup>, Ingersoll<sup>28</sup> and Vincent-Geisse *et al.*<sup>29</sup> all have a few apparently reliable directly measured data points in the near-infrared. Pontier's<sup>30</sup> data were derived from reflectance and absorbance data that he obtained over regions of longer wavelengths.

There are many other sources of information outside the visible, both in the infrared and in the ultraviolet, that are listed in Table 2. In all these cases, however, the data are only in part, or not at all, the result of refractive index measurements. Although we will compare with all these data sets, they have not been used as input to the formulation.

The following operations have been carried out on all data sets used in the fits and in the intercomparisons:

- (1) All temperatures were recalculated on the International Practical Temperature Scale of 1968<sup>31</sup>.
- (2) All pressures and densities were converted to the SI system.
- (3) In those cases where the refractive index was measured with respect to that of air,  $n_{\text{air}}$ , of specified temperature, the reported relative data  $n_{\text{rel}}$  were converted to absolute values  $n_{\text{abs}}$  by means of the equation  $n_{\text{abs}} = n_{\text{rel}} n_{\text{air}}$ , with

$$10^6 \cdot (n_{\text{air}} - 1) = \left[ 268.036 + \frac{1.476}{\lambda^2} + \frac{0.01803}{\lambda^4} \right] \cdot [1 - 0.00367(t - 20)] \cdot \frac{B}{0.1013} \quad (6)$$

as proposed by Kösters<sup>32</sup>. In Eq.(6),  $\lambda$  is the wavelength of light in vacuum, in  $\mu\text{m}$ ;  $t$  is the temperature in °C and  $B$  is the barometric pressure in MPa. This equation agrees with the one proposed by Tilton and Taylor<sup>1,2</sup> on the level of a few times  $10^{-7}$  or better. The value of the above correction is between 2 and  $3 \cdot 10^{-4}$  in  $n$ , and therefore the correction needs to be applied with care to the high-quality data in the visible range. For most data in the infrared, whose uncertainties usually exceed  $1 \cdot 10^{-3}$ , the correction is inconsequential.

#### 4. The Formulation

We have used the following representation of the wavelength, temperature and density dependence of the Lorentz-Lorenz function of light water and steam:

$$\frac{n^2 - 1}{n^2 + 2} \frac{1}{\rho^*} = a_0 + a_1 \rho^* + a_2 T^* + a_3 \lambda^{*2} T^* + a_4 / \lambda^{*2} + \frac{a_5}{\lambda^{*2} - \lambda_{UV}^{*2}} + \frac{a_6}{\lambda^{*2} - \lambda_{IR}^{*2}} + a_7 \rho^{*2} \quad (7)$$

where

$$\begin{aligned} \rho^* &= \rho / \rho_0 & \rho_0 &= 1000 \text{ kg m}^{-3} \\ \lambda^* &= \lambda / \lambda_0 & \lambda_0 &= 0.589 \text{ } \mu\text{m} \\ T^* &= T / T_0 & T_0 &= 273.15 \text{ K} \end{aligned} \quad (8)$$

$\rho$  is the density,  $\lambda$  the wavelength and  $T$  the absolute temperature. Note that, apart from an introduction of reduced (dimensionless) variables, the left-hand side of Eq. (7) is equivalent to the molar refractivity defined in Eq. (2).

The optimized values of the coefficients  $a_0$  to  $a_7$ , and of the effective infrared and ultraviolet resonances,  $\lambda_{IR}^*$  and  $\lambda_{UV}^*$ , respectively, are listed in Table 4.

The ranges of the three independent variables in which data exist that have been used in the fit are:

$$\begin{aligned} \text{temperature} & & 0 < t < 225 \text{ } ^\circ\text{C} \\ \text{density} & & 0 < \rho < 1060 \text{ kg m}^{-3} \\ \text{wavelength} & & 0.2 < \lambda < 2.5 \text{ } \mu\text{m} \end{aligned} \quad (9)$$

We do expect, but cannot substantiate by comparison with data, that the formulation will give good estimates of refractive index at temperatures much higher than given in (9), and that it will extrapolate correctly even into the supercritical regime.

#### 5. Comparison with the Selected Data Sets

In this section we compare with the data sets on which we have based the formulation (Table 3). This will enable us to analyze in some depth both the sources and the level of uncertainty of the formulation, and to pinpoint discrepancies between data sets.

In Fig. 4 we compare the refractive index data of Tilton and Taylor<sup>1,2</sup>, in liquid water from 0–60 °C and throughout the visible, with the formulation. These data have a claimed uncertainty of  $3 \cdot 10^{-7}$  in  $n$ . The departures of the data from our formulation are confined to a band of width  $\pm 15 \cdot 10^{-6}$  in  $n$ , with the exception of the data at 0 °C. The larger departure at 0 °C is due to the loss of accuracy of the equation of state, as we will argue in more detail in Sec. 6 and the Appendix. We have purposely reduced the weight at 0 °C so as not to force the formulation to fit to systematics induced by the equation of state. We will show in the Appendix, by the use of a more accurate equation of state, that the Tilton and Taylor data can be fitted more accurately than we have done here.

In Fig. 5 we compare with the high-temperature refractive indices of water vapor reported by Achtermann and Rögner<sup>5,6</sup>. These authors claim an accuracy of 2 parts in  $10^7$  in  $n$ . We fit all data, with slight systematics, to within  $\pm 6 \cdot 10^{-6}$ . The systematic departures can be reduced by about 50% by including an extra term in the formulation. We did not think the benefit of a slightly better fit outweighed the risk of uncontrolled oscillations in ranges where we had no data for constraining the formulation.

TABLE 4. Coefficients of equation (7) for the full range

$a_0 = +0.243905091$	$\lambda_{0V}^* = 0.2292020$
$a_1 = +9.53518094 \cdot 10^{-3}$	$\lambda_{R}^* = 5.432937$
$a_2 = -3.64358110 \cdot 10^{-3}$	
$a_3 = +2.65666426 \cdot 10^{-4}$	
$a_4 = +1.59189325 \cdot 10^{-3}$	
$a_5 = +2.45733798 \cdot 10^{-3}$	
$a_6 = +0.897478251$	
$a_7 = -1.63066183 \cdot 10^{-2}$	

AUTHOR: [TT 1938] Tilton-Taylor

□ 0.0 °C	◇ 25.0 °C	○ 50.0 °C
○ 5.0 °C	× 30.0 °C	○ 55.0 °C
△ 10.0 °C	* 35.0 °C	△ 60.0 °C
+ 15.0 °C	• 40.0 °C	
× 20.0 °C	□ 45.0 °C	

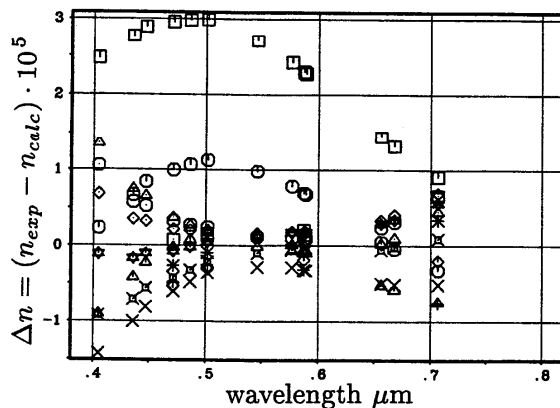


FIG. 4. Departures from the formulation of the fitted experimental  $n$  data of Tilton and Taylor<sup>1,2</sup>, plotted against wavelength.

In Figs. 6a, 6b we display the departures of the refractive index data in pressurized water, obtained by Waxler *et al.*<sup>3,4</sup>. These authors used the ambient-pressure Tilton and Taylor data as a reference. Waxler *et al.* claim an accuracy of  $5 \cdot 10^{-5}$  in  $n$ . We fit these data, after removal of two outliers, to within  $+1$  to  $-3 \cdot 10^{-4}$ . The fit was improved somewhat by adding a term quadratic in temperature, or one cubic in the density. Again, the improvement was not deemed worth the cost of uncontrolled behavior of the formulation in regions where no data exist.

In Fig. 7, we show the departures of the refractive index data in pressurized water obtained by Stanley<sup>26</sup>. Only changes in refractive index were measured, and the Tilton and Taylor data were used as a reference. The author claims an uncertainty of  $6 \cdot 10^{-5}$ . Stanley's data exceed the pressure range of the data of Waxler *et al.*<sup>3,4</sup>. Only the data beyond Waxler's range were included in our fit. Stanley made an attempt to compare his results with those of Waxler *et al.*, claiming an agreement within joint uncertainties of  $6 \cdot 10^{-5}$  and  $1 \cdot 10^{-4}$ , respectively, but he also commented on the difficulty of intercomparison since the values chosen for the independent variables were not the same for the two experiments. Our formulation makes such intercomparisons straightforward. We find that Stanley's data depart from our formulation and from the data of Waxler *et al.* in a systematic fashion. At 100 MPa, the difference between Stanley and Waxler is of the order of  $6 \cdot 10^{-4}$  in  $n$ , Stanley's data being about  $4 \cdot 10^{-4}$  higher than our formulation, and towards the end of Stanley's range his data depart from our formulation by about  $5 \cdot 10^{-4}$ . Adding terms to the formulation leads to improvement of the fit to the Stanley data at the expense of a deterioration of the fit to the data of Waxler *et al.*

Fig. 8 focuses on Flatow's data<sup>17</sup> in the ultraviolet. Other aspects of these data will be discussed at various other points of this paper. Flatow reports his data to five decimal places; the scatter is no more than a few units in the fifth decimal. In the visible, his data agree with those of Tilton and Taylor to  $1 \cdot 10^{-4}$ . In the ultraviolet above  $0.3 \mu\text{m}$ , Flatow's data depart from the formulation by  $-2 \cdot 10^{-4}$ . At lower wavelengths, the departures become larger, approaching  $10^{-3}$ , especially towards the resonance, and display systematics in temperature, the  $0^\circ\text{C}$  refractive indices being lower, the  $80^\circ\text{C}$  ones higher than the formulation.

Fig. 9 shows the departures of three old, modest-scope but apparently quite good data sources, namely Rubens<sup>27</sup>, Ingersoll<sup>28</sup> and Vincent-Geisse *et al.*<sup>29</sup>, in the infrared; these data have been used in the fit. The claimed uncertainty is of the order of  $1 \cdot 10^{-4}$ . Our formulation represents these data to better than  $6 \cdot 10^{-4}$  over a considerable range in the infrared. The infrared data of Pontier were included in the fit for wavelengths beyond  $1.2 \mu\text{m}$ . In the infrared, they agree with the formulation to about  $+1$  to  $-4 \cdot 10^{-3}$ , as indicated in Fig. 10.

This completes the intercomparisons with the basic data sets that we have used in the formulation, except for

the data of Saubade, Hall and Jasse, which are to be discussed in Sec. 6.

In summary, we represent most data to an uncertainty that is within an order of that claimed by the individual authors. Only in a few instances have we been able to put the blame on imperfections of the equation of state, namely in the case of highly accurate data near  $0^\circ\text{C}$ , to be discussed further below. In several cases, the discrepancies between data sets exceed the sum of claimed uncertainties. This is particularly so for the data on pressurized water, and is generally also the case, as we will discuss later, in the infrared and ultraviolet when the resonance frequency is approached.

## 6. Temperature Dependence of $n$ in Liquid Water, $-12$ to $100^\circ\text{C}$ , in the Visible Range

Fig. 11 displays the departures from the formulation of high-quality data in the visible, in water between  $-12$  and  $+100^\circ\text{C}$ . In addition to the data of Tilton and Taylor<sup>1,2</sup> and those of Flatow<sup>17</sup>, Hall<sup>23</sup> and Jasse<sup>24</sup>, that were used in the fit, we have included the recent data of Saubade<sup>9</sup> in supercooled water, with claimed uncertainty of  $1 \cdot 10^{-6}$ .

The comparison with our formulation, in Fig. 11, highlights three points.

1. In the range of overlap with Tilton and Taylor's data at  $5^\circ\text{C}$  and up, all data sets agree with each other and with the formulation to within approximately 1 part in  $10^4$ .
2. The Saubade and Tilton and Taylor sets agree to at least an order better. The sets show quite systematic departures from the formulation at  $0^\circ\text{C}$  and below, rising to  $1.5 \cdot 10^{-4}$  at  $-12^\circ\text{C}$ .
3. Beyond  $60^\circ\text{C}$ , the remaining data sets (Jasse and Hall) begin to depart from the formulation in a systematic way, down to  $-3 \cdot 10^{-4}$  at  $100^\circ\text{C}$ .

As to the first point, that departures between data sets exceed their combined estimated uncertainties by at least an order of magnitude, is common occurrence in data correlation which arises from incomplete knowledge of all sources of error. The second point is of considerable interest because of its relationship to deficiencies in the equation of state. The NBS/NRC<sup>8</sup> equation was not fitted to data below  $0^\circ\text{C}$ . In fact, the only highly accurate data existing in that range are those due to an extrapolation performed by Kell<sup>33</sup>. The departure of the NBS/NRC equation from the extrapolated Kell data is of the sign and magnitude required to explain a good part of the departures below  $0^\circ\text{C}$  in Fig. 11. In other words, if our present formulation were combined with an equation of state more accurate below  $0^\circ\text{C}$ , the Saubade data would be better represented. Thus, excellent refractive index data, such as those of Saubade<sup>9</sup> and of Tilton and Taylor<sup>1,2</sup>, can be used to fine-tune the equation of state of

water through the use of the Lorentz-Lorenz function. We intend to amplify on this conclusion in the Appendix.

The third point, the departures above 60 °C, are much harder to explain. In this range, the equation of state is known to be accurate on the level of a few parts in  $10^5$ . The observed departures far exceed the uncertainty of the density. We have not found a way of improving the fit. It is possible to obtain a closer fit at 100 °C, but this is at the expense of adding a term in  $T^2$  or in  $\rho^3$ , and always results in a deterioration of the fit to the data of Tilton and Taylor. We have reluctantly concluded that the Hall and Payne, and Jasse data above 60 °C are not fully consistent with the Tilton and Taylor data. Note also that correcting the Hall and Payne data for air at the same temperature, instead of air at 25 °C, increases the departures

(cf. Sec. 3). Although it was conceivable to make a different choice, we have decided to honor the primacy of the Tilton and Taylor data, until the time that data of comparable quality become available above 60 °C.

In Fig. 12, the four sets of data in supercooled water, those of Damien<sup>34</sup>, Hawkes<sup>35</sup>, Pulfrich<sup>36</sup> and Saubade<sup>9</sup>, are shown in somewhat more detail than in Fig. 11. There are systematic differences between the data obtained in the previous century, and the two more recent sets; the latter, those of Hawkes and Saubade, are in close agreement. All data show a systematic trend with temperature, which is caused in part by imperfection of the equation of state, in part by the effect of the inconsistent data above 60 °C, and, possibly, by a real anomaly in  $n$  in supercooled water. See Appendix.

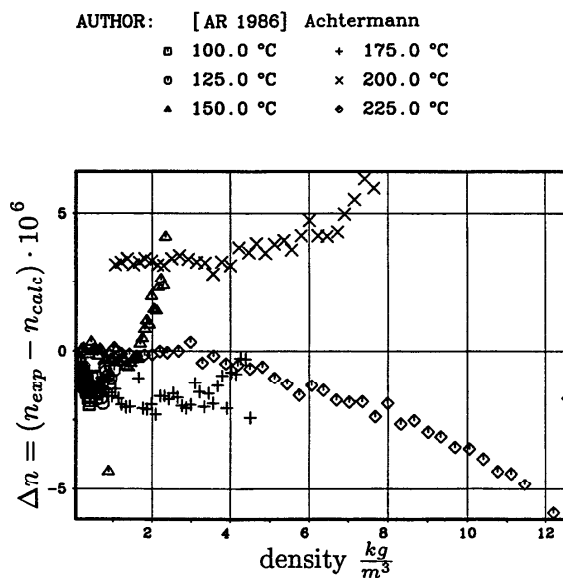


FIG. 5. Departures from the formulation of the fitted experimental  $n$  data of Achtermann and Rögner<sup>6</sup>, plotted against density.

