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Abstract: The latest model for light scattering by pure seawater was used to investigate the anomalous behavior of pure water. The results showed that water exhibits a minimum scattering at 24.6 °C, as compared to the previously reported values of minimum scattering at 22 °C or maximum scattering at 15 °C. The temperature corresponding to the minimum scattering also increases with the salinity, reaching 27.5 °C for S = 40 psu.

Keywords: light scattering; light scattering by pure water; light scattering by pure seawater; anomalous properties of water

1. Introduction

Light scattering by pure water or pure seawater is a fundamental quantity in aquatic optics. Because of hydrogen bonding, many bulk properties of water exhibit anomalous behavior with temperature that is unlike any other liquids [1,2]. For example, liquid water has a maximum density near 4 °C [3], a minimum isothermal compressibility near 46 °C [4] and a maximum refractive index near 0 °C [5]. The scattering seems to behave "anomalously" too [6]. Cohen and Eisenberg [6] measured the scattering at 436 and 546 nm by pure water at temperatures from 5 to 65 °C, and found a scattering minimum at approximately 22 °C that is consistent with their theoretical estimate using the Einstein–Smoluchowski equation and the temperature variation of the isothermal compressibility. Using the same Einstein-Smoluchowski equation, with inputs re-evaluated using newer experimental results, Buiteveld et al. [7] improved the estimate of light scattering by pure water, which showed a better agreement with the spectral values measured by Morel [8]. However, their model predicts a maximum scattering at 15 °C, which differs from Cohen and Eisenberg [6] not only in value but in the behavior as well. To the best of our knowledge, few other studies have explored the temperature behavior of scattering by water. In addition, it is still unknown whether and how this temperature dependence of scattering by water would vary in the presence of sea salts.

2. Methods

Recently, Zhang and coworkers refined the models for light scattering by pure water [9], by pure seawater [10,11], and by simple sea salt solutions [12] using the improved measurements of the key thermodynamic parameters, and their models agree with the spectral scattering measurements [13,14] for both pure water and seawater within the experimental errors (2%). Localized fluctuation in density for pure water, as well as additional fluctuations in the mixing ratio of salt ions and water for pure seawater, lead to microscopic inhomogeneities in the refractive index (n) [15], which in turn cause scattering of light. Since the fluctuations in density and mixing ratio are independent, the scattering coefficient of seawater, b (m^{-1}) can be expressed as

$$b = b_d + b_c,$$ (1)

where b_d represents the scattering due to density fluctuation, and b_c the scattering due to fluctuation of mixing ratio (concentration). Following Zhang and Hu [9],

$$b_d = \frac{8\pi^3}{\lambda^4} \left(\rho \frac{\partial n^2}{\partial \rho}\right)_T^2 kT\beta_T h(\delta), \tag{2}$$

and following Zhang et al. [11]

$$b_c = \frac{8\pi^3}{\lambda^4 N_A} \left(\frac{\partial n^2}{\partial S}\right)^2 \frac{M_w}{\rho} \frac{S}{-\partial \ln a_w / \partial S} h(\delta), \tag{3}$$

where, respectively, λ, k (=$1.38064852 \times 10^{-23}$ m^2·kg·s^{-2}·K^{-1}), and N_A (=6.022×10^{23} mol^{-1}) are the wavelength of light, the Boltzmann constant, and Avogadro's number; ρ, n, T, β_T, S, and δ are the density, the absolute refractive index, the absolute temperature, the isothermal compressibility, the mass concentration of salts, and the depolarization ratio of the seawater; and a_w and M_w (=18.01528 g mol^{-1}) are the activity and molecular weight of pure water. Also, $h(\delta) = (2+\delta)/(6-7\delta)$.

