



# Why does the ocean take up so much heat? The molecular basis for heat capacity.

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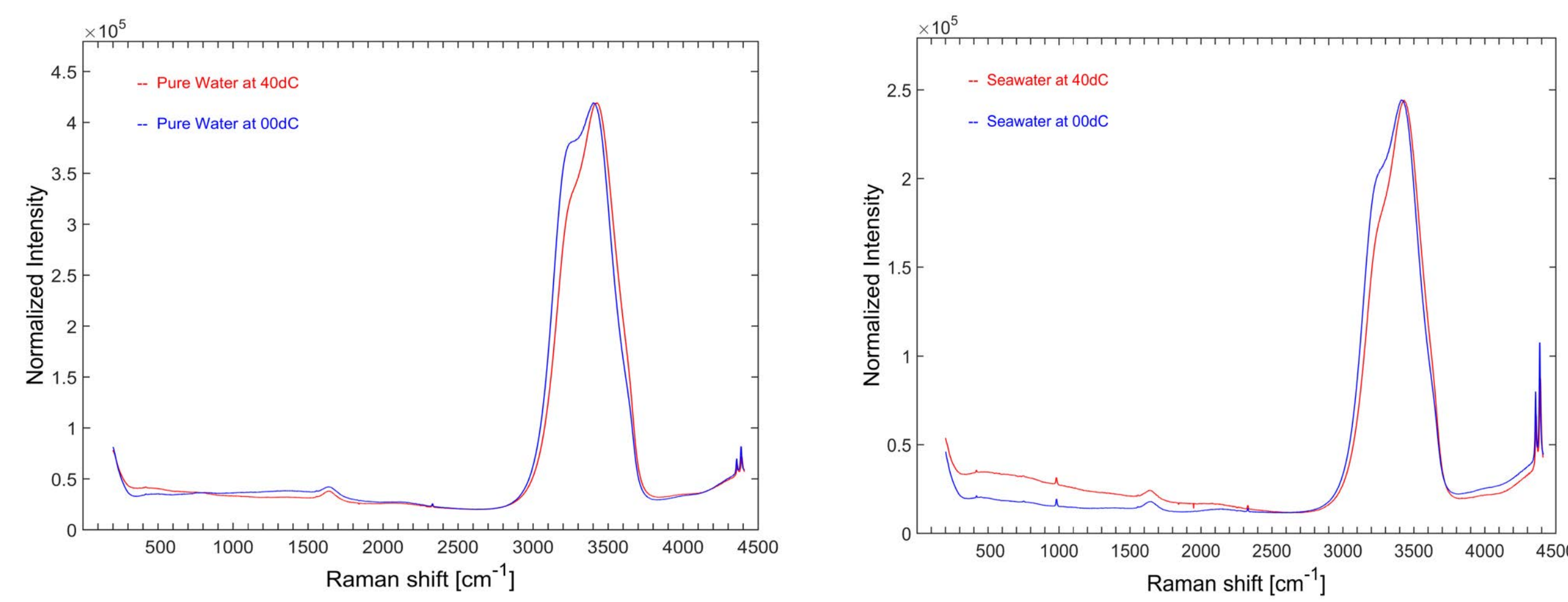
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## Abstract

