

LETTERS TO PROGRESS IN PHYSICS**Water, Hydrogen Bonding, and the Microwave Background**

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In this work, the properties of the water are briefly revisited. Though liquid water has a fleeting structure, it displays an astonishingly stable network of hydrogen bonds. Thus, even as a liquid, water possesses a local lattice with short range order. The presence of hydroxyl (O–H) and hydrogen (H···OH₂) bonds within water, indicate that it can simultaneously maintain two separate energy systems. These can be viewed as two very different temperatures. The analysis presented uses results from vibrational spectroscopy, extracting the force constant for the hydrogen bonded dimer. By idealizing this species as a simple diatomic structure, it is shown that hydrogen bonds within water should be able to produce thermal spectra in the far infrared and microwave regions of the electromagnetic spectrum. This simple analysis reveals that the oceans have a physical mechanism at their disposal, which is capable of generating the microwave background.

While water is the best studied molecule on Earth [1], it remains one of the most mysterious. The unusual properties of this solvent are generated by its hydrogen bonding network [1–4]. In the condensed state, these relatively weak bonds (H···OH₂) interlink water into a local intermolecular lattice. Conversely, the robust intramolecular hydroxyl bond (O–H) permits water to be treated as a rigid unit. Water, in the solid state, can take up to one dozen possible crystal structures. Through hydrogen bonding, each molecule is incorporated into a structure wherein the oxygen atoms assume tetrahedral coordination as illustrated in Figure 1 [1]. As for the O–H···O bond angle, it deviates only slightly from linearity in ordinary ice, or ice Ih [1; p. 200].

Yet, it is the nature of liquid water which has largely captivated the interest of physical chemists. It has been said that: “the H-bond network of liquid water is, in the average, the same as that of ice” [1; p. 223]. In liquid water, the average tetrahedral geometry of the oxygen is maintained, but at the expense of tremendous dynamic bending of the hydrogen bonds [1; p. 223]. Nonetheless, to a first approximation, and for the purposes of the discussion which is to follow, the average O–H···O bond angle will not be considered to deviate substantially from linear. The energetic dynamic bending of hydrogen bonds will be neglected.

Liquid water has been tenacious in withholding its secrets. Still, scientists have not relented in the study of this universal solvent. Some of our knowledge has come from the study of the simple water dimer [5–9], the gaseous adduct of two molecules linked by a single hydrogen bond (see Figure 2). The structure of the dimer was first elucidated in 1977 by Dyke, Mack, and Muentner [7]. In its most stable form, the water dimer displays a *trans-linear* arrangement [7], where the O–H···O linkage deviates only slightly from a linear

configuration. The stability of the *trans-linear* form has been confirmed repeatedly for this adduct, using both experimental and *ab initio* evaluations [5–9]. The energy of its hydrogen bond is ~5 kcal/mol (~21 kJ/mol; [6]).

Since the water molecules making up the dimer are somewhat rigid due to their strong hydroxyl bonds (~119 kcal/mol or ~497 kJ/mol [10; p. 9–74]), it is possible to treat this adduct as a monomer-monomer system. It is true that the dimer can undergo significant tunneling and rearrangements [5–9], but the resultant conformations do not produce the lowest energy species. As such, one can solely consider the *trans-linear* form [7] and treat each water molecule as a single, rigid unit. Under this scenario, the water dimer can be modeled as a harmonic oscillator [11–12] about the hydrogen bond. Dyke, Mack, and Muentner [7] have determined that the fundamental stretching frequency of the dimer corresponds to ~143 cm⁻¹ [7]. This frequency lies in the far infrared. It might be recalled, for instance, that NASA’s COBE FIRAS (Far Infrared Absolute Spectrophotometer) instrument scanned the sky in a frequency range from 2 to 95 cm⁻¹ [13].