In Equation (1), b_c vanishes for pure water, and the scattering of light is due entirely to density fluctuation. Replacing the density derivative in Equation (2) with pressure derivative, i.e., $\left(\rho \frac{\partial n^2}{\partial \rho}\right)_T = \frac{2n}{\beta_T} \left(\frac{\partial n}{\partial P}\right)_T$, Equation (2) becomes the Einstein–Smoluchowski equation

$$b_d = \frac{32\pi^3}{\lambda^4} \frac{n^2}{\beta_T} \left(\frac{\partial n}{\partial P}\right)_T^2 kT h(\delta) \tag{4}$$

which was used by Cohen and Eisenberg [6] and Buiteveld et al. [7] in evaluating the temperature dependence of scattering by pure water. Historically, Equation (4) was often used because the isothermal piezo-optic coefficient $(\partial n / \partial P)_T$ was relatively easier to measure, even though the uncertainty was high as compared to $n(T)$, $n(\lambda)$, or $n(S)$ [16]. However, recent theoretical development [17] has greatly improved our knowledge in $(\rho \partial n / \partial \rho)_T$. This, together with the development of Equation (3) to explicitly account for the effect of salinity on scattering [11], has advanced our capability for modeling scattering by seawater [9–11], and our confidence in using Equations (1)–(3) to evaluate its temperature effect. The formulae used in the equations to estimate n, ρ, β_T, and a_w can be found in Zhang and Hu [9] and Zhang et al. [11], and the Matlab code for the model can be accessed at https://goo.gl/jKAZgT. Light scattering by seawater is a function of salinity, temperature, and pressure. In this study, we focus on the temperature and salinity ranges of 0–60 °C and 0–40 psu under one atmospheric pressure, which cover the majority of natural inland, coastal, and oceanic surface water bodies. The presence of sea salts is expected to modify the value of δ through two contrasting effects: isotropic ions would decrease δ; whereas their electrostatic field would increase anisotropy, and hence the value of δ [18,19]. Both effects have been observed in pure salt solutions: δ for KNO$_3$ solution increases and δ for KCl solution decreases, with their respective concentrations [20]. To the best of our knowledge, however, no studies have been reported on how the δ of seawater would vary with salinity. For this study, we assumed a constant value of 0.039 for the depolarization ratio δ for pure water [21] and for seawater [8,9,22,23].

3. Results and Discussion

Light scattering by pure water at 436 and 546 nm was estimated using Equation (2) for temperatures 0–60 °C, and the values normalized to the scattering at 25 °C were compared with the measurements by Cohen and Eisenberg [6] in Figure 1. Between the two wavelengths, the temperature variations of the scattering are almost identical, showing a minimum scattering at 24.7 °C ± 0.2%. The scattering increases by 4.3% towards 0 °C and increases by 4.7% towards 60 °C at both wavelengths. The root mean square difference between our model and the measurements by Cohen and Eisenberg [6] is approximately 1.3% at both wavelengths. The refractive index model [24] used in Equations (2)