The ocean absorbs a remarkable 93% of the additional heat trapped by anthropogenic greenhouse gases due to its large size, the omnipresent stirring by wind, and the “high heat capacity” of water, yet the molecular basis for the high specific heat of water ( $C_p$ ) is not well known. It has long been established that specific heats are closely tied to molecular weight. Ironically, water has no fixed molecular weight; it exists as a bi-molecular fluid consisting of single non-hydrogen bonded (nHB)  $H_2O$  molecules and an ensemble of hydrogen bonded (HB) forms in a temperature dependent equilibrium. Here we use recent Raman spectroscopic data to show that the mean molecular weight of pure water over the range 0-40°C is 86.1-80.7 while for sea water in this temperature range the mean molecular weight is 89.4-84.5. The warming of water induces the breaking of hydrogen bonds (8.364 kJ/mol), increasing the population of the nHB form at the expense of the more compact HB forms and increasing the volume of the fluid. Our analysis shows that although warming of sea water by 10°C yields an increase of only 1.64% in the nHB form of water, this accounts for some 36% of the energy consumed. Consequently the high heat capacity of water, and water in sea water, is attributable (64%) to the large mass of the HB forms, dominantly as the tetrahedral pentamer ( $H_2O$ )<sub>5</sub>, and also (36%) to the energy required to break hydrogen bonds. The  $C_p$  for pure water decreases with increased temperature due to the decrease in the ensemble molecular weight with warming, while the  $C_p$  for sea water increases with increasing temperature due the additional work required to increase the translational energy of the large hydrated cations, which are dominantly  $Na(H_2O)_6^+$  with a molecular weight of 131.8489. The increase in the specific volume of water and sea water with rising temperature is driven by both the decrease in the population of HB forms and the overall increase in translational energy.