Given a fundamental frequency at 143 cm⁻¹, it is possible to infer the force constant for the hydrogen bond in the water dimer [11–12]. The reduced mass, μ_r , of the dimer is equal to 1.495×10^{-23} g/molecule: $\mu_r = \frac{18 \times 18}{36 \times (6.02 \times 10^{23})}$. The fundamental frequency of oscillation is related to the force constant, k , and reduced mass, μ_r , as follows:

$$\omega [\text{cm}^{-1}] = \frac{1}{2\pi c} \left(\frac{k}{\mu_r} \right)^{1/2},$$

therefore, the force constant for the dimer corresponds to a very small 0.108×10^5 dyn/cm. The force constant for the hydroxyl (O–H) bond within each molecule can be obtained from the literature [10]. It corresponds to 8.45 N/cm, which

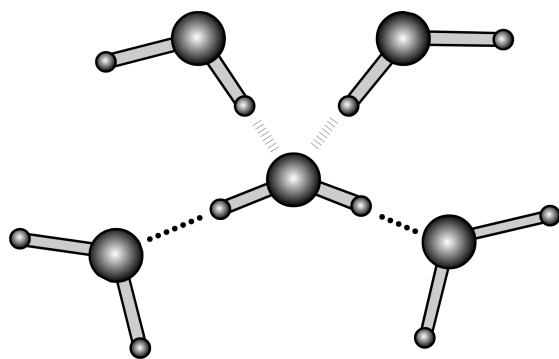


Fig. 1: Schematic representation of the water lattice. Each water molecule acts to accept and donate a total of four hydrogen bonds. Note the essentially linear O–H···O subunit.

is equivalent to 8.45×10^5 dyn/cm [10; p. 9–99].

In the ideal case, it should be possible to calculate the energy of each of these systems by considering the expression $E = \frac{1}{2} k x^2$, where k is the force constant and x is the infinitesimal displacement of the fundamental oscillation. The latter will be treated as an undetermined variable for each of these two subsystems.

Within the local water lattice, one can observe that the fundamental subunit of the dimer is also present (see Figure 1). That is, the linear O–H···O structure found within the *trans-linear* water dimer is constantly repeated. Indeed, if this were not the case, there would be little interest in studying the water dimer [5–9]. In this configuration, two bonds link every hydrogen atom to the adjacent oxygens (O–H···O): the hydrogen bond with a force constant of $\sim 0.108 \times 10^5$ dyn/cm and the hydroxyl linkage with a force constant of $\sim 8.45 \times 10^5$ dyn/cm. Since the grouping is a linear one, the displacement of the hydrogen atom must occur in the line linking the two oxygen atoms. If one isolates the hydrogen bonding system from this short range lattice, its energy will be roughly equal to $E_1 = \frac{1}{2} k_1 (x_1)^2$. Similarly, the energy for the hydroxyl system will be given by $E_2 = \frac{1}{2} k_2 (x_2)^2$. Thus, as there is a single hydrogen atom involved in the oscillation, it is immediately clear that $|x_1| = |x_2|$ and to a first approximation, $E_2/E_1 = k_2/k_1$.

Water should then be capable of sustaining thermal emissions over two very distinct regions of the electromagnetic spectrum. The first of these regions occurs in the infrared and is generated by the hydroxyl bond. A second thermal emission region exists in the far infrared or microwave region. These emissions are produced by the hydrogen bond. They represent energies which are a factor of about 80 times ($k_2/k_1 = 78$) lower than the frequencies observed for the hydroxyl bonds. Although knowledge of emission frequencies cannot be easily correlated with temperatures, this result implies that the thermal photons produced by the hydrogen bonding network might be detectable at apparent temperatures which are 80 fold below the real temperatures of the water system.

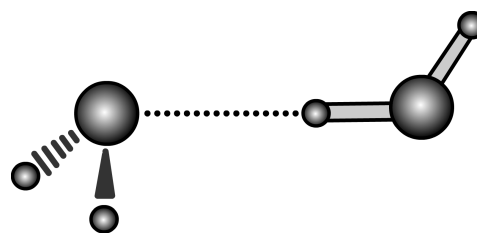


Fig. 2: Schematic representation of the *trans-linear* water dimer. Note the essentially linear O–H···O unit.