and (3) were developed using the Austin and Halikas [16] measurements, which had a temperature precision of 0.1 °C. Also, the Cohen and Eisenberg [6] data we used for comparison in Figure 1 had a temperature precision of 0.1 °C as well. Therefore, we report the temperature in this study at a precision of 0.1 °C. We denote the temperature at which the scattering reaches the minimum as T_{min} hereafter. The predicted values of T_{min} are close to the value of 22 °C measured by Cohen and Eidenberg [6], but differ significantly in both value and trend from the Buiteveld, et al. [7] model, which predicts a maximum near 15 °C. We believe the difference is largely due to the uncertainty in modeling $(\partial n / \partial P)_T$ in Equation (4) that was used by Buiteveld, et al. [7]. Austin and Halikas [16] pointed out that the measurements of the refractive index of water as a function of the pressure, i.e., $n(P)$, were of worse quality when compared to those of $n(T)$, $n(\lambda)$, or $n(S)$. Also, it is well-known that to numerically approximate a derivative, such as $\partial n / \partial P$, as a ratio of measured values is very sensitive to the uncertainties in the measurements of $n(P)$. In addition, Buiteveld, et al. [7] derived the temperature dependency of $(\partial n / \partial P)_T$ by fitting the measurements [25] between 5 and 35 °C, which also explains the relatively large deviation as shown in Figure 1 when extrapolating their model beyond 35 °C.
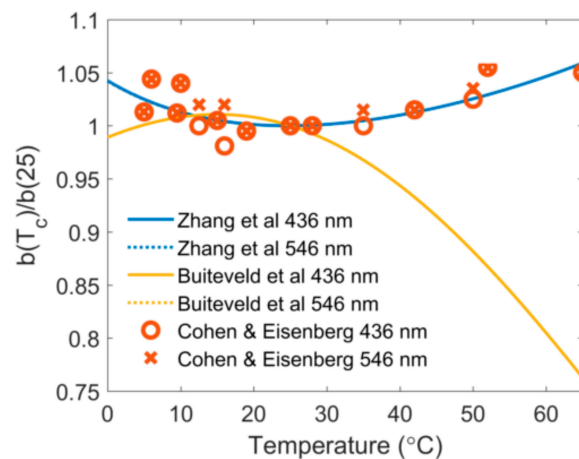

Figure 1. The temperature variations of light scattering by pure water, calculated using the Zhang and Hu [9] model (i.e., Equation (2)) at 436 and 546 nm and normalized by their respective values at 25 °C, are compared with the estimates using the Buiteveld, et al. [7] model and with the measurements by Cohen and Eisenberg [6]. Note that the normalized variations estimated by the Zhang and Hu model overlap with each other at the two wavelengths.

Several bulk properties of pure water needed to estimate the scattering coefficient behave "anomalously": density has the maximum near 4 °C [3]; isothermal compressibility has the minimum near 46 °C [4]; and the refractive index has the maximum near 0 °C [5]. Also, less apparent but indirectly relevant is that $(\partial n / \partial P)_T$, as in Equation (4), has its minimum near 50 °C [5]. Clearly, anomalous light scattering by pure water results from the combination of all of these anomalous properties, as well as its direct proportionality with the temperature (Equation (2) or (4)). Even though scattering by pure water varies strongly with wavelength, with a spectral slope of −4.28 [9], the anomalous temperature behavior of scattering varies little with wavelength (Figure 1).

The scattering coefficient at 546 nm as a function of temperature for different salinities is shown in Figure 2a for b_d (due to density fluctuation) and Figure 2b for b_c (due to concentration fluctuation). Both b_d and b_c vary with temperature in the same anomalous way, all exhibiting a minimum. Also, both T_{min} for b_d and T_{min} for b_c change with salinity—however, with differing patterns. T_{min} for b_d decreases about 20% from 24.6 °C to 19.1 °C for salinity varying from 0 to 40 psu, whereas over the same salinity range T_{min} for b_c increases slightly by ~3%, from 32.2 °C to 33.2 °C. In terms of absolute magnitude, b_d is about 2–10 times greater than b_c (Figure 2a), but in terms of change with respect to salinity, b_c is about 10 times greater than b_d (Figure 2b). As a result, the change of T_{min} for the total