AUTHOR: [WW 1963, WWS 1964] Waxler  
 □ .468  $\mu\text{m}$  + .502  $\mu\text{m}$  × .644  $\mu\text{m}$   
 ○ .480  $\mu\text{m}$  × .509  $\mu\text{m}$  × .668  $\mu\text{m}$   
 ▲ .492  $\mu\text{m}$  ○ .588  $\mu\text{m}$  \* .668  $\mu\text{m}$

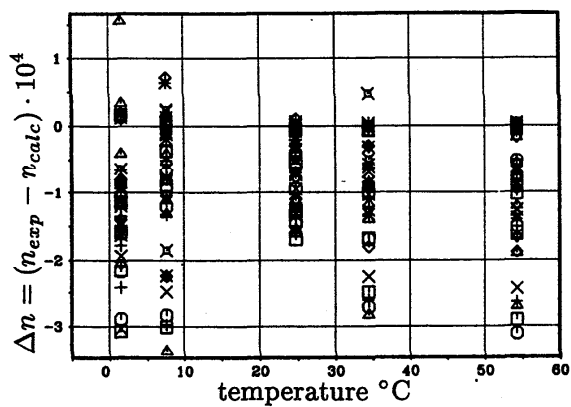


FIG. 6 (a). Departures from the formulation of the fitted experimental  $n$  data of Waxler *et al.*<sup>3,4</sup>, plotted against temperature. A few outliers have been removed.

AUTHOR: [WW 1963, WWS 1964] Waxler  
 □ .468  $\mu\text{m}$  + .502  $\mu\text{m}$  × .644  $\mu\text{m}$   
 ○ .480  $\mu\text{m}$  × .509  $\mu\text{m}$  × .668  $\mu\text{m}$   
 ▲ .492  $\mu\text{m}$  ○ .588  $\mu\text{m}$  \* .668  $\mu\text{m}$

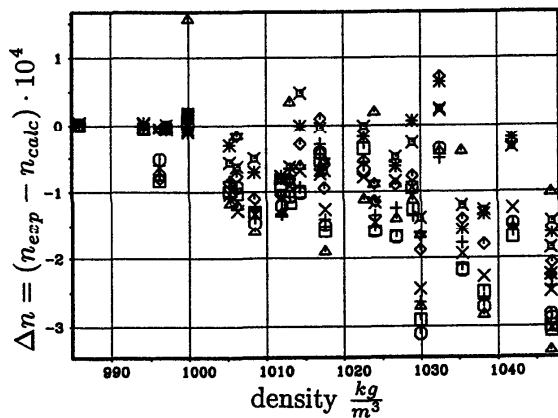


FIG. 6 (b). Departures from the formulation of the fitted experimental  $n$  data of Waxler *et al.*<sup>3,4</sup>, plotted against density. A few outliers have been removed.

AUTHOR: [S 1971] Stanley

□	1.0 °C	×	20.0 °C	•	50.0 °C
○	5.0 °C	◇	25.0 °C	◻	55.0 °C
▲	10.0 °C	×	30.0 °C	◇	60.0 °C
+	15.0 °C	*	40.0 °C		

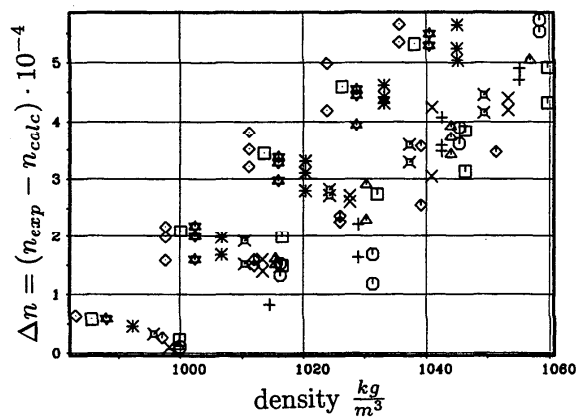


FIG. 7. Departures from the formulation, plotted against density, of the partially fitted experimental  $n$  data of Stanley<sup>26</sup> in pressurized water.

AUTHOR: [F 1903] Flatow

□	.0 °C	+	60.0 °C
○	20.0 °C	×	80.0 °C
▲	40.0 °C		

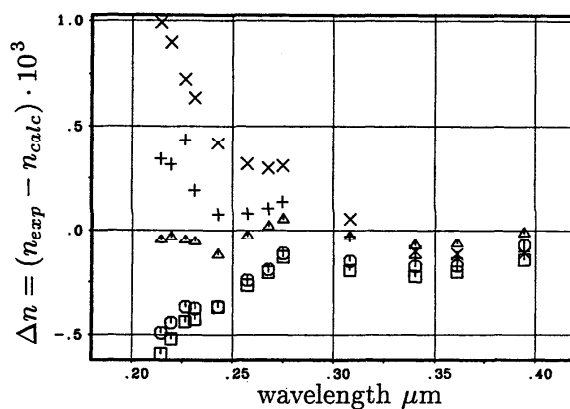


FIG. 8. Departures from the formulation of the fitted experimental  $n$  data of Flatow<sup>17</sup> in the ultraviolet, plotted against wavelength.

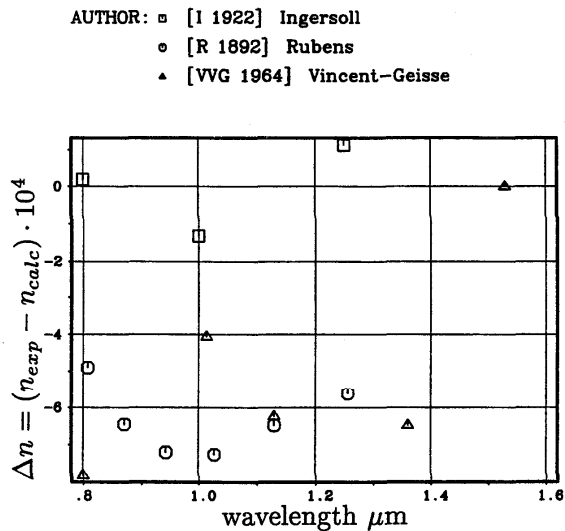


FIG. 9. Departures from the formulation of the fitted experimental  $n$  data in the infrared, those of Rubens<sup>27</sup>, Ingersoll<sup>28</sup> and Vincent-Geisse<sup>29</sup>, plotted against wavelength.

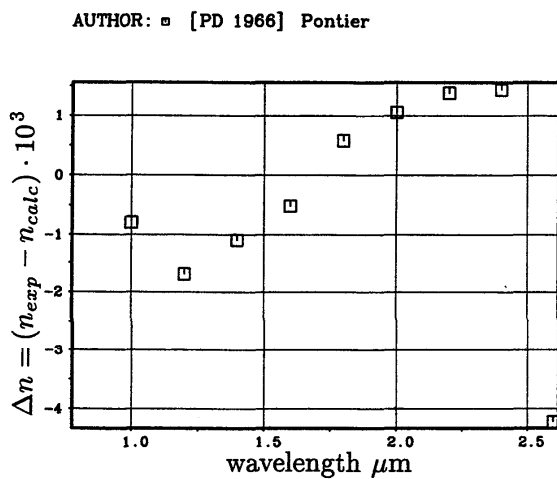


FIG. 10. Departures from the formulation of the fitted  $n$  data that Pontier<sup>30</sup> derived from reflectance measurements in the infrared; data are plotted against wavelength.



AUTHOR: □ [F 1903] Flatow + [S 1981] Saubade  
 ○ [HP 1922] Hall x [TT 1936] Tilton-Taylor  
 ▲ [J 1934] Jasse

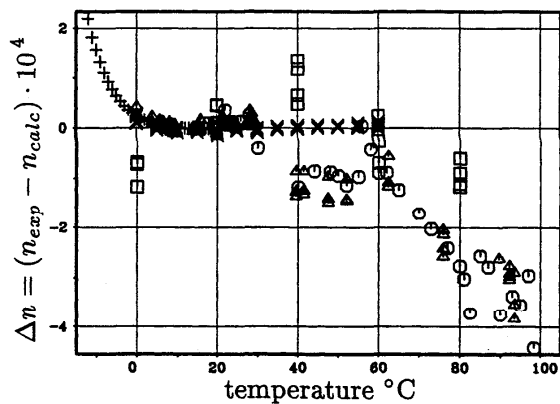


FIG. 11. Departures of all high-quality experimental data in the visible in liquid water at atmospheric pressure, plotted against temperature. They include those of Saubade<sup>9</sup> below 0°C, Tilton and Taylor<sup>1,2</sup>, Flatow<sup>17</sup>, Hall<sup>23</sup>, and Jasse<sup>24</sup>.

AUTHOR: □ [D 1881] Damien ▲ [P 1888] Pulfrich  
 ○ [HA 1948] Hawkes + [S 1981] Saubade

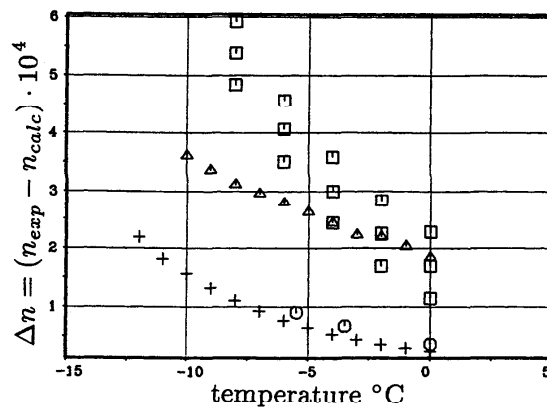


FIG. 12. Departures of all  $n$  data in supercooled water, plotted against temperature. Data are by Damien<sup>14</sup>, Hawkes<sup>35</sup>, Pulfrich<sup>36</sup>, and Saubade<sup>9</sup>.

## 7. Comparison with other Literature Data

We compare the additional data, not discussed before, with the formulation. Most comparisons are done by means of deviation plots. For sources of four or fewer data points, we have made the comparison in tabular form.

In Figs. 13–16, we compare many sources of good-quality refractive index data in the visible with our formulation. In Figs. 13 and 14, we display the deviations of a dozen high-quality sources<sup>34,37–48</sup>, mostly dating back to the 19th century. They mostly agree with the formulation on the level of  $2 \cdot 10^{-4}$ .

In Fig. 15, all sources, from late in the nineteenth century to modern times<sup>49–56</sup>, agree with the formulation on the level of  $\pm 4 \cdot 10^{-4}$ . Figure 16 compares with data<sup>23,24,34,35,57,58</sup> that span a wider temperature range than those in Fig. 15. The systematics above 60 °C discussed earlier are present here as well.

Figure 17, for the sake of completion, compares some quite old data<sup>59–62</sup> of lower quality with the formulation.

Figures 18 and 19 compare all data in pressurized water with the formulation. The data of Waxler *et al.*<sup>3,4</sup> and of Stanley<sup>26</sup> were discussed in Sec. 5. Rosen<sup>25</sup> obtained his data at room temperature in a wedge-shaped pressure cell, with the fluid confined to a rubber bag pressurized externally by glycerine. Rosen recorded his refractive index data to the 4th decimal, and estimated the uncertainty due to temperature variations to be no larger than 0.0001 for water at 2020 bar. The deviation plot shows that in Waxler's range, the Rosen and Waxler data agree with our formulation and with each other on the level of  $3 \cdot 10^{-4}$ . Beyond Waxler's range, the data of Rosen and those of Stanley diverge from the formulation in opposing directions. The data in pressurized water obtained by Poindexter<sup>63</sup>, Fig. 19, show very large departures, up to  $8 \cdot 10^{-3}$ .

We will now turn to the data sources in the ultraviolet. In Fig. 20, we show the departures of the data of Bayen<sup>49</sup>. Near the visible, these data average about  $2 \cdot 10^{-4}$  below our formulation. Their departures become large only when the resonance is approached, but are still no worse than about  $1 \cdot 10^{-3}$ .

In Fig. 21 we have collected a number of data sources<sup>17,50–52,54</sup>, and, for comparison, have included the Flatow data that we fitted. The departures from the formulation are confined to  $\pm 5 \cdot 10^{-4}$ , except near the resonance. In Fig. 22, we compare with other data sets<sup>43,64,65</sup> in the UV. These data, in general, agree on the  $2 \cdot 10^{-4}$  level with the formulation, with the exception of three data points by Simon<sup>65</sup>, at wavelengths between 2.3 and 2.4  $\mu\text{m}$ , which we have omitted because they departed by much larger amounts.

In Fig. 23, we compare with the data set of Schulz<sup>18</sup>. This is an interesting set since it spans a range from 15 to 100 °C in the ultraviolet. The data were taken in a thermostated hollow prism by a differential method, with a spectral line in the visible as a reference, for which the refractive index of water in the range of 15 to 100 °C was

calculated from existing data sources, such as Tilton and Taylor<sup>1,2</sup>, Jasse<sup>24</sup> and several other sources we have used here. The measurements were done photographically, by means of the method of minimum deviation. Schulz claims an uncertainty of  $7 \cdot 10^{-5}$  in  $n$ . He measured the refractive index against air, which he argued, not quite convincingly, to be effectively at room temperature, given the shape of the gradient around his cell. He then corrected the data to air of the same temperature. The publication does not contain the original data, but only a table of smoothed values. The thesis containing the data turned out to be inaccessible. For these reasons, we have not used the Schulz data in the fit, even though they contain information that could address the question of whether the UV resonance shifts with temperature.

From Fig. 23 it is obvious that the Schulz data show substantial systematic departures from our formulation. At the highest wavelength, they agree well with the formulation at all temperatures, roughly at the level of accuracy claimed. At the highest temperatures and lowest wavelengths, however, the departures grow to  $-7 \cdot 10^{-3}$ . These departures are an order of magnitude larger than those of other data at these low wavelengths, (Figs 20–22); also, in the visible the highest-temperature Schulz data depart from the formulation by  $-3 \cdot 10^{-3}$ , an order of magnitude worse than the Jasse data that were used as a reference. In summary, there is no way we could have incorporated the body of data of Schulz without seriously compromising the fit to the high-quality data in the visible.

The data sets of Flatow<sup>17</sup> and of Schulz<sup>18</sup> contain information on the temperature dependence of the molar refractivity near the UV resonance. Since the Schulz data do not have the correct temperature dependence in part of the visible, we have not used them to establish an eventual temperature dependence of the resonance wavelength. We have made an attempt to describe the temperature dependence of the Flatow data near the UV resonance by means of a linear temperature dependence of the resonance wavelength. Although this device leads to an improvement of the fit to Flatow's data near the UV resonance, a serious deterioration of the fit resulted elsewhere, including in the infrared.

We now turn to the data in the infrared. Except for the data in Refs. 27, 28, 29 discussed in Sec. 5, none of these contain directly-measured refractive indices. Instead, the real part of the refractive index is derived from the complex refractive index, which is obtained as a result of measurements of reflectance and absorbance over large ranges of wavelength. One such source is Pontier<sup>30</sup>, whose data we have used to guide our formulation (Fig. 10). In Fig. 24 we compare with the compilation of Centeno<sup>66</sup>. The correlation is close to our formulation in the visible and nearby infrared. Departures become large and systematic near the resonance.

In Fig. 25 we compare a variety of values proposed by scientists at the University of Kansas in the 1970s, and again based on absorbance and reflection measurements performed by this group over a range of wavelengths

and temperatures<sup>67-70</sup>. Large disagreements with our formulation, and discrepancies of several percent between the different sets, are visible near the resonances. Surprisingly, these data sets also show appreciable systematic offsets in the visible, where little doubt exists about the value of the refractive index. One of these sets, that by Pinkley *et al.*<sup>70</sup>, contains measurements near the IR resonance, slightly outside our range, over a range of temperatures. The observed temperature effects were of the same order as the accuracy of the data, so that we have not tried to derive the temperature dependence of the IR resonance from these data.

