

The Origin of Water's Dielectric Excess Wing

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Abstract—It is demonstrated that the thermal origin of the excess wing in the THz portion of the dielectric spectrum of water is the same as that of the main dielectric peak. The implication is that models positing the free rotation of water molecules to account for the Excess wing are not correct. A self-terminating Proton cascade is one possible explanation.

I. INTRODUCTION

THE dielectric relaxation of pure water has fascinated the scientific community since it was first measured. The main dielectric relaxation loss peak for water can be found at 18 GHz at room temperature and it can be modelled adequately for the most part by a Debye function [1, 2].

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1+i\omega\tau} \quad (1)$$

Where $\Delta\varepsilon$ is the dielectric strength, τ is the characteristic relaxation time and ε_∞ is the contribution to the permittivity arising from high frequency processes. As with many of water's properties it is a mystery, as the microscopic details of the molecular dipole moment cannot predict the macroscopic properties of bulk water's dielectric relaxation, especially when the H-bonded nature of water is considered. Moreover, this picture is further disturbed above 100 GHz with the appearance of an excess wing, whereby the dielectric losses are notably higher than that predicted by the Debye model. Traditionally this is accounted for by the assumption of one or two more dielectric processes in the THz region of the spectrum. Molecular Dynamic simulation then suggests that these are the result of relaxations by single unattached water molecules [3, 4].

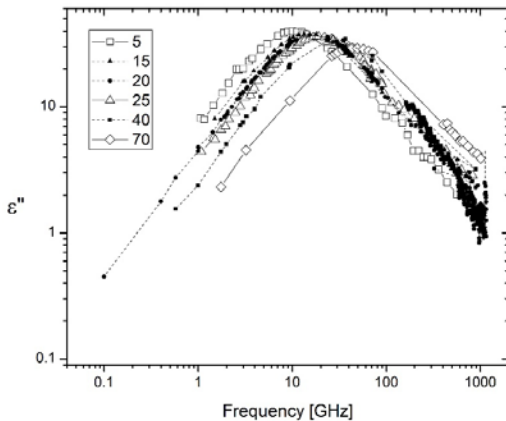


Fig. 1 – The measured dielectric spectra of pure water as a function of frequency (100 MHz to 1 THz) in the temperature range 5 °C to 70 °C. As the temperature is varied the spectra shift towards the higher frequencies in line with the Arrhenius law, $\tau = \tau_0 \exp(E/kT)$, where τ is the relaxation time defined in equation 1 and E is the energy of activation.

To confirm this we made temperature based measurements of pure water using an open ended coaxial probe and an Agilent N5245A PNA-X vector network analyzer from 1 MHz to 50 GHz. These were augmented by measurements using a custom

Time domain THz spectrometer, providing spectra up to 2 THz. The results are shown in Fig. 1.

II. RESULTS

By normalizing the spectra presented in Figure 1 by the peak frequency and the peak amplitude for each temperature, a Master plot was created. Surprisingly all temperature curves collapse to a unified figure in this representation (see Fig.2). The implication of such a unification is that the thermal character of the excess is the same as that of the main dielectric loss peak. As the energy of activation of the main peak is 23 kJ/mol – the breaking of an H-bond – the origin of the excess

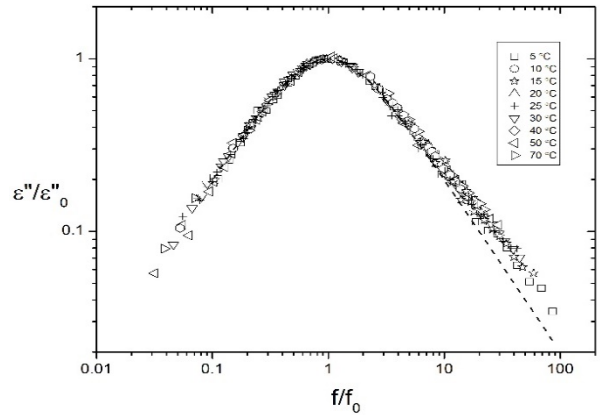


Fig. 2. The Master plot for pure water. All normalized temperature slices collapse to the same curve. The implication is that the thermal origin of the excess wing is the same as that of the main dielectric peak and involves the break of H-bonds. This rules out the orientation of unbound water molecules as the source of the excess wing.

wing must perforce also involve the breaking of an H-bond. The paper posits that a previously neglected mechanism is responsible for both the main dielectric peak and the excess wing – A self-terminating proton cascade inside the water cluster.