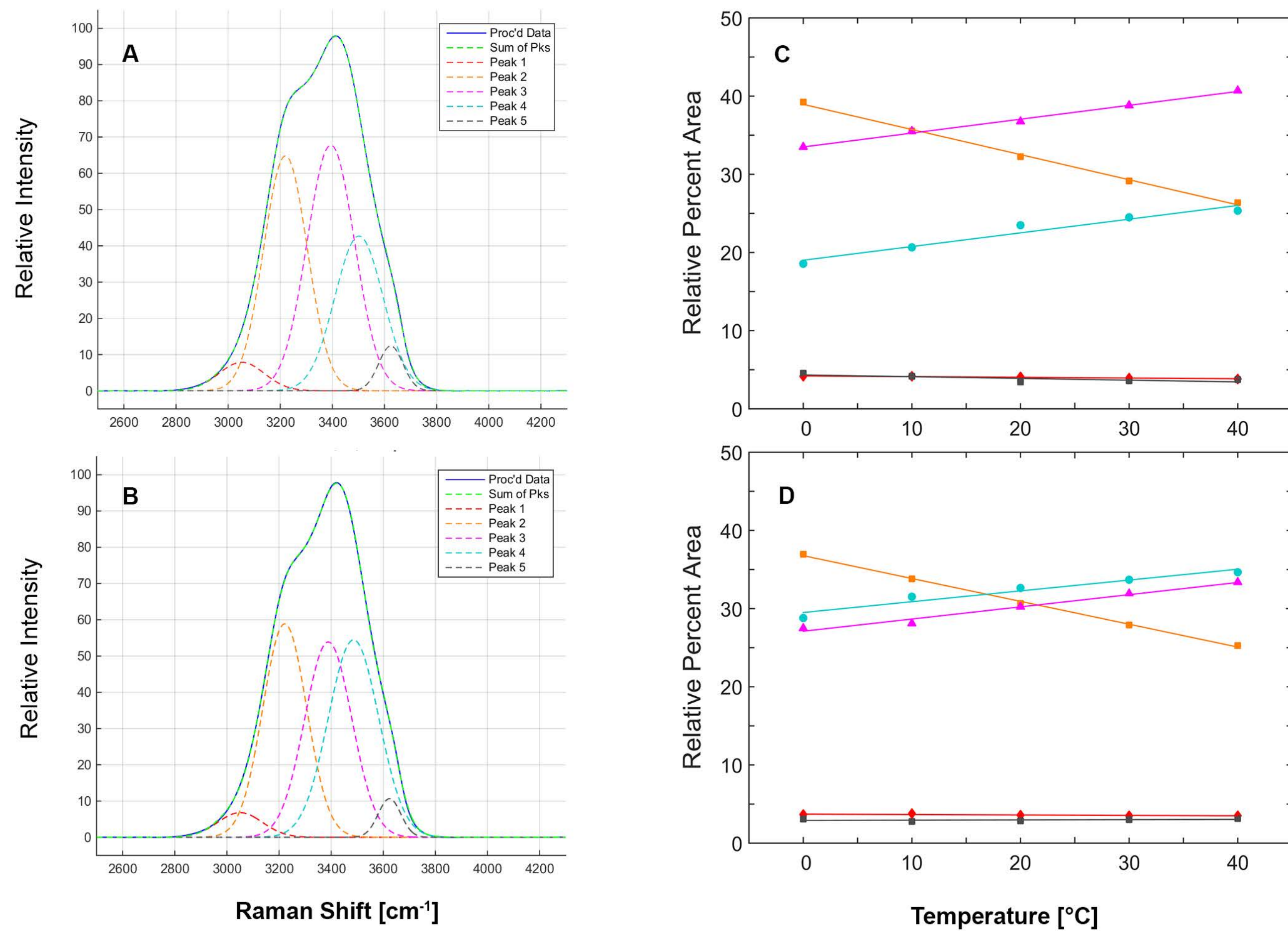
## Experimental

### Laser Raman Spectroscopy



**Figure 1.** Raman spectra of pure water (left panel) and sea water (right panel) at 40°C (red) and 0°C (blue). Note the presence of both the water bending modes (1650  $cm^{-1}$ ) and water stretching modes (2900-3800  $cm^{-1}$ ) in each spectra plus the addition of the sulfate ion peak at 981  $cm^{-1}$  in the sea water spectra. Also note the change in the distinctive shape of the bending mode peaks with increasing temperature for both water types.