The compilation by Zolotarev<sup>71,72</sup> (Fig. 26), which is based, in part, on his own measurements of absorbance and disturbed total internal reflection over very large ranges of wavelength, agrees quite well with our formulation up to 2.0  $\mu\text{m}$ . His data do not display the sizable positive departures in the range from 1.5 to 2.6  $\mu\text{m}$  that are visible in Fig. 25. Beyond 2.0  $\mu\text{m}$ , the departures from our formulation become quite large.

Although, no doubt, the form of our equation is deficient near the resonances, the disagreement between the different data sets is so large that guidance for improvement of the function near the resonances is simply not available.

In Table 5, we compare the refractive indices from sources of three or fewer data points with our formulation. The data are those from Baxter *et al.*<sup>73</sup>, Cohen and Eisenberg<sup>74</sup>, Kanonnikoff<sup>75</sup>, Gladstone<sup>76</sup>, Röntgen and Zehnder<sup>77</sup> and Ruoss<sup>78</sup>. This Table illustrates again that the age of the data is not a predictor for the quality of refractive index data.

Next, we need to comment on the sole source of reliable data in water vapor prior to the work of Achtermann and Rögner. We refer to the work of Cuthbertson and Cuthbertson<sup>79</sup> in the early part of the 1900s. These

authors introduced a known amount of liquid water into their refractometer tube. They measured the change in the number of fringes as the tube was heated from a (low) reference temperature to the temperature at which all liquid had evaporated. They were able to calculate the molar refraction from the observed fringe shift, the measured temperatures, the vapor pressure at the reference temperature, the amount of water and the volume of the refractometer tube. At a wavelength close to that of Achtermann, the value of the molar refraction, converted to our units, equals 0.2080, estimated<sup>79</sup> to be accurate to 1 part in 500. This value is 1% lower than Achtermann's average.

Finally, we mention the few data sources in Table 2 that have escaped comment so far. The references to Fraunhofer<sup>80</sup> and Müttrich<sup>81</sup> have been included as historical curiosities. Müttrich's data depart from the formulation on the level of  $1 \cdot 10^{-3}$  in the visible. Yadev<sup>82</sup> gives only graphical information. The three shock-wave data points of Zeldovich<sup>83</sup> are at temperatures from 185 to 875 °C and at pressures from 35 to 150 kbar, which is outside the range of the NBS/NRC Steam Tables. Zeldovich presents estimated densities that have an uncertainty of several percents at the highest pressure. If we use his densities, and assume that the wavelength used is that of sodium light, we predict, at the lowest point (185 °C; 33–40 kbar) a range of refractive index of 1.470 – 1.475, compared to the measured value of 1.47. At the middle point (630 °C, 107–111 kbar) we predict  $n = 1.489 - 1.499$  to be compared with the measured value of 1.52. At the highest point (875 °C, 146–152 kbar) we predict  $n = 1.504 - 1.517$ , to be compared with the measured value of 1.52. Our formulation therefore appears to extrapolate smoothly to slightly below the values observed by Zeldovich.

TABLE 5. Sources of a few data points each

First Author	Code	Ref.	$n_{\text{exp}} - n_{\text{calc}}$	Nominal		
				$\lambda$ , $\mu\text{m}$	$T$ , °C	$P$ , MPa
Baxter	[BBD 1911]	73	+ $9 \cdot 10^{-6}$	0.59	20	0.1
			– $2 \cdot 10^{-5}$	0.59	25	0.1
			– $4 \cdot 10^{-5}$	0.59	30	0.1
Cohen	[CE 1965]	74	+ $3 \cdot 10^{-4}$	0.44	25	0.1
			+ $2 \cdot 10^{-5}$	0.55	25	0.1
Gladstone	[G 1870]	76	– $3 \cdot 10^{-2}$	0.32	20	0.1
			– $1 \cdot 10^{-2}$	0.36	20	0.1
			+ $5 \cdot 10^{-4}$	0.40	20	0.1
Kanonnikoff	[K 1885]	75	+ $3 \cdot 10^{-4}$	0.49	20	0.1
			+ $1 \cdot 10^{-4}$	0.59	20	0.1
			+ $1 \cdot 10^{-4}$	0.66	20	0.1
Röntgen	[RZ 1891]	77	+ $4 \cdot 10^{-5}$	0.59	19	0.1
Ruoss	[R 1893]	78	+ $4 \cdot 10^{-5}$	0.59	23	0.1

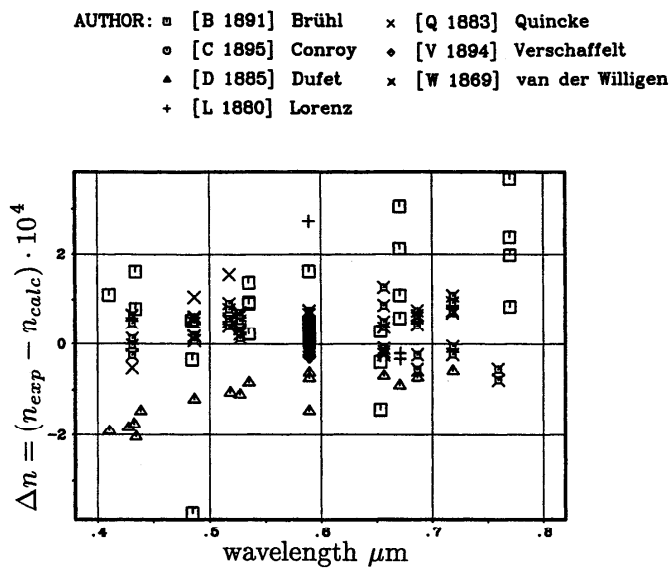


FIG. 13. Departures from the formulation of the high-quality  $n$  data in the visible and at temperatures close to ambient, of Brühl<sup>37</sup>, Conroy<sup>38</sup>, Dufet<sup>39</sup>, Lorenz<sup>40</sup>, Quincke<sup>41</sup>, Verschaffelt<sup>42</sup> and van der Willigen<sup>43</sup>, plotted against wavelength.

AUTHOR: □ [D 1881] Damien    + [W 1868] Wüllner  
 ○ [GSV 1976] Grange    × [W 1876] Wiedemann  
 ▲ [L 1862] Landolt    ♦ [W 1892] Walter

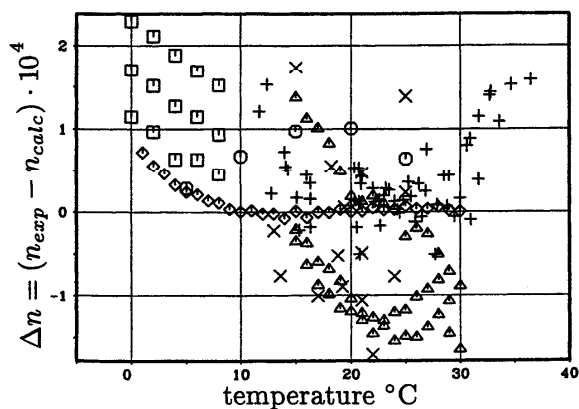


FIG. 14. Departures from the formulation of the high-quality  $n$  data in the visible and in the temperature range 0–40  $^{\circ}\text{C}$ ; the data are by Damien<sup>34</sup>, Grange<sup>44</sup>, Landolt<sup>45</sup>, Wüllner<sup>46</sup>, Wiedemann<sup>47</sup>, and Walter<sup>48</sup>.

AUTHOR: □ [B 1942] Bayen      × [GW 1931] Gregg-Wilson  
 ○ [B 1973] Boguth      ◇ [K 1940] Kruis  
 ▲ [DJ 1921] Ducleaux    × [MGF 1984] Moreels  
 + [G 1907] Gifford      \* [S 1890] Schütt

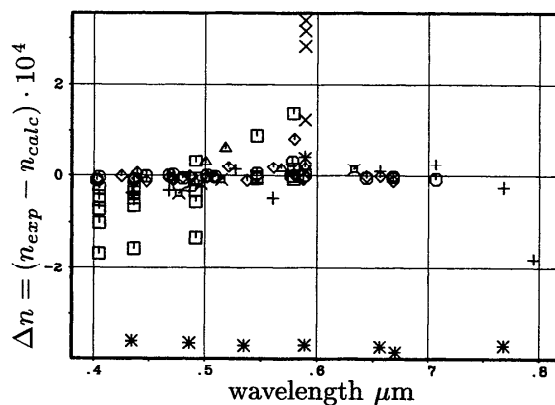


FIG. 15. Departures from the formulation of high- and medium-quality  $n$  data in the visible and at temperatures near ambient, and plotted against wavelength. The data are by Bayen<sup>49</sup>, Boguth<sup>50</sup>, Ducleaux<sup>51</sup>, Gifford<sup>52</sup>, Gregg-Wilson<sup>53</sup>, Kruis<sup>54</sup>, Moreels<sup>55</sup>, and Schütt<sup>56</sup>. Two outliers by Bayen have been removed.

AUTHOR: □ [B 1899] Bender      + [HA 1948] Hawkes  
 ○ [D 1881] Damien      × [J 1934] Jasse  
 ▲ [HP 1922] Hall      ◇ [K 1888] Ketteler

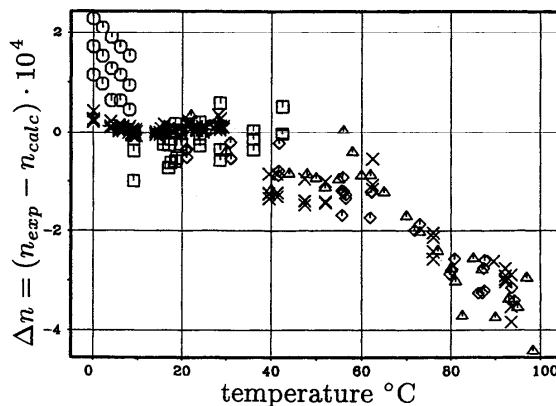


FIG. 16. Departures from the formulation of medium- and high-quality  $n$  data in the visible and in the temperature range of 0 to 100  $^{\circ}C$ . The data are by Bender<sup>57</sup>, Damien<sup>54</sup>, Hall<sup>23</sup>, Hawkes<sup>35</sup>, Jasse<sup>24</sup> and Ketteler<sup>58</sup>.

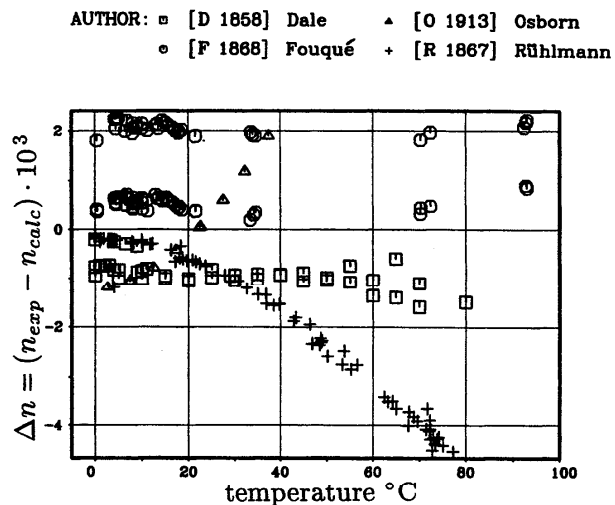


FIG. 17. Departures from the formulation of low-quality  $n$  data in the visible as a function of temperature. The data are those of Dale<sup>59</sup>, Fouqué<sup>60</sup>, Osborn<sup>61</sup>, and Rühlmann<sup>62</sup>. An outlier of Rühlmann at 15 °C has been removed.

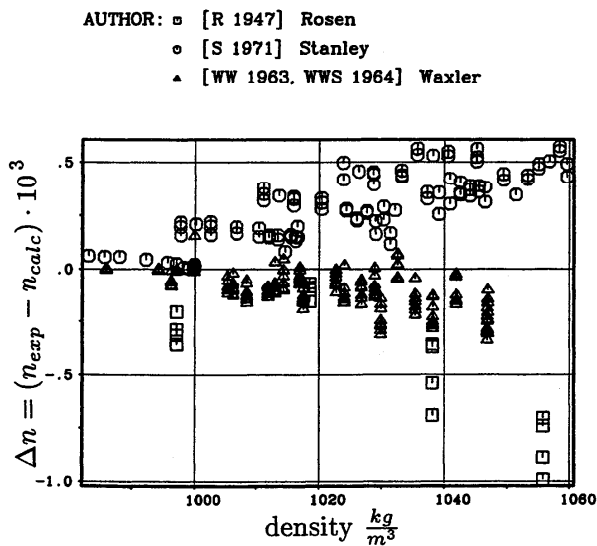


FIG. 18. Departures from the formulation for  $n$  data in pressurized water. The data are those of Waxler *et al.*<sup>3,4</sup>, Rosen<sup>25</sup> and Stanley<sup>26</sup> and are plotted versus density. An outlier has been removed from the Rosen data.

AUTHOR: □ [PR 1934] Poindexter

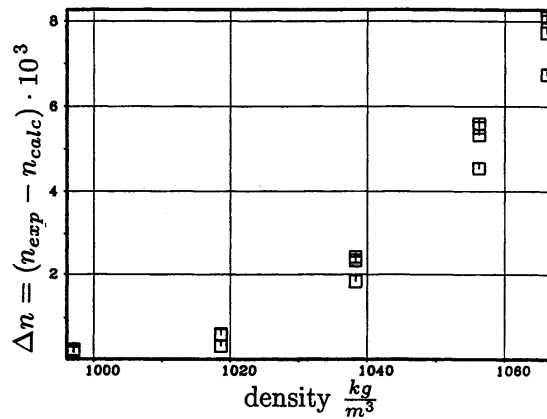


FIG. 19. Departures from the formulation of the low-quality Poindexter data<sup>63</sup> in pressurized water, plotted versus density.

AUTHOR: □ [B 1942] Bayen

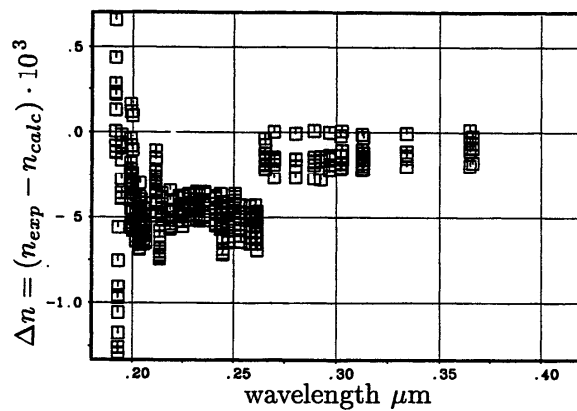


FIG. 20. Departures from the formulation of the  $n$  data of Bayen<sup>49</sup> in the ultraviolet plotted versus wavelength.

AUTHOR: □ [B 1973] Boguth    + [DJ 1921] Ducleaux  
 ○ [F 1903] Flatow        × [K 1940] Kruis  
 ▲ [G 1907] Gifford

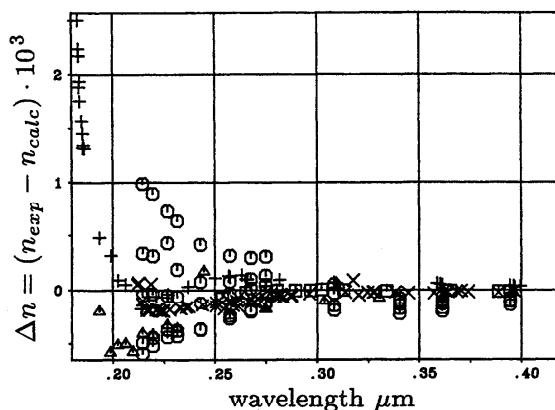


FIG. 21. Departures from the formulation of  $n$  data in the ultraviolet plotted versus wavelength. The data are by Boguth<sup>50</sup>, Ducleaux<sup>51</sup>, Flatow<sup>17</sup>, Gifford<sup>52</sup> and Kruis<sup>54</sup>.