III. DISCUSSION

The implication for a collapse of all temperature slices to a single curve in the master plot representation is that the main peak and the excess wing of the dielectric spectrum share the same thermal origin and the same energy of activation. This stands in contrast to the various models, based on the multiple Debye fits [3, 4] and molecular dynamic simulation [5]. Obviously, the excess wing relates to mobilities faster than characteristic time for the reorganization of the main water cluster (8.28 ps at 25 °C). Consequently, as the frequency is increased, these elements of the relaxation mechanism dominate. Phenomenologically, this can be described by a modification to the dielectric strength at frequencies higher than the main peak frequency. We posit the following, modified Debye formula [6],

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon \cdot (1 + f(\omega))}{1 + i\omega\tau}$$

$$\text{where } f(\omega) = \begin{cases} 0 & \omega < \omega_c \\ A(\omega\tau)^q & \omega \geq \omega_c \end{cases}, \quad (5)$$

to account for the existence of an excess wing, thermodynamically identified with the main dielectric relaxation peak. Here, $\omega_c > 1/\tau$ is a cut-off frequency, from which the existence of the wing is noticeable.

From the temperature fittings one derives $A = (6.9 \pm 0.2) \times 10^{-3}$ and $q = 1.27 \pm 0.06$, where the standard deviation of the dataset is used as the error estimate. The parameters A and q can further be associated to a new microscopic time scale,

$$A^{1/q} = \frac{\tau_0}{\tau} \quad (6)$$

whereby τ_0 is representative of the underlying fast mobilities, responsible for the excess wing. At room temperature one finds that τ_0 is estimated to be about 0.17 ps, a typical lifetime for proton mobility. One could be tempted to consider excess protons as the source of the excess wing. However, their concentration is too low to be relevant at these frequencies. While excess protons in pure water from auto-disassociation are necessarily in very low concentrations, the disassociation process conceals many rearrangements between different types of protonated water that do not result in a free proton. These rearrangements would lead to a rapid reorganisation of the H-bonded network and the consequent apparent dipole moment of the cluster. This view can be supported by the Molecular Dynamic Simulation (MD) studies by Geissler and Chandler [7] of auto-ionization in water. Their studies produced a number of significant conclusions: 1) that auto-ionization would be the result of a cooperative fluctuation of water molecules, in short a cluster, 2) that the initial transitional state - the separation of the water molecule to H^+ and OH^- ions - would usually terminate to another neutral water molecule within 10 Å and, 3) that the time required for the formation of the intermediate state is 0.15 ps. This time scale coincides with τ_0 as defined above. As their model is essentially a Grotthuss mechanism, the dominant energy of activation is the cleavage of an H-bond, related to the motion of the proton through the H-bonded network of water molecules, rather than the dissolving of the O-H bond. They further concluded that there should be an observable signature of this process. A more recent evaluation of this model by Hassanali et al. [8] reveals that the neutralization event – the fast recombination of the Proton and the Hydroxyl ion – does indeed dominate. Using their published distribution of recombination times, one can estimate that recombination events outweigh auto-ionization events by a factor of at least 1000. The initiator of these events is a local density fluctuation. As each recombination leads to a reorganization of its local environment.

The final model is illustrated in Fig.3. A local density fluctuation leads to a local disassociation event that precipitates a cascade of disassociation/recombination events before eventually recombining to leave the cluster neutral, but rearranged. Consequently the apparent dipole moment of the cluster is changed.

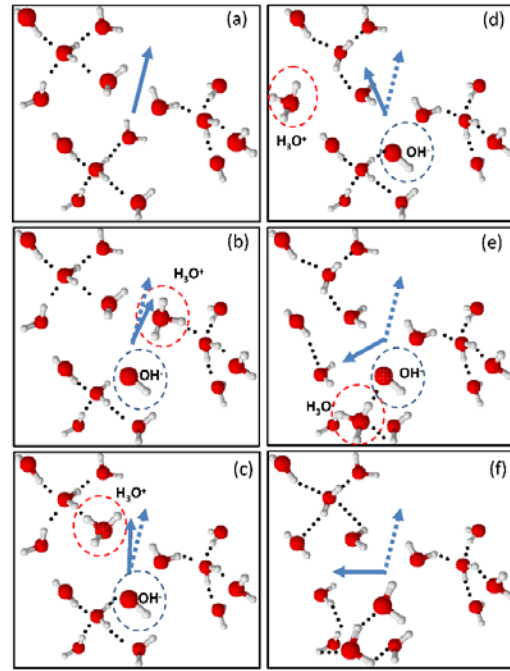


Fig. 3 - A schematic illustrating the concept of a proton cascade. The blue arrow in frame (a) represents the apparent dipole moment of the cluster. The dotted lines trace out the H-bond between nearest neighbors. The cascade is initiated by density fluctuations leading to a condition such that local molecular fields are high enough to permit a proton transfer in frame (b), resulting in the formation of a hydronium ion (circled red) and a hydroxyl ion (circled blue). The time scale between frames is in the region of 0.17 ps. The proton migrates through the cluster by the formation of metastable Hydronium (frames (c) to (e)). The last frame (f) represents the closing of the loop as the excess H_3O^+ is neutralized by the uncompensated OH^- . The resulting reorganization of the cluster leads to a change in the apparent dipole moment, represented by the solid blue arrow in frame (f), compared to the dotted blue arrow representing the original dipole moment vector.

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