

Some background info on the measurement of water temperature with Raman spectroscopy

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Hi Carl et al:

I promised this info a while back but a lot of things got in the way (you really don't want to know) so please accept my apology for the delay and let's look at how temperature can be measured via Raman spectroscopy.

Leonard et al (1977, 1979) are the first that I know of to attempt this measurement. From Figure 1 in Leonard et al (1979), we can see that their theory is based upon a equilibrium between two forms of water: polymer and monomer; and that this equilibrium is temperature dependent. Chemists would refer to these two forms as non-hydrogen bonded (nHB or free H₂O) and hydrogen bonded water (HB). So far so good ... but it quickly gets more complicated as the HB forms range in size from dimers to octamers or larger. We don't need to go down that rabbit hole now (maybe later). For their instrument, Leonard et al "integrated the signal" from 3100-3400 cm⁻¹ for one band and 3400-3700 cm⁻¹ for the other. Converting to nm: 637-649 and 650-662 or there abouts (see table attached.)

Becucci et al (1999) attempted to quantify & improve the accuracy of this technique by collecting the full spectra in this range and fitting two gaussian peaks to the data. From these peaks they then calculated the marker ratio where $R = (H_1/W_1)/(H_2/W_2)$ where H_i and W_i are the height and width of the two gaussian peaks respectively. Unfortunately, they did not report the wave-lengths nor the Raman shifts for their two gaussian peaks (at least not that I have found!) While this is a far more complicated procedure than the one planned, it does show us that R is more sensitive to temperature than salinity by a factor of about 2.

About 16 years ago, we had a post-doc (Rachel Dunk) who took a second look at the work of Becucci et al (1999) using a more refined spectrometer and fitted 3 gaussian peaks with the hope of teasing out T & S individually. A powerpoint of her results is attached. While her presentation is a far better graphical description of what is happening, the end result is the same: R or M is intimately linked to T & S. These two parameters can not be teased apart. Additionally, as Becucci found, the ratio is twice as sensitive to a change in 1 deg C vs a change of 1 in salinity. If we remember that the

bottom water of the world ocean has a salinity between 34.5 and 35.5, we could guess a salinity of 35 and not be off by more than about 0.25 deg C in temperature. We would do better with a CTD handy.

For what it is worth, Rachel fixed her gaussian peaks at 3250 and 3450 cm⁻¹ equivalent to 643.2 and 651.6 nm.

There is a lot more complexity to this story and I could send a suite of our papers where we have followed other spectroscopists who have shown that the water bending band actually has 5 overlapping gaussian peaks (2 nHB stretching modes and 2 HB stretching modes plus a bending overtone). We have used this as a basis for calculating the enthalpy of the hydrogen bond in sea water and used this to show how "water structure" (actually the degree of hydrogen bonding) affects all kinds of water bulk properties including density, heat capacity, and viscosity. But I will save those papers for another time.

I hope that this info helps in some way and I hope to see you all tomorrow,
Ed.
