Visible and near-ultraviolet absorption spectrum of liquid water: comment

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Measurements of the absorption of pure water have been described [Appl. Opt. **38,** 1216 (1999)]. This comment on that paper disputes the claims that (1) their list of references on pure water absorption is complete, (2) their result ". . . provides reliable data in the 320–420-nm region . . . ," and (3) their data agree well with existing data in the literature. The clearest demonstration of these points is made by plotting their data and its associated error bars together with plots of other data in the literature that should be considered significantly more reliable. Finally, for practical applications that require absorption data, a suggestion is made for the best choice of absorption coefficients in the range of 196 nm $\leq \lambda \leq$ 700 nm. © 2000 Optical Society of America

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The recent paper "Visible and near-ultraviolet absorption spectrum of liquid water" by Litjens, Quickenden and Freeman (LQF)[1] claims (1) to provide a ". . . complete listing of all the data published between 1891 and 1997 on optical absorption by pure liquid water in the 300–700-nm spectral region . . . ," (2) to present new measurements on the absorption of pure water that provide reliable data in the 320–420-nm range, and (3) that these data are consistent with previously published data in the 420–700-nm region.

First, in just the period 1976–1997, there are at least 12 references (and probably others) that they do not list.[2–13] In addition, Querry et al. have provided a review with extensive references covering the spectrum, from x ray to far infrared.[14] Finally, Price[15] recently pointed out that deep-sea ice has spectral absorption coefficients that agree well with the data of Pope and Fry (P&F)[2] for pure water, especially at the minimum around 420 nm.[16]

Some of the most important data that were not referenced were that of Smith and Baker (S&B),[11] Sogandares and Fry (S&F),[3] and P&F. The S&B data are their best estimate of a consistent data set based on an analysis of published data and their measurements of the diffuse attenuation coefficient in the 300–400-nm region. This data set is particularly important because it has been used extensively in the field of ocean optics since its publication in 1981. S&F obtained their data using photothermal deflection spectroscopy which is essentially independent of scattering effects in the sample but is an extraordinarily difficult technique to implement. The S&F data showed significantly lower absorption in the blue than the S&B data. The P&F data, which are perhaps the most reliable, were obtained by use of a new integrating cavity technique[17,18] that is also essentially free of scattering effects in the sample. It is relatively simple to implement and is very sensitive to weak absorption; the effective path lengths through a weak absorber in an 8-cm-diameter integrating cavity are of the order of 10 m.

Data from S&B, S&F, P&F, and Quickenden and Irvin (Q&I)[19] are plotted in Fig. 1 together with the LQF data. Because the data are displayed most appropriately on a log scale that cannot show negative values, the four values of λ for which LQF obtained negative values of the absorption coefficient are not included in the plot. The absorption coefficients quoted by Q&I and LQF are base 10, $I/I_0 = 10^{-\alpha' L}$. For presentation in Fig. 1, they have been converted to base e, $I/I_0 = \exp(-\alpha L)$, where $\alpha = 2.303\alpha'$. The error bars quoted in each of the references are also shown. For 380 nm $\leq \lambda \leq$ 700 nm, the data of P&F are most reliable; consequently, to minimize clutter in Fig. 1, the only S&B and S&F data shown are for $\lambda \leq$ 380 nm. The Q&I data cover the range 196 nm

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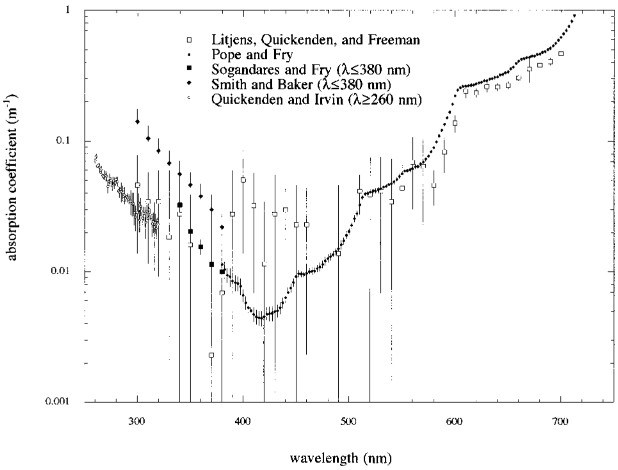

Fig. 1. Measurements of the absorption coefficient of pure water as a function of wavelength. In each case, error bars are those quoted by the respective authors.

≤λ ≤ 320 nm and appear to be relatively good, especially because such extraordinary measures were taken to eliminate organic impurities. Their data are shown for 260 nm ≤λ ≤ 320 nm.

It is clear from Fig. 1 that the LQF data cannot, in fact, be considered particularly reliable in comparison with the other data sets. Its error bars are sufficiently large so that there is not a serious disagreement with most of the other data shown in Fig. 1. However, their results above 600 nm do appear to be systematically lower than the results of P&F; in fact, for λ > 600 nm their data are also systematically lower than the literature mean shown in their Fig. 1.

In summary, the most reliable data for 380 nm ≤λ ≤ 700 nm appear to be those of P&F. For 196 nm ≤λ ≤ 320 nm, the most reliable data are probably those of Q&I. There does not seem to be a best choice of data covering the gap 320 nm ≤λ ≤ 380 nm. However, for present applications that require absorption coefficients, a best guess would be a straight-line extrapolation (on the log plot) between the 320-nm data of Q&I and the 380-nm data of P&F. Such an extrapolation fits smoothly to the data at both ends and has a shape similar to the S&B data over this wavelength range. Except for the point at 340 nm, the S&F data are consistent with the extrapolation. The LQF data do not appear to play a useful role. The S&B data are almost certainly biased to the high side by organic contaminants that absorb in the UV, but their data do provide an upper limit.

There remains an obvious need for new data on the ultraviolet absorption spectrum of pure water. Use of the conventional direct transmission technique appears limited in this spectral range as indicated by the increasing size of the error bars in the Q&I data as the absorption coefficient drops below $\sim 0.05\ m^{-1}$. On the other hand, extension of the integrating cavity technique down to a wavelength ≈250 nm is straightforward and, based on the previous results, is probably the optimum choice of techniques to obtain this data.

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