scattering coefficient, b is dominated by b_c, and increases from 24.6 °C to 27.5 °C for S from 0–40 psu (Figure 3). It is well known that T_{max} for density [26] and T_{min} for isothermal compressibility [27] decrease with the salinity. Here, we show for the first time that T_{min} for light scattering increases with salinity, which is largely due to the temperature variation of scattering introduced by sea salts. Table 1 lists the variations of T_{min} for b_d, b_c, and b at different salinities.
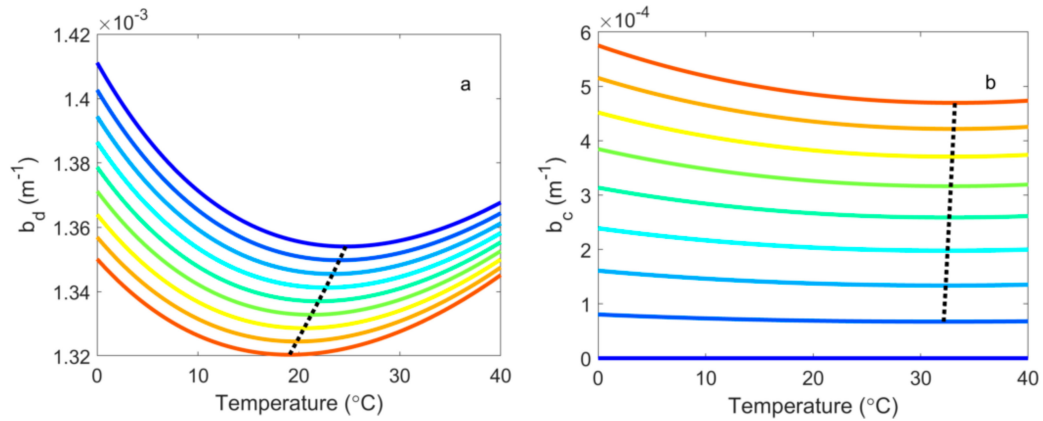

Figure 2. Light scattering by pure seawater at 546 nm as a function of temperature and salinity. (**a**) b_d, the scattering due to density fluctuation; and (**b**) b_c, the scattering due to concentration fluctuation. Lines of progressive colors from blue to red correspond to different salinities from 0 to 40 psu, at 5 psu increments. The dotted line in each plot connects T_{min} at different salinities.
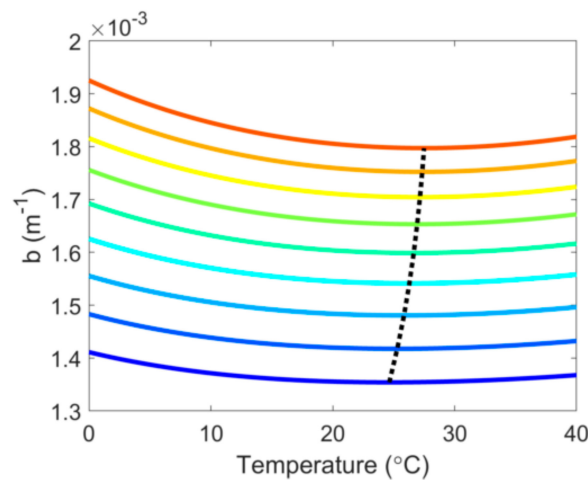

Figure 3. Total scattering coefficient by pure seawater at 546 nm as a function of temperature and salinity. Lines of progressive colors from blue to red correspond to different salinities from 0 to 40 psu at 5 psu increments. The dotted line connects T_{min} at different salinities.

Table 1. Temperatures (T_{min} in °C) at which the scattering of light at 546 nm by pure seawater due to density fluctuations (b_d), concentration fluctuations (b_c), and their total (b) reach the minimum for various salinities (S).

S (psu)	0	5	10	15	20	25	30	35	40
b_d (m^{-1})	24.6	24.0	23.4	22.7	22.0	21.2	20.5	19.8	19.1
b_c (m^{-1})		32.2	32.3	32.5	32.7	32.8	33.0	33.1	33.2
b (m^{-1})	24.6	25.3	25.9	26.3	26.6	26.9	27.2	27.3	27.5

In conclusion, using the latest scattering models for water and seawater, we find that water exhibits an anomalous light scattering behavior, with a minimum occurring at 24.6 °C for pure water, and that this minimum increases with the salinity, reaching 27.5 °C at 40 psu. This temperature behavior changes little spectrally. Caution should be exercised when using the Buiteveld, et al. [7] model, which predicts a temperature behavior of scattering that is inconsistent with the measurements [6] or the results of this study.

Author Contributions: X.Z. and L.H. conceived and designed the experiments; X.Z. wrote the paper.

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