AUTHOR: □ [R 1930] Roberts  
 ○ [S 1894] Simon  
 ▲ [W 1869] van der Willigen

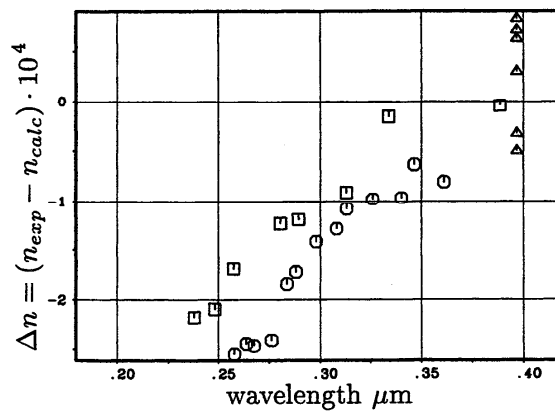


FIG. 22. Departures from the formulation of the  $n$  data in the ultraviolet plotted versus wavelength. The data are by Roberts<sup>64</sup>, Simon<sup>65</sup> and van der Willigen<sup>43</sup>. Three points by Simon below  $.25 \mu\text{m}$  in wavelength, with negative deviations down to  $-0.01$  at  $\lambda = 0.22 \mu\text{m}$ ., have been omitted.



AUTHOR: □ [S 1955] Schulz

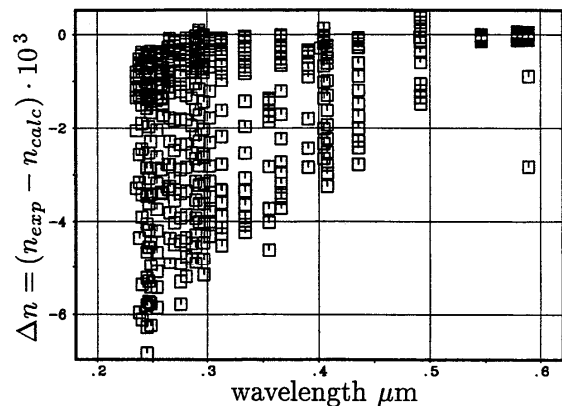


FIG. 23. Departures from the formulation of the refractive index data of Schulz<sup>18</sup> plotted against wavelength. The data are a composite, prepared by Schulz, of his own data in the ultraviolet in the range of 0–100 °C, and by others in the visible.

AUTHOR: □ [C 1941] Centeno

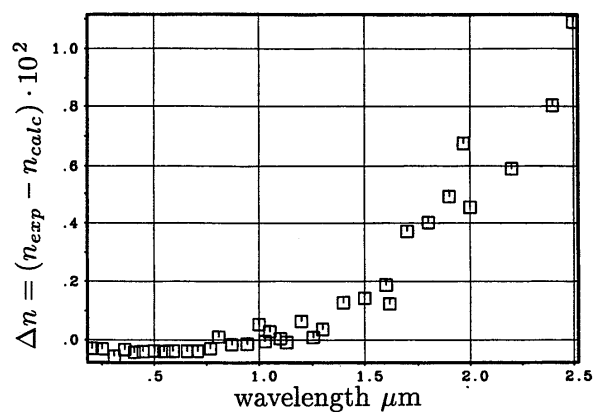


FIG. 24. Departures from the formulation of  $n$  data derived from reflectance and absorbance data in the infrared plotted versus wavelength. The plot is cut off at 2.6  $\mu m$ , beyond which the deviations become very large. The data are those of Centeno<sup>66</sup>.

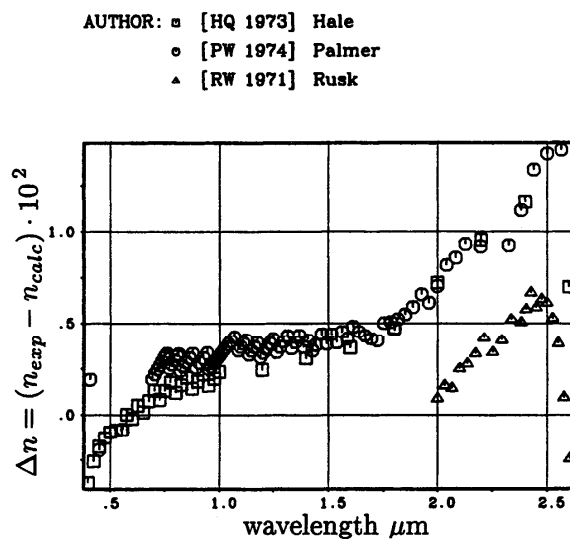


FIG. 25. Departures from the formulation of the refractive index data calculated from reflectance and absorbance over large ranges of wavelength. The predictions are due to Hale<sup>67</sup>, Palmer<sup>68</sup>, and Rusk<sup>69</sup>.

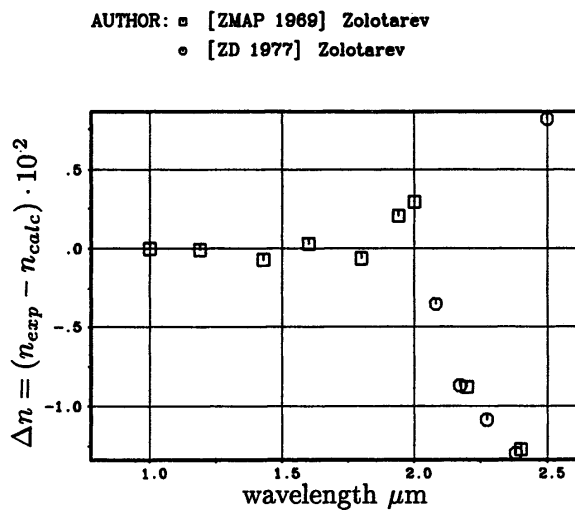


FIG. 26. Departures of the Zolotarev's<sup>71,72</sup> refractive index data, both measured and predicted from reflectance and absorbance over large ranges of wavelength.

TABLE 6. Estimated uncertainty of the refractive index formulation

Wavelength $\mu\text{m}$	Temperature $^{\circ}\text{C}$	Pressure MPa	State	Est. uncert. in $n$ absolute
visible	5–60	ambient	liquid	$15 \cdot 10^{-6}$
visible	60–100	ambient	liquid	$(1-3) \cdot 10^{-4}$
visible	–12–5	ambient	liquid	$12 \cdot 10^{-5}$
visible	0–60	150	liquid	$2 \cdot 10^{-4}$
visible	100–225	0–2	vapor	$5 \cdot 10^{-6}$
IR to 1.3	ambient	ambient	liquid	$7 \cdot 10^{-4}$
IR 1.3–2.0	ambient	ambient	liquid	$3 \cdot 10^{-3}$
IR 2.0–2.5	ambient	ambient	liquid	$1 \cdot 10^{-2}$
UV to 0.21	0–100	ambient	liquid	$5 \cdot 10^{-4}$

In the following ranges there are no supporting data

visible	0–374	0–0.1 $P_{\text{sat}}$	vapor	$5 \cdot 10^{-6}$
visible	100–374	$P_{\text{sat}}$ to 200	liquid	$1 \cdot 10^{-3}$
visible	> 374	up to $1/3 \rho_c$	dilute	$1 \cdot 10^{-5}$
visible	> 374	beyond $\rho_c$	dense	$2 \cdot 10^{-3}$

## 8. Estimate of Reliability of the Formulation

We summarize the reliability estimates for the refractive index values predicted by the formulation in the ranges where data exist in Table 6. The estimates are based on the observed departures of reliable data sets from the formulation, as presented and discussed in the preceding sections, and on the accuracy of these data sets, as far as known and confirmed. The uncertainty of the formulation is smallest in liquid water between 0 and 60  $^{\circ}\text{C}$ , at ambient pressure and in the visible, and in water vapor between 100 and 225  $^{\circ}\text{C}$ , at pressures up to 20 bar and in the visible. Above 60  $^{\circ}\text{C}$ , there is a marked loss of reliability. The uncertainty also increases somewhat for pressurized water below 60  $^{\circ}\text{C}$ ; it increases considerably in the ultraviolet and infrared, and grows very rapidly near the resonances, especially in the infrared where no direct measurements exist.

It is not possible to give an estimate of reliability in ranges where no data exist. The form of the equation is simple enough, however, that large oscillations are not expected to occur. To the extent that our hypothesis is valid that the Lorentz-Lorenz function depends weakly on temperature and density at fixed wavelength, and that the effective resonance frequencies are independent of density and temperature, we may hope that the formulation, in the visible, will predict the refractive index on the level of  $1 \cdot 10^{-3}$  or better in liquid water and in dense supercritical states at all temperatures. We may also be hopeful that the formulation will be very good in water

vapor at densities up to  $10 \text{ kg m}^{-3}$  at all temperatures, with “very good” meaning an uncertainty no larger than one or two units in the fifth decimal. The number of significant figures in the tabulated value we will present is one to several decimals more than the estimates of uncertainty presented here; this permits the programmer to check the accuracy of his/her formulation of the correlation, and assures that derivative properties are obtained with good approximation.

## 9. Tabulation of the Refractive Index

In Table 7, we list the refractive index of water as calculated from our formulation for 6 wavelengths ranging from the infrared through the visible to the ultraviolet, as a function of pressure and temperature. The wavelengths chosen in the ultraviolet are cadmium lines used by Flatow; in the visible, we chose a strong potassium line (0.40441), the strongest sodium line (0.58900) and a He-Ne laser wavelength (0.6328). In the infrared, we used two mercury spectroscopic standards. The transition from 6 to 5 significant digits indicates the transition from vapor to liquid states. The number of decimals listed at any particular state point exceeds our estimate of the reliability at that point by one to several orders of magnitude. In Table 8, saturation values, the refractive indices are given in the temperature range of most interest to the user. The user of Tables 7 and 8 is strongly advised to check Table 6 and Sec. 8 for estimates of the reliability in the region of application.

TABLE 7. Refractive Index of Water for Wavelength 0.36105  $\mu\text{m}$ ,  $T$  in  $^{\circ}\text{C}$ ,  $P$  in MPa—Continued

$T \setminus P$	.1	.2	.3	.5	1.0	2.0	3.0	5.0	10.0	20.0	30.0	50.0	100.0
0	1.39450	1.39452	1.39454	1.39458	1.39468	1.39489	1.39509	1.39550	1.39650	1.39848	1.40041	1.40414	1.41276
10	1.39422	1.39423	1.39425	1.39429	1.39439	1.39458	1.39477	1.39515	1.39609	1.39795	1.39977	1.40328	1.41147
20	1.39336	1.39338	1.39340	1.39344	1.39353	1.39371	1.39390	1.39426	1.39516	1.39694	1.39869	1.40206	1.40996
30	1.39208	1.39210	1.39212	1.39216	1.39224	1.39242	1.39260	1.39296	1.39384	1.39557	1.39726	1.40055	1.40825
40	1.39046	1.39047	1.39049	1.39053	1.39062	1.39079	1.39097	1.39132	1.39218	1.39389	1.39556	1.39879	1.40636
50	1.38854	1.38855	1.38857	1.38861	1.38869	1.38887	1.38904	1.38939	1.39025	1.39195	1.39360	1.39681	1.40431
60	1.38636	1.38638	1.38639	1.38643	1.38652	1.38669	1.38687	1.38721	1.38808	1.38977	1.39143	1.39463	1.40211
70	1.38395	1.38396	1.38398	1.38402	1.38410	1.38428	1.38446	1.38481	1.38568	1.38739	1.38905	1.39228	1.39978
80	1.38132	1.38134	1.38135	1.38139	1.38148	1.38166	1.38184	1.38219	1.38308	1.38481	1.38649	1.38975	1.39730
90	1.37849	1.37851	1.37852	1.37856	1.37865	1.37884	1.37902	1.37938	1.38028	1.38204	1.38376	1.38706	1.39471
100	1.000217	1.37549	1.37551	1.37554	1.37564	1.37582	1.37601	1.37638	1.37731	1.37911	1.38086	1.38423	1.39200
120	1.000205	1.36891	1.36893	1.36897	1.36907	1.36927	1.36946	1.36986	1.37084	1.37275	1.37460	1.37814	1.38624
140	1.000194	1.000392	1.000594	1.36169	1.36180	1.36202	1.36223	1.36266	1.36372	1.36578	1.36776	1.37153	1.38007
160	1.000185	1.000372	1.000563	1.000955	1.35384	1.35408	1.35432	1.35479	1.35595	1.35819	1.36035	1.36442	1.37353
180	1.000176	1.000354	1.000535	1.000905	1.001883	1.34542	1.34568	1.34621	1.34750	1.34999	1.35237	1.35681	1.36661
200	1.000168	1.000338	1.000510	1.000860	1.001776	1.33595	1.33625	1.33686	1.33833	1.34113	1.34378	1.34870	1.35934
220	1.000161	1.000324	1.000488	1.000821	1.001684	1.003578	1.32591	1.32661	1.32832	1.33154	1.33454	1.34005	1.35171
240	1.000155	1.000310	1.000467	1.000785	1.001604	1.003367	1.005356	1.31528	1.31731	1.32109	1.32456	1.33081	1.34370
260	1.000149	1.000298	1.000449	1.000753	1.001533	1.003189	1.005009	1.30254	1.30505	1.30962	1.31372	1.32092	1.33531
280	1.000143	1.000287	1.000431	1.000723	1.001468	1.003035	1.004726	1.008637	1.29109	1.29684	1.30183	1.31030	1.32652
300	1.000138	1.000276	1.000415	1.000696	1.001410	1.002900	1.004486	1.008041	1.27457	1.28229	1.28860	1.29881	1.31730
320	1.000133	1.000266	1.000401	1.000670	1.001356	1.002779	1.004278	1.007566	1.018960	1.26507	1.27358	1.28628	1.30762
340	1.000128	1.000257	1.000387	1.000647	1.001307	1.002669	1.004094	1.007169	1.016975	1.24309	1.25591	1.27248	1.29747
360	1.000124	1.000249	1.000374	1.000625	1.001261	1.002569	1.003929	1.006829	1.015615	1.20763	1.23380	1.25704	1.28681
380	1.000120	1.000241	1.000362	1.000605	1.001219	1.002477	1.003779	1.006530	1.014578	1.044349	1.20190	1.23944	1.27562
400	1.000117	1.000233	1.000350	1.000586	1.001180	1.002393	1.003642	1.006264	1.013740	1.036702	1.13359	1.21888	1.26389
420	1.000113	1.000226	1.000340	1.000568	1.001143	1.002314	1.003517	1.006024	1.013037	1.032552	1.07481	1.19431	1.25161
440	1.000110	1.000220	1.000330	1.000551	1.001108	1.002241	1.003400	1.005806	1.012431	1.029730	1.05880	1.16539	1.23882
460	1.000107	1.000213	1.000320	1.000535	1.001075	1.002172	1.003292	1.005607	1.011900	1.027606	1.05079	1.13557	1.22556
480	1.000104	1.000207	1.000311	1.000520	1.001045	1.002108	1.003199	1.005422	1.011426	1.025911	1.04563	1.11137	1.21198
500	1.000101	1.000202	1.000303	1.000506	1.001016	1.002048	1.003097	1.005251	1.011000	1.024505	1.04190	1.09457	1.19828

TABLE 7. Refractive Index of Water for Wavelength 0.36105  $\mu\text{m}$ ,  $T$  in  $^{\circ}\text{C}$ ,  $P$  in MPa—Continued