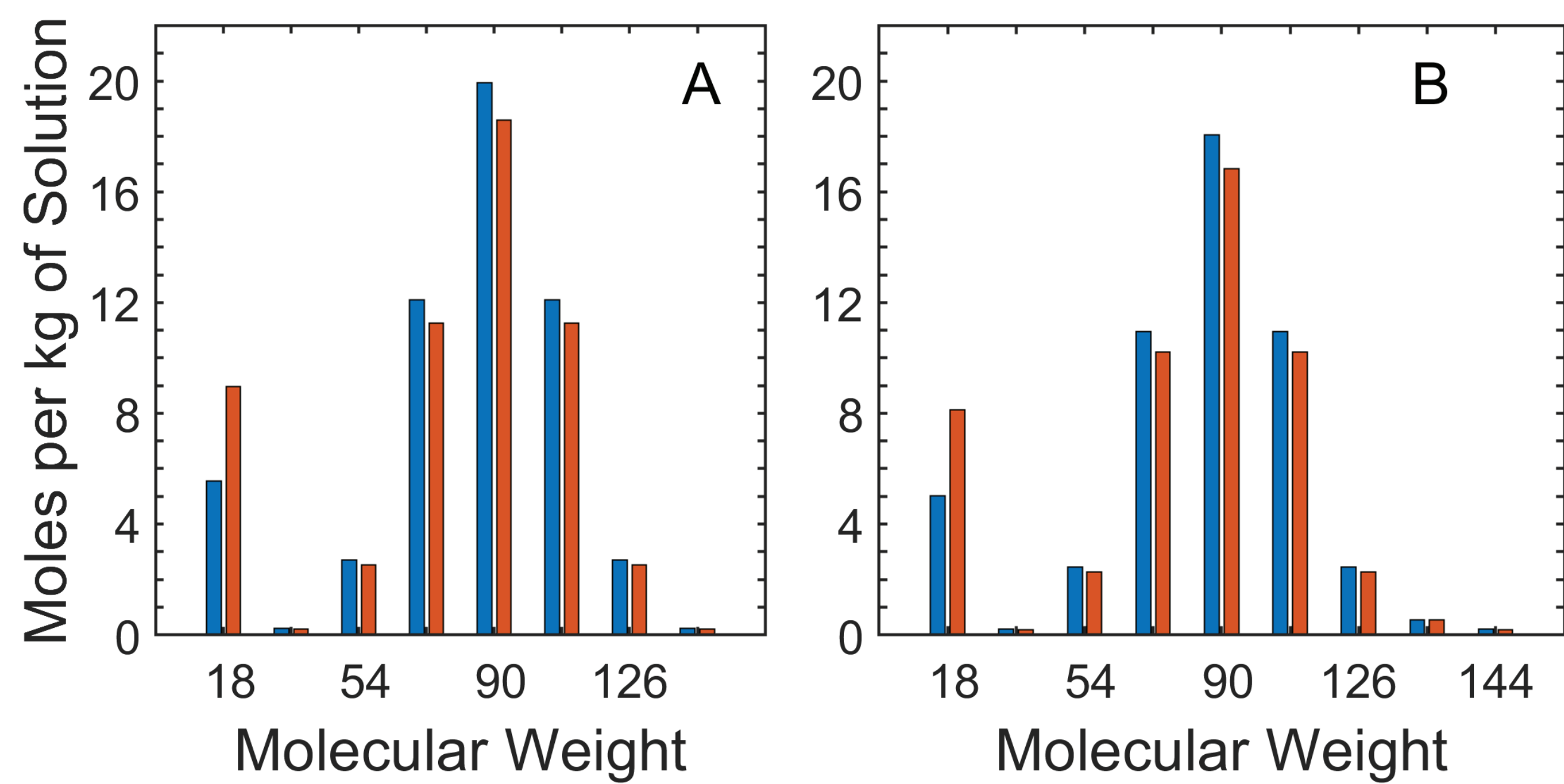
### Gaussian fitting



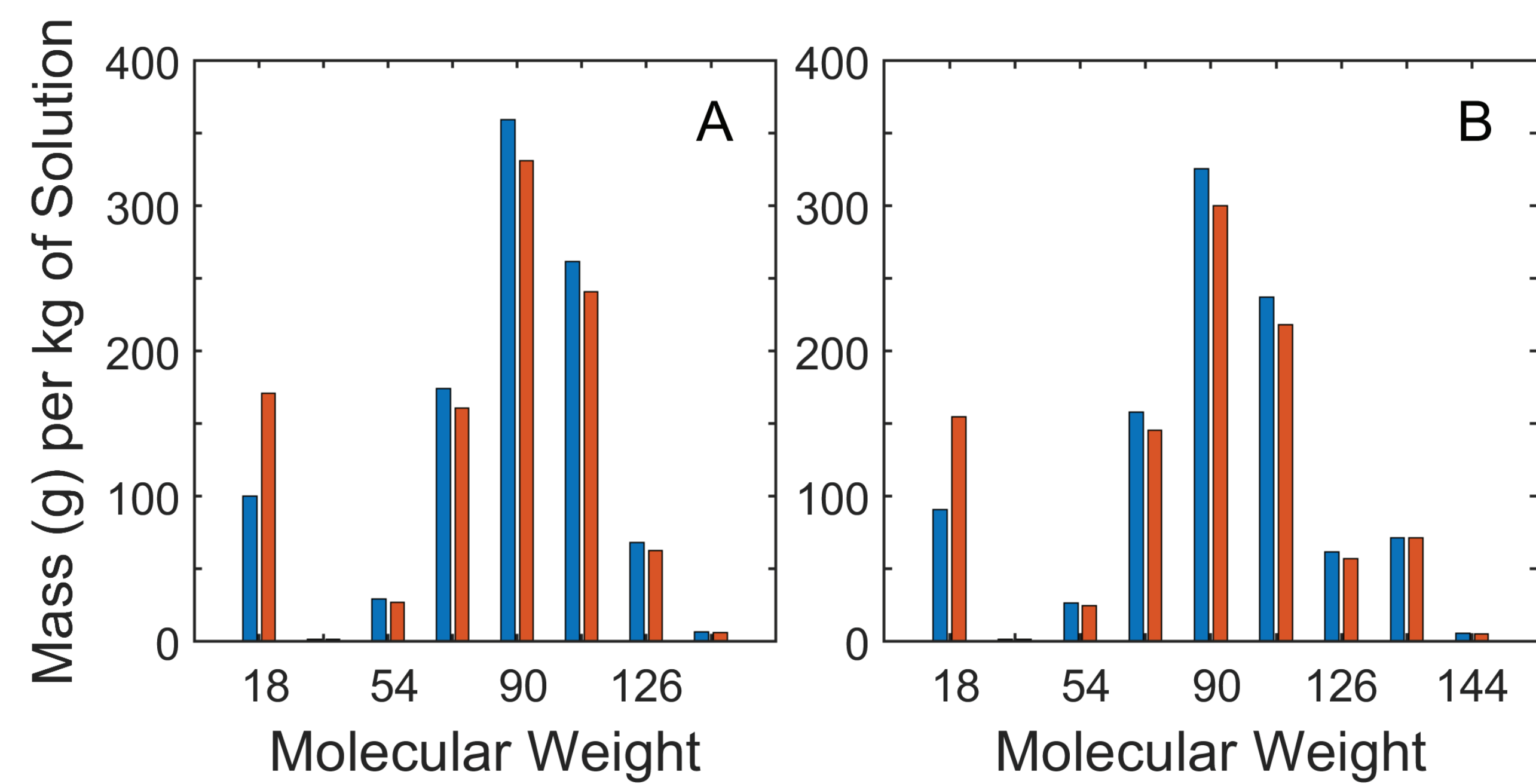
**Figure 2.** Comparisons of the spectra of pure water (A) and sea water (B) both at 20°C. The spectra are deconvoluted into their 5 Gaussian components (Walrafen et al., 1986; Carey & Korenowski, 1988; Furic et al., 2000). In the sea water sample peaks 3 and 4 associated with the single water molecule modes are reversed in peak area and height compared to the pure water spectra. In the right-hand panels (C & D) we show the temperature dependence of the areas of these same peaks. The red and blue lines that have a positive trend with T are for the nHB form of water. In pure water Peak 3 (red line; asymmetrical stretching) is dominant; in sea water peak 4 (blue line; symmetrical stretching) is dominant. These results clearly show the effect of ions in capturing water from the bulk fluid to populate the solvation shell.

## Calculations

### Molecular weight of pure water & sea water



**Figure 3.** Schematic of one possible distribution (moles/kg of solution) of water species (clusters) in pure water (A) or seawater (B) with a salinity ( $S_p$ ) of 35 at temperatures of 0°C (blue bars) and 40°C (red bars). We assumed that the pentamer forms are dominant and the other HB forms have a Gaussian distribution around the pentamer. In (B) the additional pair of bars between molecular weights 126 & 144 are the cations with water solvation spheres and an ensemble molecular weight of 131.8489. The solvated cation concentrations do not vary with temperature.



**Figure 4.** (A) Schematic of the same distribution of water species (clusters) as in Figure 3 converted to mass/kg of solution in pure water (A) or seawater (B) with a salinity ( $S_p$ ) of 35 at temperatures of 0°C (blue bars) and 40°C (red bars). As in Figure 3, the additional pair of bars in (B) between molecular weights 126 & 144 are the mass of the cations with water solvation spheres and an ensemble molecular weight of 131.8489. Again, the solvated cation concentrations do not vary with temperature.