The thermodynamics of hydrogen bond rearrangements in the liquid phase have recently been examined [14]. This work gives a value of 1.5 ± 0.5 kcal/mol (~ 6.3 kJ/mol) for the rearrangement energy. As these energies are directly associated with the formation and breaking of hydrogen bonds, it implies that the true energy of these bonds is closer to 1.5 ± 0.5 kcal/mol in the liquid state, not the 5 kcal/mol obtained from dimer studies [6]. Therefore, the appropriate force constant for the hydrogen bond in liquid water could be nearly 3 fold lower, yielding a ratio of force constants (k_2/k_1) in a range of 80–240. Consequently, the hydrogen bonding system in water could produce a thermal spectrum reporting a temperature which is 80–240 fold lower than the true temperature of the water system.

An analysis of the hydrogen bonding system within water helps to explain how the oceans of the Earth could produce a thermal spectrum with an apparent temperature much lower than their physical temperature [15, 16]. This occurs despite the fact that sea water contains cations and anions [17, 18]. Note that the molar concentration and the physical influence of the salts in sea water (mostly NaCl at ~ 0.12 M) does not interfere significantly with the H-bonding network of ~ 110 M hydrogen atoms [17, 18]. For instance, studies of the effects of cations and anions on the water system, tend to utilize ion concentrations which are more than 10 times those found in sea water [17, 18]. It is interesting however, that while the lifetimes of the first excited state for the hydroxyl (O–H···) stretch in liquid water is on the order of ~ 1 psec, this value increases to ~ 2.6 psec in the vicinity of chloride ions [19, 20]. Nonetheless, it is unlikely that the presence of ions in the oceans will dramatically alter the conclusions reached herein, even though the presence of ions can produce small changes in the first solvation shell [17, 18].

Maréchal [1; p. 220] illustrates how liquid water displays strong hydroxyl absorption bands at 1644 cm^{-1} (H–O–H bending) and 3400 cm^{-1} (hydrogen bonded O–H stretch). Importantly, the spectra also revealed broad and powerful libration bands (hindered rotations about the hydrogen bond; O···H) at $\sim 700 \text{ cm}^{-1}$ and hydrogen bond stretches (O···H) centered at $\sim 200 \text{ cm}^{-1}$ which extend to lower frequencies. Since water is a good absorber in the far infrared, these studies were executed on samples which were only $1\text{-}\mu\text{m}$ thick. Consequently, it would not be unexpected that the supporting matrix and a small sample thickness could alter both the

position and amplitude of the hydrogen bonding stretching and libration bands. The findings reported by Maréchal [1; p. 220] are interesting, but inconclusive as related to the hydrogen bond itself.

Reflecting on the paucity of supportive data, in this very difficult experimental region of the far infrared, it seems that much more needs to be learned about the emissions due to hydrogen bonds in nature. In particular, the lack of a signal specifically assigned to hydrogen bonds from water on Earth gives cause for concern. This is because the microwave background [21] was assigned to the universe [22] when virtually nothing was known about the spectroscopic signature of the hydrogen bond.

Consideration of these findings reveals why the author has advanced [15, 16] that the microwave background [21] does not correspond to an astrophysical signal [22], but instead is generated by the oceans [15, 16, 23]. Water has the means to generate thermal emissions in the far infrared and microwave regions. The fundamental oscillator involved is best represented by the dimer subunit and its associated hydrogen bond within liquid water itself. In the gas phase, the dimer is known to have a fundamental frequency in the far infrared [7], very close to the region sampled by the COBE FIRAS instrument [13]. It is quite reasonable to expect that the emissions from the oceans occur in the same region.

In summary, the microwave background can be understood as follows: photons are being produced by the oceans and they are then scattered in the atmosphere such that a completely isotropic signal is observed [15]. The isotropy of the microwave background was first reported by Penzias and Wilson [21]. The signal is independent of temperature variations on the globe, since the hydrogen bonding energy system is already fully occupied at earthly temperatures. This explains why the microwave background is independent of seasonal changes [21]. Satellite data obtained by COBE strengthen the idea that the Earth does produce the microwave background [24, 25]. This hypothesis has not been refuted either by the three year [26] or five year WMAP findings.

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Dedication

This work is dedicated to my wife, Patricia.

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