$T \setminus P$	.1	.2	.3	.5	1.0	2.0	3.0	5.0	10.0	20.0	30.0	50.0	100.0
0	1.34896	1.34898	1.34900	1.34903	1.34912	1.34930	1.34947	1.34982	1.35068	1.35238	1.35403	1.35723	1.36460
10	1.34870	1.34872	1.34873	1.34876	1.34885	1.34901	1.34918	1.34950	1.35031	1.35190	1.35346	1.35647	1.36347
20	1.34795	1.34796	1.34798	1.34801	1.34809	1.34824	1.34840	1.34871	1.34949	1.35101	1.35251	1.35540	1.36215
30	1.34682	1.34684	1.34685	1.34688	1.34696	1.34711	1.34727	1.34757	1.34833	1.34981	1.35126	1.35408	1.36067
40	1.34540	1.34542	1.34543	1.34546	1.34554	1.34569	1.34584	1.34614	1.34689	1.34835	1.34978	1.35255	1.35903
50	1.34373	1.34375	1.34376	1.34379	1.34387	1.34402	1.34417	1.34447	1.34521	1.34666	1.34808	1.35083	1.35725
60	1.34184	1.34185	1.34187	1.34190	1.34197	1.34212	1.34227	1.34257	1.34331	1.34477	1.34619	1.34894	1.35535
70	1.33974	1.33976	1.33977	1.33980	1.33988	1.34003	1.34018	1.34049	1.34123	1.34270	1.34413	1.34689	1.35332
80	1.33746	1.33748	1.33749	1.33752	1.33760	1.33775	1.33791	1.33822	1.33897	1.34046	1.34191	1.34470	1.35118
90	1.33501	1.33502	1.33504	1.33507	1.33515	1.33531	1.33546	1.33578	1.33655	1.33806	1.33954	1.34238	1.34893
100	1.000195	1.33240	1.33242	1.33245	1.33253	1.33269	1.33285	1.33317	1.33397	1.33552	1.33702	1.33992	1.34658
120	1.000184	1.32669	1.32671	1.32674	1.32683	1.32700	1.32717	1.32751	1.32836	1.33000	1.33160	1.33464	1.34160
140	1.000174	1.000352	1.000534	1.32042	1.32052	1.32071	1.32089	1.32126	1.32218	1.32395	1.32566	1.32891	1.33626
160	1.000166	1.000334	1.000506	1.000858	1.31360	1.31381	1.31401	1.31442	1.31543	1.31737	1.31923	1.32274	1.33058
180	1.000158	1.000318	1.000481	1.000813	1.001691	1.30628	1.30651	1.30696	1.30808	1.31024	1.31229	1.31613	1.32459
200	1.000151	1.000304	1.000458	1.000773	1.001595	1.29804	1.29830	1.29882	1.30010	1.30253	1.30482	1.30908	1.31827
220	1.000145	1.000291	1.000438	1.000737	1.001512	1.003213	1.28928	1.28989	1.29137	1.29417	1.29678	1.30155	1.31164
240	1.000139	1.000279	1.000420	1.000705	1.001440	1.003023	1.004809	1.28001	1.28177	1.28506	1.28808	1.29350	1.30468
260	1.000133	1.000268	1.000403	1.000676	1.001376	1.002863	1.004497	1.26887	1.27106	1.27504	1.27861	1.28488	1.29737
280	1.000128	1.000257	1.000387	1.000649	1.001318	1.002725	1.004242	1.007753	1.25884	1.26386	1.26822	1.27560	1.28970
300	1.000124	1.000248	1.000373	1.000624	1.001265	1.002603	1.004027	1.007217	1.24436	1.25111	1.25663	1.26555	1.28166
320	1.000119	1.000239	1.000359	1.000602	1.001217	1.002494	1.003839	1.006790	1.017015	1.23600	1.24345	1.25458	1.27320
340	1.000115	1.000231	1.000347	1.000581	1.001173	1.002395	1.003674	1.006434	1.015232	1.21665	1.22793	1.24246	1.26432
360	1.000111	1.000223	1.000335	1.000561	1.001132	1.002305	1.003525	1.006128	1.014010	1.18534	1.20844	1.22889	1.25498
380	1.000108	1.000216	1.000325	1.000543	1.001094	1.002223	1.003391	1.005859	1.013079	1.039775	1.18025	1.21339	1.24516
400	1.000105	1.000209	1.000314	1.000525	1.001058	1.002147	1.003268	1.005620	1.012326	1.032917	1.11956	1.19524	1.23485
420	1.000101	1.000203	1.000305	1.000509	1.001025	1.002076	1.003154	1.005404	1.011694	1.029193	1.06704	1.17349	1.22405
440	1.000098	1.000197	1.000296	1.000494	1.000994	1.002010	1.003050	1.005208	1.011150	1.026660	1.05271	1.14782	1.21277
460	1.000096	1.000191	1.000287	1.000480	1.000964	1.001948	1.002953	1.005028	1.010672	1.024753	1.04553	1.12129	1.20107
480	1.000093	1.000186	1.000279	1.000466	1.000937	1.001890	1.002862	1.004862	1.010246	1.023231	1.04090	1.09969	1.18906
500	1.000090	1.000181	1.000272	1.000454	1.000911	1.001836	1.002777	1.004709	1.009862	1.021969	1.03756	1.08468	1.17693

TABLE 7. Refractive Index of Water for Wavelength 0.40441  $\mu\text{m}$ ,  $T$  in  $^{\circ}\text{C}$ ,  $P$  in MPa — Continued

$T \backslash P$	.1	.2	.3	.5	1.0	2.0	3.0	5.0	10.0	20.0	30.0	50.0	100.0
0	1.34415	1.34417	1.34419	1.34422	1.34431	1.34448	1.34465	1.34500	1.34585	1.34751	1.34914	1.35228	1.35952
10	1.34389	1.34391	1.34393	1.34396	1.34404	1.34420	1.34436	1.34468	1.34548	1.34704	1.34857	1.35153	1.35841
20	1.34315	1.34317	1.34318	1.34321	1.34329	1.34344	1.34360	1.34391	1.34467	1.34617	1.34763	1.35048	1.35711
30	1.34205	1.34206	1.34208	1.34211	1.34218	1.34233	1.34248	1.34278	1.34352	1.34498	1.34641	1.34918	1.35565
40	1.34065	1.34067	1.34068	1.34071	1.34078	1.34093	1.34108	1.34138	1.34211	1.34354	1.34495	1.34767	1.35404
50	1.33901	1.33902	1.33904	1.33906	1.33914	1.33929	1.33943	1.33973	1.34045	1.34188	1.34328	1.34598	1.35229
60	1.33714	1.33716	1.33717	1.33720	1.33728	1.33742	1.33757	1.33787	1.33859	1.34002	1.34142	1.34412	1.35042
70	1.33508	1.33510	1.33511	1.33514	1.33522	1.33536	1.33551	1.33581	1.33654	1.33799	1.33939	1.34211	1.34843
80	1.33284	1.33285	1.33287	1.33290	1.33297	1.33312	1.33328	1.33358	1.33432	1.33578	1.33721	1.33995	1.34632
90	1.33042	1.33044	1.33045	1.33048	1.33056	1.33071	1.33087	1.33118	1.33194	1.33343	1.33487	1.33767	1.34411
100	1.000192	1.32786	1.32787	1.32791	1.32798	1.32814	1.32830	1.32862	1.32940	1.33092	1.33240	1.33525	1.34180
120	1.000182	1.32224	1.32226	1.32229	1.32237	1.32254	1.32271	1.32305	1.32388	1.32550	1.32706	1.33006	1.33690
140	1.000172	1.000348	1.000528	1.31608	1.31617	1.31635	1.31653	1.31690	1.31780	1.31954	1.32122	1.32442	1.33164
160	1.000164	1.000330	1.000500	1.000848	1.30936	1.30956	1.30976	1.31017	1.31115	1.31306	1.31489	1.31835	1.32606
180	1.000156	1.000314	1.000475	1.000803	1.001670	1.302149	1.302376	1.30283	1.30393	1.30605	1.30807	1.31185	1.32016
200	1.000149	1.000300	1.000453	1.000763	1.001575	1.294039	1.294298	1.29481	1.29607	1.29846	1.30072	1.30490	1.31395
220	1.000143	1.000287	1.000433	1.000728	1.001494	1.003174	1.285422	1.28602	1.28748	1.29023	1.29280	1.29749	1.30742
240	1.000137	1.000275	1.000415	1.000696	1.001423	1.002986	1.004751	1.27629	1.27803	1.28126	1.28423	1.28957	1.30057
260	1.000132	1.000264	1.000398	1.000668	1.001359	1.002828	1.004442	1.26532	1.26748	1.27139	1.27491	1.28108	1.29338
280	1.000127	1.000254	1.000382	1.000641	1.001302	1.002692	1.004191	1.007659	1.25544	1.26039	1.26467	1.27194	1.28583
300	1.000122	1.000245	1.000368	1.000617	1.001250	1.002571	1.003978	1.007130	1.24117	1.24782	1.25326	1.26204	1.27790
320	1.000118	1.000236	1.000355	1.000594	1.001202	1.002463	1.003793	1.006707	1.016807	1.23293	1.24028	1.25123	1.26958
340	1.000114	1.000228	1.000343	1.000574	1.001159	1.002366	1.003629	1.006355	1.015047	1.21386	1.22498	1.23930	1.26083
360	1.000110	1.000221	1.000331	1.000554	1.001118	1.002277	1.003482	1.006503	1.013840	1.18298	1.20577	1.22593	1.25163
380	1.000107	1.000213	1.000321	1.000536	1.001080	1.002196	1.003349	1.005788	1.012920	1.039289	1.17796	1.21064	1.24195
400	1.000103	1.000207	1.000311	1.000519	1.001045	1.002120	1.003228	1.005551	1.012176	1.032515	1.11807	1.19274	1.23179
420	1.000100	1.000201	1.000301	1.000503	1.001012	1.002050	1.003116	1.005338	1.011551	1.028837	1.06622	1.17129	1.22114
440	1.000097	1.000195	1.000292	1.000488	1.000982	1.001985	1.003013	1.005144	1.011014	1.026335	1.05206	1.14596	1.21002
460	1.000094	1.000189	1.000284	1.000474	1.000953	1.001924	1.002917	1.004967	1.010541	1.024451	1.04497	1.11978	1.19849
480	1.000092	1.000184	1.000276	1.000461	1.000925	1.001867	1.002827	1.004803	1.010121	1.022947	1.040 04	1.09846	1.18665
500	1.000089	1.000179	1.000268	1.000448	1.000900	1.001814	1.002743	1.004651	1.009742	1.021700	1.03710	1.08364	1.17468

TABLE 7. Refractive Index of Water for Wavelength 0.58900  $\mu\text{m}$ ,  $T$  in  $^{\circ}\text{C}$ ,  $P$  in MPa — Continued

$T \setminus P$	.1	.2	.3	.5	1.0	2.0	3.0	5.0	10.0	20.0	30.0	50.0	100.0
0	1.33432	1.33434	1.33436	1.33439	1.33447	1.33464	1.33481	1.33514	1.33596	1.33756	1.33913	1.34216	1.34914
10	1.33408	1.33409	1.33411	1.33414	1.33422	1.33437	1.33453	1.33484	1.33560	1.33711	1.33859	1.34144	1.34807
20	1.33336	1.33338	1.33339	1.33342	1.33350	1.33365	1.33379	1.33409	1.33483	1.33627	1.33769	1.34043	1.34682
30	1.33230	1.33231	1.33233	1.33236	1.33243	1.33257	1.33272	1.33301	1.33372	1.33513	1.33651	1.33918	1.34542
40	1.33095	1.33097	1.33098	1.33101	1.33108	1.33123	1.33137	1.33165	1.33236	1.33374	1.33510	1.33773	1.34387
50	1.32937	1.32938	1.32940	1.32943	1.32950	1.32964	1.32978	1.33007	1.33077	1.33214	1.33349	1.33610	1.34218
60	1.32757	1.32759	1.32760	1.32763	1.32770	1.32785	1.32799	1.32827	1.32897	1.33035	1.33170	1.33431	1.34038
70	1.32559	1.32560	1.32562	1.32564	1.32572	1.32586	1.32600	1.32629	1.32700	1.32839	1.32975	1.33237	1.33846
80	1.32342	1.32344	1.32345	1.32348	1.32355	1.32370	1.32385	1.32414	1.32486	1.32627	1.32764	1.33029	1.33644
90	1.32109	1.32111	1.32112	1.32115	1.32123	1.32138	1.32153	1.32182	1.32256	1.32399	1.32539	1.32809	1.33431
100	1.000188	1.31862	1.31864	1.31867	1.31874	1.31890	1.31905	1.31935	1.32011	1.32158	1.32301	1.32576	1.33208
120	1.000177	1.31320	1.31322	1.31325	1.31333	1.31349	1.31366	1.31398	1.31478	1.31635	1.31786	1.32075	1.32735
140	1.000168	1.000339	1.000514	1.30725	1.30734	1.30752	1.30769	1.30804	1.30891	1.31060	1.31222	1.31531	1.32229
160	1.000160	1.000322	1.000487	1.000826	1.30076	1.30096	1.30116	1.30154	1.30250	1.30434	1.30611	1.30945	1.31690
180	1.000152	1.000307	1.000463	1.000783	1.001629	1.29380	1.29402	1.29445	1.29552	1.29757	1.29952	1.30317	1.31121
200	1.000146	1.000293	1.000441	1.000744	1.001536	1.28596	1.28621	1.28670	1.28792	1.29023	1.29242	1.29647	1.30521
220	1.000139	1.000280	1.000422	1.000710	1.001457	1.003095	1.27762	1.27820	1.27961	1.28228	1.28476	1.28930	1.29890
240	1.000134	1.000268	1.000404	1.000679	1.001387	1.002912	1.004632	1.26878	1.27046	1.27360	1.27648	1.28164	1.29228
260	1.000128	1.000258	1.000388	1.000651	1.001325	1.002758	1.004332	1.25816	1.26025	1.26405	1.26746	1.27343	1.28533
280	1.000124	1.000248	1.000373	1.000625	1.001270	1.002625	1.004086	1.007468	1.24859	1.25338	1.25754	1.26458	1.27803
300	1.000119	1.000239	1.000359	1.000602	1.001219	1.002507	1.003879	1.006952	1.23475	1.24121	1.24648	1.25500	1.27036
320	1.000115	1.000230	1.000346	1.000580	1.001173	1.002402	1.003698	1.006541	1.016390	1.22676	1.23389	1.24452	1.26230
340	1.000111	1.000222	1.000334	1.000559	1.001130	1.002307	1.003539	1.006198	1.014674	1.20825	1.21905	1.23295	1.25382
360	1.000107	1.000215	1.000323	1.000540	1.001090	1.002221	1.003396	1.005903	1.013497	1.17826	1.20040	1.21997	1.24491
380	1.000104	1.000208	1.000313	1.000523	1.001054	1.002141	1.003266	1.005644	1.012600	1.038313	1.17338	1.20514	1.23553
400	1.000101	1.000202	1.000303	1.000506	1.001019	1.002068	1.003148	1.005414	1.011874	1.031709	1.11509	1.18775	1.22568
420	1.000098	1.000196	1.000294	1.000491	1.000987	1.002000	1.003039	1.005206	1.011266	1.028123	1.06457	1.16690	1.21534
440	1.000095	1.000190	1.000285	1.000476	1.000957	1.001936	1.002938	1.005017	1.010741	1.025683	1.05077	1.14226	1.20455
460	1.000092	1.000184	1.000277	1.000462	1.000929	1.001877	1.002845	1.004844	1.010281	1.023846	1.04386	1.11676	1.19334
480	1.000090	1.000179	1.000269	1.000449	1.000902	1.001821	1.002757	1.004685	1.009871	1.022381	1.03940	1.09600	1.18184
500	1.000087	1.000174	1.000262	1.000437	1.000877	1.001769	1.002676	1.004537	1.009502	1.021165	1.03618	1.08155	1.17020

TABLE 7. Refractive Index of Water for Wavelength 0.63280  $\mu\text{m}$ ,  $T$  in  $^{\circ}\text{C}$ ,  $P$  in MPa — Continued