		0	10	20	30	40
	nHB/nHB	0.1111	0.1318	0.1545	0.1793	0.2060
	%-nHB	10.000	11.645	13.384	15.202	17.083
	%-HB	90.000	88.355	86.616	84.798	82.917

Calculation of pure water molecular weight				Mass Water / kg pw = 1000.00g			
N-mer	Wt (%)	Mol Wt		Mass water × (%-nHB or %-HB) × wt % × mol wt			
1	100.0	18.0153	1801.51	2097.84	2411.16	2738.70	3077.59
2	0.1773	36.0306	57.50	56.45	55.34	54.18	52.98
3	3.2403	54.0459	1576.14	1547.34	1516.88	1485.04	1452.10
4	19.3629	72.0612	12557.84	12328.33	12085.65	11831.97	11569.50
5	39.9050	90.0765	32350.59	31759.33	31134.18	30480.67	29804.50
6	29.0443	108.0918	28255.14	27738.73	27192.72	26621.94	26031.37
7	7.5608	126.1071	8581.22	8424.39	8258.56	8085.21	7905.86
8	0.7093	144.1224	920.02	903.20	885.43	866.84	847.61
Ensemble PW molecular wt:				86.1	84.9	83.5	82.2

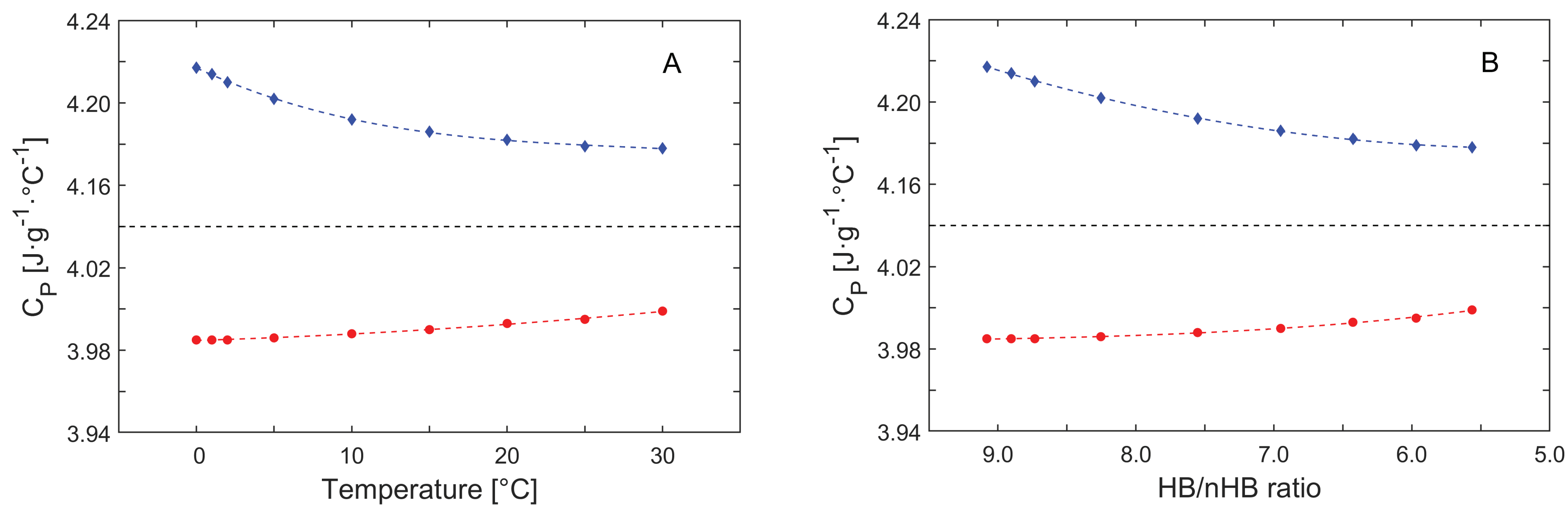
Calculation of sea water molecular weight				Mass Water / kg sw = 906.236g			
N-mer	Wt (%)	Mol Wt		Mass water × (%-nHB or %-HB) × wt % × mol wt			
1	100.0	18.0153	1632.59	1901.14	2185.08	2481.91	2789.02
2	0.1773	36.0306	52.11	51.16	50.15	49.10	48.01
3	3.2403	54.0459	1428.36	1402.25	1374.65	1345.80	1315.94
4	19.3629	72.0612	11380.37	11172.37	10952.45	10722.56	10484.70
5	39.9050	90.0765	29317.27	28781.45	28214.91	27622.68	27009.91
6	29.0443	108.0918	25605.82	25137.84	24643.02	24125.76	23590.57
7	7.5608	126.1071	7776.61	7634.49	7484.21	7327.11	7164.57
8	0.7093	144.1224	833.75	818.52	802.40	785.56	768.14
Solv $H_2O$ + cations:				131.8489	9422.19	9422.19	9422.19
Ensemble SW molecular wt:				89.4	88.3	87.1	85.8

**Table 1.** Calculation of the ensemble molecular weight for pure water and seawater ( $S_p = 35$ ) as a function of temperature. N-mer weight-% is 100% for n=1 and a Gaussian distribution for n=2-8 (where a=0.443012, b=90.0765 and c=18.0153) times the n-mer molecular weight. The ensemble molecular weight is calculated as the sum of n-mer mass × molecular weight products divided by the sum of the n-mer masses (plus the cations in the case of seawater).

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## Specific Heats



**Figure 5.** Specific Heats ( $C_p$ , Cox and Smith, 1959) for pure water (blue diamonds) and seawater ( $S_p = 35$ , red dots) as a function of temperature (A) and the molar ratio of HB to nHB water molecules (B). Pure water has a higher  $C_p$  which decreases as temperature rises while seawater has a smaller  $C_p$  that increases with increasing temperature and decreasing salinity.

The specific heat of the hydrated salts can now be calculated by difference:

$$C_p[\text{hyd-salts}] = (1000 * C_p[\text{sw}] - 906.236 * C_p[\text{pw}]) / (35.179 + 0.54198 * 6 * 18.0153)$$

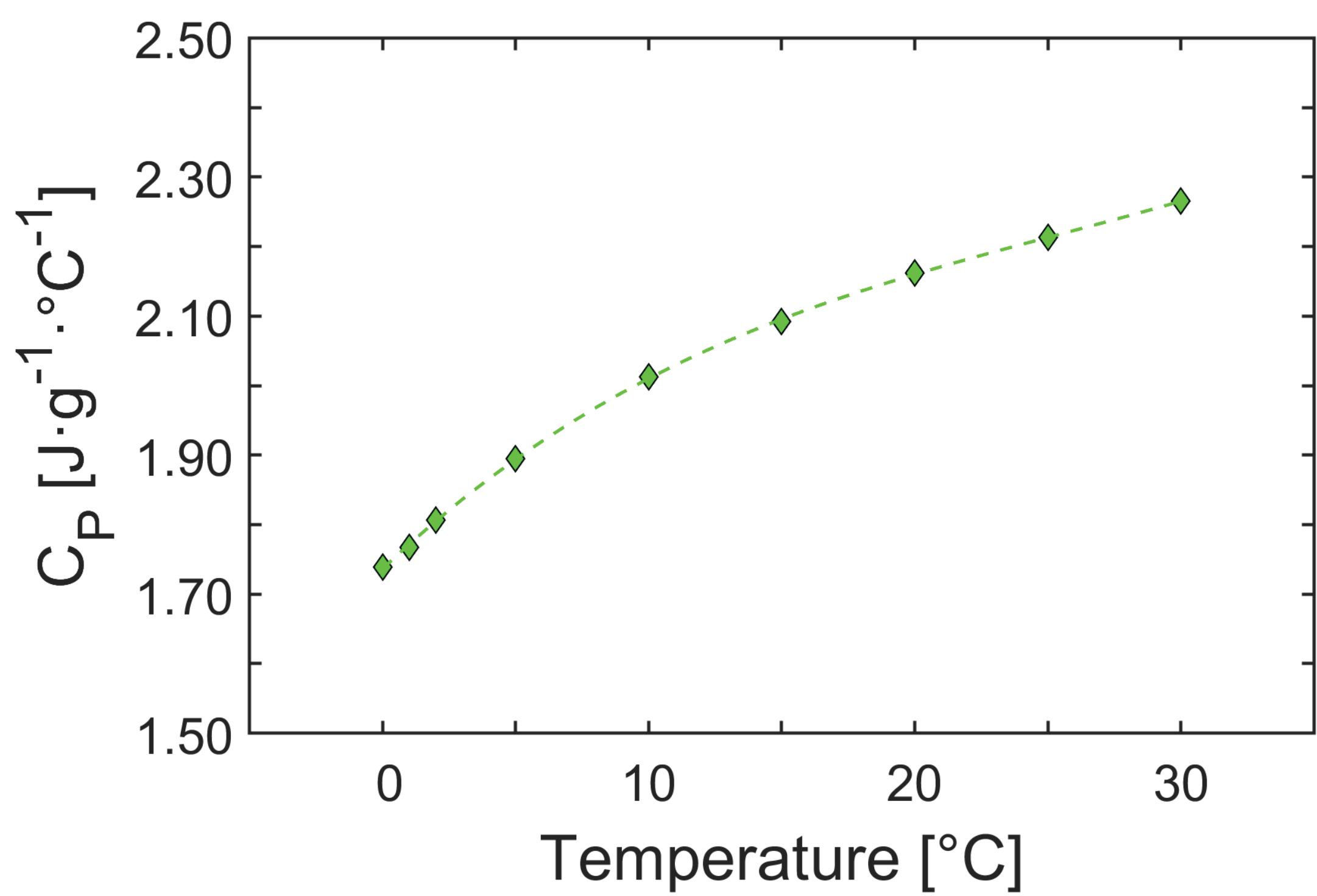


Figure 6. Specific heat of the salts (plus solvation water) dissolved in 1 kg of seawater calculated by the difference between the  $C_p$  of pure water and sea-water.

## Summary & Conclusions

- Hydrogen bonding of water molecules plays several important roles contributing to the large specific heat of water:
  - Hydrogen bonds make the formation of water molecule clusters possible causing the effective molecular weight of water to be almost five-fold larger than the singlet form and substantially increasing the specific heat of water in this process.