$T \backslash P$	.1	.2	.3	.5	1.0	2.0	3.0	5.0	10.0	20.0	30.0	50.0	100.0
0	1.33306	1.33308	1.33310	1.33313	1.33321	1.33338	1.33354	1.33387	1.33469	1.33629	1.33785	1.34086	1.34781
10	1.33282	1.33283	1.33285	1.33288	1.33296	1.33311	1.33327	1.33358	1.33434	1.33584	1.33731	1.34015	1.34675
20	1.33211	1.33212	1.33214	1.33217	1.33224	1.33239	1.33254	1.33284	1.33357	1.33501	1.33641	1.33914	1.34551
30	1.33105	1.33107	1.33108	1.33111	1.33118	1.33133	1.33147	1.33176	1.33247	1.33387	1.33524	1.33790	1.34411
40	1.32972	1.32973	1.32975	1.32977	1.32985	1.32999	1.33013	1.33041	1.33112	1.33250	1.33384	1.33646	1.34257
50	1.32814	1.32816	1.32817	1.32820	1.32827	1.32841	1.32855	1.32883	1.32953	1.33090	1.33224	1.33484	1.34090
60	1.32636	1.32637	1.32638	1.32641	1.32648	1.32663	1.32677	1.32705	1.32775	1.32912	1.33047	1.33306	1.33910
70	1.32438	1.32439	1.32441	1.32444	1.32451	1.32465	1.32480	1.32508	1.32579	1.32717	1.32852	1.33113	1.33720
80	1.32223	1.32224	1.32226	1.32229	1.32236	1.32250	1.32265	1.32294	1.32366	1.32506	1.32643	1.32907	1.33518
90	1.31991	1.31992	1.31994	1.31997	1.32004	1.32019	1.32034	1.32064	1.32137	1.32280	1.32419	1.32687	1.33306
100	1.000187	1.31745	1.31747	1.31750	1.31757	1.31773	1.31788	1.31818	1.31893	1.32040	1.32182	1.32455	1.33085
120	1.000177	1.31206	1.31207	1.31211	1.31219	1.31235	1.31251	1.31284	1.31363	1.31519	1.31670	1.31958	1.32615
140	1.000167	1.000338	1.000513	1.30614	1.30622	1.30640	1.30658	1.30693	1.30779	1.30947	1.31109	1.31416	1.32111
160	1.000159	1.000321	1.000486	1.000824	1.29968	1.29988	1.30007	1.30046	1.30141	1.30325	1.30501	1.30833	1.31575
180	1.000152	1.000306	1.000462	1.000780	1.001624	1.29275	1.29297	1.29340	1.29446	1.29650	1.29845	1.30208	1.31008
200	1.000145	1.000292	1.000440	1.000742	1.001531	1.28494	1.28519	1.28569	1.28690	1.28920	1.29138	1.29541	1.30412
220	1.000139	1.000279	1.000421	1.000708	1.001452	1.003085	1.27665	1.27723	1.27863	1.28128	1.28376	1.28828	1.29784
240	1.000133	1.000268	1.000403	1.000677	1.001383	1.002903	1.004618	1.26785	1.26952	1.27264	1.27551	1.28066	1.29125
260	1.000128	1.000257	1.000387	1.000649	1.001321	1.002749	1.004318	1.25728	1.25935	1.26313	1.26653	1.27248	1.28433
280	1.000123	1.000247	1.000372	1.000623	1.001266	1.002616	1.004073	1.007445	1.24774	1.25252	1.25665	1.26367	1.27706
300	1.000119	1.000238	1.000358	1.000600	1.001215	1.002499	1.003867	1.006931	1.23396	1.24039	1.24565	1.25413	1.26943
320	1.000115	1.000230	1.000345	1.000578	1.001169	1.002395	1.003687	1.006520	1.016338	1.22600	1.23311	1.24369	1.26140
340	1.000111	1.000222	1.000333	1.000558	1.001126	1.002300	1.003528	1.006178	1.014628	1.20756	1.21832	1.23217	1.25296
360	1.000107	1.000214	1.000322	1.000539	1.001087	1.002214	1.003385	1.005884	1.013454	1.17768	1.19974	1.21924	1.24409
380	1.000104	1.000208	1.000312	1.000521	1.001050	1.002135	1.003256	1.005627	1.012560	1.038194	1.17282	1.20447	1.23475
400	1.000100	1.000201	1.000302	1.000505	1.001016	1.002061	1.003138	1.005397	1.011838	1.031610	1.11473	1.18714	1.22493
420	1.000097	1.000195	1.000293	1.000489	1.000984	1.001994	1.003030	1.005190	1.011231	1.028036	1.06437	1.16636	1.21464
440	1.000095	1.000189	1.000284	1.000475	1.000954	1.001930	1.002929	1.005002	1.010708	1.025604	1.05061	1.14181	1.20388
460	1.000092	1.000184	1.000276	1.000461	1.000926	1.001871	1.002836	1.004829	1.010249	1.023773	1.04372	1.11640	1.19272
480	1.000089	1.000179	1.000268	1.000448	1.000900	1.001816	1.002749	1.004670	1.009841	1.022312	1.03928	1.09570	1.18126
500	1.000087	1.000174	1.000261	1.000436	1.000875	1.001764	1.002667	1.004523	1.009473	1.021100	1.03607	1.08130	1.16966



TABLE 7. Refractive Index of Water for Wavelength 1.01398  $\mu\text{m}$ ,  $T$  in  $^{\circ}\text{C}$ ,  $P$  in MPa — Continued

$T \backslash P$	.1	.2	.3	.5	1.0	2.0	3.0	5.0	10.0	20.0	30.0	50.0	100.0
0	1.32612	1.32614	1.32615	1.32618	1.32626	1.32643	1.32659	1.32691	1.32770	1.32926	1.33078	1.33371	1.34048
10	1.32591	1.32592	1.32594	1.32597	1.32604	1.32619	1.32634	1.32664	1.32739	1.32885	1.33028	1.33305	1.33947
20	1.32524	1.32526	1.32527	1.32530	1.32537	1.32552	1.32566	1.32595	1.32666	1.32806	1.32944	1.33209	1.33829
30	1.32424	1.32425	1.32427	1.32430	1.32437	1.32451	1.32465	1.32493	1.32562	1.32699	1.32832	1.33091	1.33696
40	1.32296	1.32298	1.32299	1.32302	1.32309	1.32323	1.32337	1.32364	1.32433	1.32567	1.32699	1.32953	1.33549
50	1.32145	1.32147	1.32148	1.32151	1.32158	1.32172	1.32185	1.32213	1.32281	1.32415	1.32545	1.32798	1.33388
60	1.31974	1.31975	1.31977	1.31979	1.31986	1.32000	1.32014	1.32042	1.32110	1.32244	1.32375	1.32627	1.33216
70	1.31784	1.31785	1.31787	1.31789	1.31796	1.31810	1.31824	1.31852	1.31921	1.32056	1.32188	1.32442	1.33033
80	1.31576	1.31578	1.31579	1.31582	1.31589	1.31603	1.31618	1.31646	1.31716	1.31853	1.31986	1.32243	1.32840
90	1.31353	1.31354	1.31356	1.31359	1.31366	1.31381	1.31395	1.31424	1.31495	1.31635	1.31771	1.32032	1.32636
100	1.000184	1.31116	1.31117	1.31120	1.31128	1.31142	1.31157	1.31187	1.31260	1.31403	1.31542	1.31809	1.32422
120	1.000173	1.30594	1.30596	1.30599	1.30607	1.30623	1.30639	1.30670	1.30748	1.30900	1.31047	1.31328	1.31969
140	1.000165	1.000332	1.000504	1.30021	1.30030	1.30047	1.30064	1.30098	1.30183	1.30347	1.30504	1.30805	1.31483
160	1.000156	1.000315	1.000477	1.000810	1.29396	1.29415	1.29434	1.29471	1.29564	1.29744	1.29916	1.30240	1.30965
180	1.000149	1.000300	1.000454	1.000767	1.001596	1.28722	1.28744	1.28786	1.28890	1.29089	1.29279	1.29635	1.30417
200	1.000143	1.000287	1.000433	1.000729	1.001505	1.27964	1.27988	1.28037	1.28155	1.28380	1.28593	1.28987	1.29838
220	1.000137	1.000274	1.000414	1.000696	1.001428	1.003034	1.27157	1.27213	1.27351	1.27610	1.27853	1.28295	1.29230
240	1.000131	1.000263	1.000396	1.000666	1.001360	1.002854	1.004541	1.26300	1.26464	1.26769	1.27050	1.27554	1.28590
260	1.000126	1.000253	1.000380	1.000638	1.001299	1.002704	1.004247	1.25269	1.25472	1.25843	1.26175	1.26758	1.27918
280	1.000121	1.000243	1.000366	1.000613	1.001245	1.002574	1.004007	1.007323	1.24339	1.24807	1.25212	1.25899	1.27211
300	1.000117	1.000234	1.000352	1.000590	1.001196	1.002459	1.003804	1.006818	1.22992	1.23622	1.24137	1.24968	1.26468
320	1.000113	1.000226	1.000340	1.000569	1.001150	1.002356	1.003628	1.006416	1.016077	1.22215	1.22912	1.23950	1.25686
340	1.000109	1.000218	1.000328	1.000549	1.001109	1.002264	1.003472	1.006080	1.014395	1.20409	1.21465	1.22823	1.24863
360	1.000105	1.000211	1.000317	1.000530	1.001070	1.002179	1.003332	1.005792	1.013243	1.17477	1.19644	1.21559	1.23996
380	1.000102	1.000204	1.000307	1.000513	1.001034	1.002101	1.003205	1.005539	1.012365	1.037598	1.17002	1.20111	1.23084
400	1.000099	1.000198	1.000297	1.000497	1.001001	1.002030	1.003090	1.005314	1.011655	1.031122	1.11293	1.18413	1.22124
420	1.000096	1.000192	1.000288	1.000482	1.000969	1.001963	1.002983	1.005111	1.011059	1.027607	1.06338	1.16373	1.21117
440	1.000093	1.000186	1.000280	1.000467	1.000940	1.001901	1.002885	1.004926	1.010546	1.025217	1.04984	1.13961	1.20064
460	1.000090	1.000181	1.000272	1.000454	1.000912	1.001843	1.002793	1.004757	1.010096	1.023417	1.04307	1.11462	1.18970
480	1.000088	1.000176	1.000264	1.000441	1.000886	1.001789	1.002708	1.004601	1.009695	1.021981	1.03870	1.09426	1.17846
500	1.000086	1.000171	1.000257	1.000429	1.000862	1.001738	1.002628	1.004456	1.009334	1.020791	1.03554	1.08010	1.16708

TABLE 7. Refractive Index of Water for Wavelength 2.32542  $\mu\text{m}$ ,  $T$  in  $^{\circ}\text{C}$ ,  $P$  in MPa — Continued

$T \setminus P$	.1	.2	.3	.5	1.0	2.0	3.0	5.0	10.0	20.0	30.0	50.0	100.0
0	1.27651	1.27652	1.27654	1.27656	1.27663	1.27676	1.27689	1.27715	1.27780	1.27907	1.28030	1.28269	1.28817
10	1.27652	1.27653	1.27654	1.27657	1.27663	1.27675	1.27688	1.27712	1.27773	1.27892	1.28008	1.28233	1.28755
20	1.27616	1.27617	1.27618	1.27621	1.27627	1.27639	1.27650	1.27674	1.27732	1.27846	1.27958	1.28175	1.28679
30	1.27552	1.27554	1.27555	1.27557	1.27563	1.27574	1.27586	1.27609	1.27665	1.27777	1.27886	1.28097	1.28589
40	1.27466	1.27467	1.27468	1.27471	1.27476	1.27488	1.27499	1.27522	1.27578	1.27688	1.27795	1.28003	1.28488
50	1.27361	1.27362	1.27363	1.27365	1.27371	1.27382	1.27394	1.27416	1.27472	1.27581	1.27688	1.27895	1.28377
60	1.27238	1.27239	1.27240	1.27243	1.27248	1.27260	1.27271	1.27294	1.27350	1.27459	1.27567	1.27774	1.28255
70	1.27100	1.27101	1.27102	1.27105	1.27110	1.27122	1.27133	1.27156	1.27213	1.27324	1.27432	1.27640	1.28124
80	1.26947	1.26948	1.26950	1.26952	1.26958	1.26969	1.26981	1.27004	1.27062	1.27174	1.27284	1.27496	1.27984
90	1.26781	1.26782	1.26783	1.26786	1.26792	1.26804	1.26815	1.26839	1.26898	1.27013	1.27125	1.27340	1.27836
100	1.000160	1.26602	1.26604	1.26606	1.26612	1.26625	1.26637	1.26661	1.26722	1.26840	1.26954	1.27174	1.27679
120	1.000151	1.26206	1.26207	1.26210	1.26216	1.26230	1.26243	1.26269	1.26333	1.26459	1.26581	1.26813	1.27343
140	1.000143	1.000290	1.000439	1.25764	1.25771	1.25786	1.25800	1.25829	1.25899	1.26035	1.26166	1.26415	1.26977
160	1.000137	1.000275	1.000416	1.000706	1.25276	1.25292	1.25308	1.25340	1.25417	1.25567	1.25710	1.25981	1.26583
180	1.000130	1.000262	1.000396	1.000670	1.001394	1.24746	1.24764	1.24800	1.24887	1.25054	1.25213	1.25510	1.26162
200	1.000125	1.000251	1.000378	1.000638	1.001316	1.24142	1.24162	1.24203	1.24302	1.24492	1.24670	1.25001	1.25714
220	1.000120	1.000240	1.000362	1.000609	1.001250	1.002656	1.23493	1.23541	1.23657	1.23875	1.24079	1.24452	1.25237
240	1.000115	1.000231	1.000347	1.000583	1.001192	1.002502	1.003980	1.22798	1.22937	1.23196	1.23433	1.23859	1.24733
260	1.000111	1.000222	1.000334	1.000560	1.001140	1.002373	1.003727	1.21951	1.22125	1.22439	1.22722	1.23216	1.24198
280	1.000106	1.000214	1.000321	1.000539	1.001094	1.002261	1.003521	1.006435	1.21186	1.21586	1.21932	1.22517	1.23631
300	1.000103	1.000206	1.000310	1.000519	1.001052	1.002163	1.003347	1.005998	1.20060	1.20600	1.21041	1.21752	1.23030
320	1.000099	1.000199	1.000299	1.000501	1.001013	1.002076	1.003195	1.005651	1.014160	1.19417	1.20017	1.20908	1.22393
340	1.000096	1.000192	1.000289	1.000484	1.000978	1.001996	1.003062	1.005362	1.012695	1.17883	1.18795	1.19966	1.21718
360	1.000093	1.000186	1.000280	1.000468	1.000945	1.001924	1.002942	1.005114	1.011693	1.15359	1.17242	1.18900	1.21002
380	1.000090	1.000181	1.000271	1.000454	1.000914	1.001858	1.002834	1.004897	1.010931	1.033231	1.14964	1.17670	1.20242
400	1.000087	1.000175	1.000263	1.000440	1.000886	1.001797	1.002735	1.004703	1.010316	1.027543	1.09976	1.16214	1.19439
420	1.000085	1.000170	1.000256	1.000427	1.000859	1.001740	1.002644	1.004529	1.009801	1.024463	1.05614	1.14452	1.18590
440	1.000083	1.000165	1.000248	1.000415	1.000834	1.001687	1.002560	1.004371	1.009358	1.022372	1.04421	1.12351	1.17697
460	1.000080	1.000161	1.000242	1.000403	1.000811	1.001637	1.002482	1.004226	1.008969	1.020802	1.03825	1.10163	1.16764
480	1.000078	1.000157	1.000235	1.000392	1.000788	1.001591	1.002409	1.004093	1.008623	1.019551	1.03442	1.08374	1.15800
500	1.000076	1.000153	1.000229	1.000382	1.000768	1.001548	1.002341	1.003969	1.008312	1.018515	1.03164	1.07127	1.14820