  - The breaking of hydrogen bonds during warming consumes a substantial amount of heat energy:
    - It takes 42.042 kJ to heat 1kg water from 0°C to 10°C.
    - Warming of water by 10°C increases the amount of single  $H_2O$  molecules by 1.64%, or 0.913 moles.
    - The strength of the hydrogen bond is close to 8.364 kJ  $mol^{-1}$ , and two hydrogen bonds must be broken to free one  $H_2O$  molecule, so liberating 0.913 moles of  $H_2O$  takes 15.27 kJ.
    - Thus, 36% of the heat required to raise the temperature of water by 10°C is accounted for by the work done to break hydrogen bonds.
    - And, 64% of the heat required to raise the temperature of water by 10°C is accounted for by the increase in kinetic energy of molecules with an ensemble molecular weight of 86.1-84.9 (for pure water) or 89.4-88.3 (for sea water).
- In the case of seawater, the recruitment of single water molecules from the ensemble population into the hydration sphere around a cation reduces the population of the large molecular weight HB forms more than the nHB form:
  - This results in the lower specific heat of seawater compared to pure water within the oceanic temperature range.
  - The retention of water molecules in the hydration shell around cations makes it increasingly difficult for the cations to achieve the mean kinetic energy defined by rising temperature thereby increasing the specific heat of sea water as temperature increases.
- Identical processes account for the expansion of water on warming: the loss of the compact Walrafen pentamers, and the rise of the singlet  $H_2O$  form.

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