TABLE 8. Refractive indices of water and steam at state of saturation

T (°C)	λ = 0.22650 μm		λ = 0.36105 μm		λ = 0.40441 μm		λ = 0.58900 μm		λ = 0.63280 μm		λ = 1.01398 μm		λ = 2.32542 μm	
	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''	n'	n''
0	0.0006	1.39448	1.00002	1.34895	1.00002	1.34414	1.00002	1.33431	1.00002	1.33305	1.00002	1.32610	1.00002	1.27650
5	0.0009	1.39442	1.00003	1.34889	1.00002	1.34408	1.00002	1.33425	1.00002	1.33299	1.00002	1.32606	1.00002	1.27656
10	0.0012	1.39420	1.00003	1.34868	1.00003	1.34388	1.00003	1.33406	1.00003	1.33280	1.00003	1.32589	1.00003	1.27651
15	0.0017	1.39383	1.00005	1.34836	1.00004	1.34356	1.00004	1.33375	1.00004	1.33250	1.00004	1.32561	1.00004	1.27637
20	0.0023	1.39335	1.00006	1.34793	1.00006	1.34314	1.00006	1.33353	1.00006	1.33210	1.00006	1.32523	1.00005	1.27615
25	0.0032	1.39276	1.00009	1.34741	1.00008	1.34262	1.00008	1.33285	1.00007	1.33161	1.00007	1.32476	1.00007	1.27586
30	0.0042	1.39207	1.00011	1.34681	1.00010	1.34203	1.00010	1.33228	1.00010	1.33104	1.00010	1.32423	1.00009	1.27551
35	0.0056	1.39129	1.00015	1.34613	1.00013	1.34137	1.00013	1.33164	1.00013	1.33040	1.00013	1.32362	1.00012	1.27511
40	0.0074	1.39044	1.00019	1.34539	1.00017	1.34064	1.00017	1.33094	1.00016	1.32970	1.00016	1.32295	1.00016	1.27465
45	0.0096	1.38952	1.00024	1.34458	1.00022	1.33984	1.00021	1.33018	1.00021	1.32894	1.00021	1.32222	1.00020	1.27415
50	0.0123	1.38852	1.00031	1.34372	1.00028	1.33899	1.00027	1.32936	1.00026	1.32813	1.00026	1.32144	1.00026	1.27360
55	0.0158	1.38747	1.00038	1.34280	1.00035	1.33809	1.00034	1.32848	1.00033	1.32726	1.00033	1.32061	1.00033	1.27300
60	0.0199	1.38635	1.00048	1.34183	1.00043	1.33713	1.00043	1.32756	1.00042	1.32634	1.00041	1.31973	1.00041	1.27237
65	0.0250	1.38517	1.00059	1.34080	1.00053	1.33612	1.00053	1.32659	1.00051	1.32538	1.00051	1.31880	1.00050	1.27170
70	0.0312	1.38393	1.00073	1.33973	1.00066	1.33507	1.00065	1.32558	1.00063	1.32437	1.00063	1.31783	1.00062	1.27099
75	0.0386	1.38265	1.00089	1.33862	1.00080	1.33397	1.00079	1.32452	1.00077	1.32332	1.00077	1.31681	1.00075	1.27025
80	0.0474	1.38131	1.00108	1.33745	1.00097	1.33283	1.00096	1.32341	1.00093	1.32222	1.00093	1.31576	1.00091	1.26947
85	0.0578	1.37992	1.00130	1.33625	1.00117	1.33164	1.00115	1.32227	1.00113	1.32108	1.00112	1.31466	1.00110	1.26865
90	0.0701	1.37848	1.00156	1.33500	1.00140	1.33042	1.00138	1.32109	1.00135	1.31991	1.00134	1.31353	1.00132	1.26780
95	0.0845	1.37700	1.00185	1.33371	1.00167	1.32915	1.00165	1.31987	1.00160	1.31869	1.00160	1.31235	1.00157	1.26692
100	0.1013	1.37547	1.00220	1.33239	1.00197	1.32784	1.00195	1.31861	1.00190	1.31744	1.00189	1.31114	1.00186	1.26601
110	0.1432	1.37228	1.00303	1.32961	1.00273	1.32511	1.00269	1.31597	1.00263	1.31482	1.00262	1.30861	1.00257	1.26410
120	0.1985	1.36891	1.00411	1.32669	1.00370	1.32224	1.00365	1.31320	1.00356	1.31206	1.00355	1.30594	1.00349	1.26206
130	0.2700	1.36537	1.00549	1.32362	1.00493	1.31922	1.00487	1.31028	1.00475	1.30915	1.00473	1.30313	1.00465	1.25990
140	0.3612	1.36166	1.00720	1.32040	1.00647	1.31605	1.00639	1.30722	1.00623	1.30611	1.00621	1.30019	1.00611	1.25762
150	0.4757	1.35779	1.00933	1.31704	1.00838	1.31274	1.00828	1.30403	1.00807	1.30293	1.00805	1.29710	1.00791	1.25522
160	0.6177	1.35375	1.01193	1.31352	1.01072	1.30928	1.01059	1.30069	1.01032	1.29961	1.01029	1.29388	1.01011	1.25270
170	0.7915	1.34954	1.01508	1.30986	1.01355	1.30568	1.01338	1.29721	1.01305	1.29614	1.01301	1.29052	1.01278	1.25006
180	1.0019	1.34515	1.01887	1.30604	1.01694	1.30192	1.01674	1.29358	1.01632	1.29253	1.01627	1.28701	1.01599	1.24729
190	1.2542	1.34058	1.02338	1.30207	1.02100	1.29801	1.02074	1.28979	1.02023	1.28876	1.02016	1.28335	1.01982	1.24438
200	1.5536	1.33582	1.02873	1.29792	1.02580	1.29392	1.02549	1.28584	1.02485	1.28483	1.02477	1.27953	1.02435	1.24133
210	1.9062	1.33085	1.03503	1.29359	1.03146	1.28966	1.03107	1.28172	1.03030	1.28073	1.03020	1.27534	1.02969	1.23813
220	2.3178	1.32567	1.04242	1.28907	1.03809	1.28522	1.03763	1.27742	1.03669	1.27645	1.03658	1.27157	1.03596	1.23476
230	2.7951	1.32025	1.05106	1.28435	1.04585	1.28056	1.04529	1.27292	1.04417	1.27197	1.04403	1.26701	1.04329	1.23123
240	3.3447	1.31459	1.06114	1.27940	1.05490	1.27569	1.05423	1.26820	1.05288	1.26727	1.05271	1.26243	1.05184	1.22750

TABLE 8. Refractive indices of water and steam at state of saturation — Continued

$T$ (°C) \ $p$ (MPa)	$\lambda = 0.22650$ $\mu\text{m}$		$\lambda = 0.36105$ $\mu\text{m}$		$\lambda = 0.40441$ $\mu\text{m}$		$\lambda = 0.58900$ $\mu\text{m}$		$\lambda = 0.63280$ $\mu\text{m}$		$\lambda = 1.01398$ $\mu\text{m}$		$\lambda = 2.32542$ $\mu\text{m}$		
	$n'$	$n''$	$n'$	$n''$	$n'$	$n''$	$n'$	$n''$	$n'$	$n''$	$n'$	$n''$	$n'$	$n''$	
200	1.5536	1.3582	1.002873	1.29792	1.002580	1.29392	1.002549	1.28584	1.002485	1.28483	1.002477	1.27953	1.002435	1.24133	1.002129
210	1.9062	1.33085	1.003303	1.29359	1.003146	1.28966	1.003107	1.28172	1.003030	1.28073	1.003020	1.27554	1.002969	1.23813	1.002598
220	2.3178	1.32567	1.004242	1.28907	1.003809	1.28522	1.003763	1.27742	1.003669	1.27645	1.003658	1.27137	1.003596	1.23476	1.003148
230	2.7951	1.32025	1.005106	1.28435	1.004585	1.28056	1.004529	1.27292	1.004417	1.27197	1.004403	1.26701	1.004329	1.23123	1.003792
240	3.3447	1.31459	1.006114	1.27940	1.005490	1.27569	1.005423	1.26820	1.005288	1.26727	1.005271	1.26243	1.005184	1.22750	1.004544
250	3.9736	1.30864	1.007288	1.27420	1.006543	1.27057	1.006464	1.26325	1.006303	1.26234	1.006283	1.25763	1.006179	1.22357	1.005419
260	4.6894	1.30238	1.008654	1.26873	1.007769	1.26519	1.007675	1.25803	1.007484	1.25714	1.007460	1.25256	1.007337	1.21940	1.006439
270	5.4999	1.29578	1.010245	1.26295	1.009197	1.25949	1.009085	1.25252	1.008859	1.25165	1.008831	1.24720	1.008686	1.21498	1.007628
280	6.4132	1.28878	1.012103	1.25682	1.010864	1.25345	1.010732	1.24666	1.010465	1.24582	1.010432	1.24150	1.010262	1.21025	1.009017
290	7.4380	1.28132	1.014282	1.25028	1.012819	1.24700	1.012663	1.24041	1.012348	1.23960	1.012309	1.23542	1.012109	1.20519	1.010646
300	8.5838	1.27332	1.016853	1.24325	1.015125	1.24008	1.014941	1.23370	1.014570	1.23291	1.014524	1.22889	1.014289	1.19971	1.012570

## 10. Summary and Conclusions

We have obtained a relatively simple formulation of the refractive index of water and water vapor, that, with ten adjustable constants, but coupled with an equation of state, represents adequately the reliable data and sometimes highly accurate data sets in the visible, infrared and ultraviolet, in liquid, vapor, pressurized and supercooled water. The formulation rests on the assumptions that the Lorentz-Lorenz function depends only weakly on density and temperature, and that the ultraviolet and infrared resonances in the formulation are not dependent on temperature. Both hypotheses, although not in conflict with the available experimental results, should be subjected to scrutiny. The first one, quite well supported by very accurate, be it patchy, data, deserves closer investigation because it shows such an utterly remarkable indifference to the state of water, a substance thoroughly researched because of its unusual structural behavior. One experiment that could have come a long way towards substantiating our hypothesis is that of Scheffler<sup>16</sup>, which bridged the vapor and liquid regions through the supercritical regime. Unfortunately, lack of knowledge of the temperature dependence of the refractive index of the prism used in the experiment puts its results into serious doubt. A repeat of this experiment, with careful attention to the temperature dependence of the refractive index of the prism, would not only test our hypothesis, but also enable the refractive index to be used as an *in situ* probe of the density of supercritical steam in power cycles.

Our formulation enables the unraveling of the refraction virials from the gas nonideality. A recent paper by Burns *et al.*<sup>19</sup> contains experimental values of the refractivity second virial for a number of simple gases. It also gives the theoretical expression for this property, in terms of molecular parameters, and calculates the various contributions to the second refractivity virial in a number of cases. The theoretical expressions for the first and second refraction virial indicate that the first,  $A_R$ , is proportional to the molecular polarizability, and that by

far the largest contribution to the second virial  $B_R$  comes from a term proportional to the cube of the molecular polarizability. It follows that the ratio of the second refractivity virial to the cube of the first and made dimensionless by means of a molar volume  $NR_0^3$ , with  $N_A$  Avogadro's number and  $R_0$  a typical molecular size should be roughly constant, independent of the substance considered. In Table 9, we test this ratio for the fluids for which it has been measured, calculated or both. It is gratifying to note that the second refraction virial obtained by us for water is of the order of magnitude observed for other fluids. The signs of both the second and the third virials are the same as for those fluids for which they are known with any certainty<sup>19,22</sup>. We conclude that the behavior of the molar refraction as formulated here is in reasonable agreement with that found for other fluids. This statement does not imply that the present authors understand why the refractive index of water behaves in such an uncomplicated fashion.

The second assumption, that the resonances are not sensitive to temperature, was made for lack of data indicating otherwise. This hypothesis is, of course, only one aspect of the very empirical approach we took to wavelength dependence. Incorporation of more resonances, and much more careful treatment of damping near the resonances, should lead to theoretically much better founded expressions for wavelength-dependence. At present, the data base is simply not there for testing alternative expressions.

Finally, a word about the recent formulations proposed for the complex refractive index<sup>30,66-71</sup> over large ranges of wavelengths, a topic of great importance in communications and in military applications. If these formulations would take into account the very accurate knowledge of the real refractive index in the visible, near infrared and near ultraviolet, as available in our formulation, it would seem that, at least in ranges near the visible, major improvement of the formulation of the complex refractive index might result, and discrepancies of several percents noted by us in Sec. 7 might be resolved.

TABLE 9. Refractivity virial values; visible range, ambient temperature

Substance	Ref	$A_R \cdot 10^6$ $\text{m}^3 \text{mol}^{-1}$	$B_R \cdot 10^{12}$ $\text{m}^6 \text{mol}^{-2}$	$C_R \cdot 10^{18}$ $\text{m}^9 \text{mol}^{-3}$	$R_0$ nm	$N_A R_0^3 \cdot 10^4$ $\text{m}^3$	$N_A R_0^3 B_R / A_R^3$
C <sub>2</sub> H <sub>4</sub>	21	10.65	20	-1300	0.42	0.45	0.75
Ar	19	4.2	1.55		0.34	0.24	0.50
CO <sub>2</sub>	19	6.7	1-4		0.40	0.39	0.13-0.52
Xe	19	10.6	15-25		0.41	0.42	0.53-0.88
CH <sub>3</sub> F	19	7.1	1.5-2.5		0.38	0.33	0.13-0.23
H <sub>2</sub> O	this paper	3.71	3.2	-98	0.30	0.16	1.00

## 11. Nomenclature

$a_i$	adjustable parameter
$A_R, B_R, C_R$	molar-refraction virial coefficients
$B$	barometric pressure
$LL$	Lorentz-Lorenz function
$N_A$	Avogadro's number
$n$	refractive index (of water)
$n_{\text{air}}$	refractive index (of air)
$P$	pressure
$T$	absolute temperature
$t$	Celsius temperature

## Greek Symbols

$\alpha$	molecular polarizability
$\delta$	incremental change
$\epsilon_0$	permittivity of vacuum
$\lambda$	wavelength
$\rho$	density

## Superscripts

*	reduced (dimensionless) variable
---	----------------------------------

## Subscripts

$i$	running index
IR	nearest infrared resonance in water
m	molar
o	reference value
R	referring to molar refractivity
UV	nearest ultraviolet resonance in water

## 12. Acknowledgements

The Executive Committee of the International Association for the Properties of Steam authorized this study, and provided travel funds for one of us (P.S.) to initiate the work at NIST. Two of us, (J.M.H.L.S. and J.S.G.) received support from the Office of Standard Reference Data at NIST. Two of us (P.S. and J.S.) acknowledge support by The Deutsche Forschungsgemeinschaft (DFG Str 117/28-1). We have made extensive use of the data compilation, evaluation and correction prepared earlier by K. Scheffler and I. Thormählen at the Technische Universität München. We have profited from discussions about molar refractivity with Prof. G. Walrafen from Howard University, and about refractivity virials with Dr. H.-J. Achtermann from the Technische Universität Hannover. Prof. Ph. Hill from University of British Columbia, and Prof. W. Wagner from the Ruhr Universität Bochum have contributed their insights about the properties of supercooled water; both they and Prof. H. Sato from Keio University, Yokohama, provided us with prepublication information on their respective formulations of the equation of state of water and steam. Prof. M.R. Querry from the University of Kansas commented on an earlier version of the manuscript.

## 13. References

- L. W. Tilton, *J. Res. Natl. Bur. Stand.* **17**, 639 (1936).
- L. W. Tilton and J. K. Taylor, *J. Res. Natl. Bur. Stand. (U. S.)* **20**, 419 (1938).
- R. M. Waxler and C. E. Weir, *J. Res. Natl. Bur. Stand.* **67A**, 163 (1963).
- R. M. Waxler, C. E. Weir, and H. R. Schamp, *J. Res. Natl. Bur. Stand. (U. S.)* **68**, 489 (1964).
- H.-J. Achtermann, Ph. D. Thesis University of Hanover, FRG (1978).
- H.-J. Achtermann and H. Rögner, in: *Proc. 10th Internat. Conf. Prop. Steam*, V. V. Sytchev and A. A. Aleksandrov, Editors. MIR publishers, Moscow, 1986. Vol. 2, p. 29.
- I. Thormählen, J. Straub and U. Grigull, *J. Phys. Chem. Ref. Data* **14**, 933 (1985).
- L. Haar, J. S. Gallagher, and G. S. Kell, *NBS/NRC Steam Tables*, Hemisphere, New York (1984).
- Ch. Saubade, *J. Physique* **42**, 359 (1981).
- A. Michels and J. Hamers, *CSSR, Physica* **4**, 995 (1937).
- A. Michels and A. Botzen, *Physica* **15**, 769 (1949).
- A. D. Buckingham, *Trans. Farad. Soc.* **52**, 747 (1956).
- J. A. Lorentz, *Ann. Phys. Wied.* **9**, 641 (1880).
- L. Lorenz, *Ann. Phys. Wied.* **11**, 70 (1880).
- M. Born and E. Wolf, *Principles of Optics* (Pergamon, London, 1959).
- K. Scheffler, J. Straub and U. Grigull, *Proc. 8th Symposium of Thermophys. Prop.* ASME 1981. J. V. Sengers, ed, Vol. **11**, 311.
- E. Flatow, *Ann. Phys. Wied.* **12**, 85 (1903).
- D. Schulz, *Wissensch. Zeitsch. Päd. Hochschule Potsdam* **2**, 45, (1955).
- R. C. Burns, C. Graham and A. R. M. Weller, *Mol. Phys.* **59**, 41 (1986).
- H.-J. Achtermann, *Festschrift Prof. Rögner*, in press.
- H.-J. Achtermann, T. K. Bose and G. Magnus, 10th Symp. Thermo-physical Prop., A. Cezairliyan and J. V. Sengers, Edts., *Int. J. Thermophys* **11**, 133 (1990).
- H.-J. Achtermann, H. D. Baehr and T. K. Bose, *J. Chem. Thermodyn.*, **21**, 1023 (1989).
- E. E. Hall and A. R. Payne, *Phys. Rev.* **20**, 249 (1922).
- O. Jasse, *C. R. Acad. Sci.* **198**, 163 (1934).
- J. S. Rosen, *J. Opt. Soc. Am.* **37**, 932 (1947).
- E. M. Stanley, *J. Chem. Eng. Data* **16**, 454 (1971).
- H. Rubens, *Ann. Phys. Wied.* **45**, 238 (1892). H. Rubens and E. Ladenburg, *Ber. Dtsch. Phys. Ges.* **11**, 16 (1909).
- L. R. Ingersoll, *J. Opt. Soc. Am.* **6**, 663 (1922).
- J. Vincent-Geisse, G. Vagner and F. Gans, *Revue d'Optique* **43**, 15 (1964).
- L. Pontier and C. Dechambeno, *Ann. de Geophys.* **22**, 633 (1966).
- "The 1968 International Practical Temperature Scale," *Metrologia* **5**, (1969).
- Kösters, *Phys. Zeitschr.* **34**, 223 (1934).
- G. S. Kell, *J. Chem. Eng. Data*, **20**, 97 (1975).
- B. C. Damien, *J. Phys. (Paris)* **10**, 198 (1881).
- J. B. Hawkes and R. W. Astheimer, *J. Opt. Soc. Am.* **38**, 804 (1948).
- C. Pulfrich, *Ann. Phys. Wied.* **34**, 326 (1888).
- J. W. Brühl, *Ber. Deutsch. Chem. Gesells.* **24**, 644 (1891).
- S. J. Conroy, *Proc. R. Soc. London* **58**, 228 (1895).
- M. H. Dufet, *J. Phys. (Paris)* **4**, 389 (1885).
- L. Lorenz, *Vidensk. Selsk. Skv.* **10**, 485 (1875); *Ann. Phys. Wied* **11**, 70 (1880).
- G. Quincke, *Ann. Phys. Wied.* **19**, 401 (1883).
- J. Verschaffelt, *Bull. Acad. R. Sci. Belg.* **27**, 49 (1894).
- V. S. M. van der Willigen, *Ann. Phys. Pogg.* **122**, 191 (1864); *Arch. Mus. Teyler* **2**, 199 (1869).
- B. W. Grange, W. H. Stevenson and P. Viskenta, *Appl. Opt.* **15**, 858 (1976).
- H. Landolt, *Ann. Phys. Pogg.* **117**, 353 (1862).
- A. Wüllner, *Ann. Phys. Pogg.* **133**, 1 (1868).
- E. Wiedemann, *Ann. Phys. Pogg.* **158**, 375 (1876).

- <sup>48</sup>B. Walter, *Ann. Phys. Wied.* **46**, 423 (1892).  
<sup>49</sup>M. Bayen, *J. Phys. Radium* **8**, 57 (1942).  
<sup>50</sup>W. Boguth, *Microscopica Acta* **74**, 217 (1973).  
<sup>51</sup>J. Ducleaux and P. Jeantet, *J. Phys. (Paris)* **2**, 346 (1921); *J. Phys. (Paris)* **5**, 92 (1924).  
<sup>52</sup>J. W. Gifford, *Proc. R. Soc. London* **78**, 406 (1907).  
<sup>53</sup>N. Gregg-Wilson and R. Wright, *J. Phys. Chem.* **35**, 3011 (1931).  
<sup>54</sup>A. Kruis and W. Geffken, *Zeitschr. f. Physik. Chem.* **B45**, 438 (1940).  
<sup>55</sup>E. Moreels, C. de Greef and R. Finsy, *Appl. Optics* **23**, 3010 (1984).  
<sup>56</sup>F. Schütt, *Z. Phys. Chem.* **5**, 348 (1890).  
<sup>57</sup>C. Bender, *Ann. Phys. Wied.* **65**, 343 (1899).  
<sup>58</sup>E. Ketteler, *Ann. Phys. Wied.* **30**, 285 (1887); **33**, 506 (1888).  
<sup>59</sup>T. P. Dale and J. H. Gladstone, *Phil. Trans. Roy. Soc. London* **148**, 887 (1858).  
<sup>60</sup>M. F. Fouqué, *Ann. Obs. (Paris)* **9**, 172 (1867).  
<sup>61</sup>F. A. Osborn, *Phys. Rev.* **1**, 198 (1913).  
<sup>62</sup>R. Rühlmann, *Ann. Phys. Pogg.* **132**, 177 (1867).  
<sup>63</sup>F. E. Poindexter and J. Rosen, *Phys. Rev.* **45**, 760 (1934).  
<sup>64</sup>R. W. Roberts, *Philos. Mag.* **9**, 361 (1930).  
<sup>65</sup>H. T. Simon, *Ann. Phys. Wied.* **53**, 542 (1894).  
<sup>66</sup>U. M. Centeno, *J. Opt. Soc. Am.* **31**, 244 (1941).  
<sup>67</sup>G. M. Hale and M. R. Querry, *Appl. Opt.* **12**, 555 (1973).  
<sup>68</sup>K. F. Palmer and D. Williams, *J. Opt. Soc. Am.* **64**, 1107 (1974).  
<sup>69</sup>A. N. Rusk and D. Williams, *J. Opt. Soc. Am.* **61**, 895 (1971).  
<sup>70</sup>L. W. Pinkley, P. P. Sethna, and D. Williams, *J. Opt. Soc. Am.* **67**, 494 (1977).  
<sup>71</sup>V. M. Zolotarev, B. M. Mikhailov, L. I. Alperovich and S. I. Popov, *Opt. and Spectrosc.* **27(5)**, 430 (1969); *Optics Comm.* **1(6)**, 301 (1970).  
<sup>72</sup>V. M. Zolotarev and A. V. Denium, *Opt. and Spectrosc.* **43(2)**, 157 (1977).  
<sup>73</sup>G. P. Baxter, L. L. Burges, and H. W. Daudt, *J. Am. Chem. Soc.* **33**, 893 (1911).  
<sup>74</sup>G. Cohen and H. Eisenberg, *J. Chem. Phys.* **43**, 3881 (1965).  
<sup>75</sup>J. Kanonnikoff, *J. Prakt. Chem.* **31**, 321 (1885).  
<sup>76</sup>J. H. Gladstone, *Phil. Trans. Roy. Soc. London* **160**, 887 (1870).  
<sup>77</sup>W. C. Röntgen and L. Zehnder, *Ann. Phys. Wied.* **44**, 24 (1891).  
<sup>78</sup>H. Ruoss, *Ann. Phys. Wied.* **48**, 531 (1893).  
<sup>79</sup>C. Cuthbertson and M. Cuthbertson, *Phil. Trans.* **A213**, 1 (1913).  
<sup>80</sup>J. Fraunhofer, *Gilberts Annalen* **56**, 276 (1817).  
<sup>81</sup>A. Müttrich, *Ann. Phys. Wied.* **121**, 398 (1864).  
<sup>82</sup>H. S. Yadev, *J. Appl. Phys.* **44**, 2197 (1973).  
<sup>83</sup>Y. B. Zeldovich, S. B. Kromer, M. V. Sinitsyn and K. B. Yushko, *Sov. Phys. Dokl.* **6** 494 (1961).  
<sup>84</sup>G. S. Kell and E. Whalley, *J. Chem. Phys.* **62**, 3496 (1975).  
<sup>85</sup>Ph. G. Hill, Prepublication results (1989).  
<sup>86</sup>A. Saul and W. Wagner, *J. Phys. Chem. Ref. Data*, **18**, 1537, (1989).  
<sup>87</sup>H. Sato, Proc. 11th ICPS, Prague, 1989. To be published, Hemisphere, Washington, DC (1990).  
<sup>88</sup>R. Speedy, *J. Phys. Chem.* **86**, 3002, (1982).  
<sup>89</sup>P. Schiebener, J. Straub, J. M. H. Levelt Sengers and J. S. Gallagher, Proc. 11th ICPS, Prague, 1989. To be published, Hemisphere, Washington, DC, (1990).

## Appendix

### Optimum Formulation of the Refractive Index of Liquid Water below 60 °C, in the Visible Range, at Atmospheric Pressure.

Inconsistencies between data sets, and slight imperfections of the equation of state, have prevented us from representing the best refractive index data in liquid water to their full claimed accuracy (1 ppm or better). In view of the many scientific and practical uses of the refractive index of liquid water in the visible, it appears worthwhile to optimize the coefficients of our formulation, Eq. 7, by fitting solely to the data of Tilton and Taylor<sup>1,2</sup> and of Saubade<sup>9</sup> in liquid and supercooled water at atmospheric pressure, in the visible and below 60 °C, with the best equation of state available in this range. Before presenting the result of such a formulation, let us briefly digress on the sources and accuracy of the density of liquid and supercooled water, which limits the accuracy to be obtained in the refractive index formulation in this range.

The most accurate source of densities of liquid and compressed water from 0 to 150 °C and up to 100 MPa in pressure is the data of Kell, Whalley and collaborators obtained at the National Research Council in Canada, and reevaluated in an authoritative paper by the authors<sup>84</sup>, who claim an uncertainty of 20 ppm in density. In addition, densities in water at atmospheric pressure were formulated by Kell<sup>33</sup>, who also extrapolated this formulation to -30 °C. Kell notes that his equation does not extrapolate well. Comparing with a literature value at -30 °C, he notes a difference of 1 part in 1000, the literature value being lower. For the range of 0 to 40 °C, Kell claims a precision in density of 1 part in 10<sup>6</sup> or better, and absolute accuracy of better than 1 part in 10<sup>5</sup>. Haar et al.<sup>8</sup>, Hill<sup>85</sup>, Wagner and Saul<sup>86</sup>, and recently Sato<sup>87</sup>, all fit the Kell and Whalley data for pressurized water to the claimed accuracy of 20 ppm. Haar *et al.* did not use any data below 0 °C in their fit. Wagner and Saul, Hill and Sato<sup>87</sup> used a variety of equilibrium data below 0 °C at higher pressures, and they also used the extrapolated Kell data for supercooled water at atmospheric pressure.

A perusal of Figs. 11 and 12 makes it very clear that there are systematics in the refractive index formulation that far exceed the expected uncertainty of the various equation-of-state formulations. Using Table 1 as a guide, we note that an increase in density assignment of 1·10<sup>-5</sup> leads to a percentage decrease in *LL* of the same amount, and to a decrease in the predicted refractive index of

3·10<sup>-6</sup>. The observed departures are up to two orders of magnitude higher. For an optimum formulation of the Tilton and Taylor data it is necessary to eliminate the data of others above 60 °C because they are not fully consistent. This elimination also has a very beneficial effect at the low-temperature end of the data. A refit of the Tilton and Taylor, and Saubade data alone, based on the NBS/NRC equation, however, still leaves departures as large as 15·10<sup>-5</sup> at the lowest temperature, -12 °C. Refits using Kell's equation<sup>33</sup>, Hill's equation<sup>85</sup>, and the equation of Wagner and Saul<sup>86</sup>, all lead to considerable improvement at the lowest temperature, with only marginal differences between the three and a maximum deviation of about 6·10<sup>-5</sup> in *n* at -12 °C. The best results are obtained if Sato's new equation<sup>87</sup> is used.

In Table A1, we present the coefficients of a formulation based on the Tilton and Taylor data, Saubade's data, and Sato's equation. In Fig. A1, we show the departures of the refractive index data from this formulation. Note that for use of the formulation given in Table A1 it is necessary to use Sato's equation for conversion of pressures to densities. The remaining systematics in the visible are limited to ±1·10<sup>-5</sup>, and will require additional terms in the formulation in order to improve wavelength-dependence. The remaining systematics in supercooled water are no larger than 3·10<sup>-5</sup>; they might indicate an anomaly in the refractive index of a nature similar to those found for many other properties of supercooled water<sup>88</sup>; in the absence of an estimate of the uncertainty of the density at -12 °C, this remains speculation. For further detail, we refer to Ref. 89.

Table A1. Coefficients of Equation (7) for Atmospheric Liquid Water

$a_0 = + 0.236901076$	$\lambda_{0v} = 0.2292020$
$a_1 = + 0.262728490 \cdot 10^{-1}$	$\lambda_{1r} = 5.432937$
$a_2 = - 0.384585572 \cdot 10^{-2}$	
$a_3 = + 0.270774991 \cdot 10^{-3}$	
$a_4 = + 0.163659909 \cdot 10^{-2}$	
$a_5 = + 0.242035967 \cdot 10^{-2}$	
$a_6 = + 0.899681358$	
$a_7 = - 0.257595113 \cdot 10^{-1}$	

To be used for liquid water with Sato's equation<sup>87</sup>, in the range of -12 to +60 °C, at atmospheric pressure and in the visible.



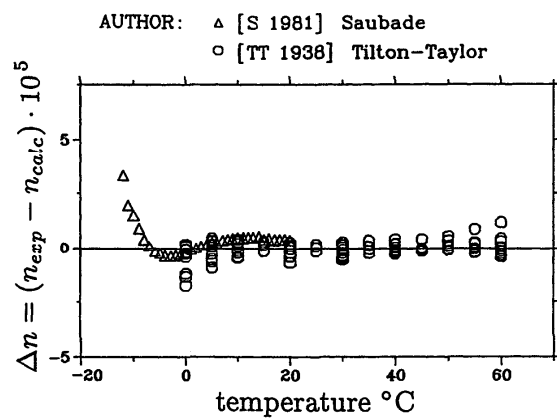


FIG. A1. Departures of the data of Tilton and Taylor<sup>1,2</sup> and of Saubade<sup>9</sup> in liquid water at atmospheric pressure from an alternative formulation based on Sato's equation for the density of water.