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The Close Correlation of MRET Treated Bulk Water and Nanoconfined Water Ionic Activity (Review)

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Abstract: MRET (Molecular Resonance Effect Technology) activated water exhibits a direct physical and functional correlation with nanoconfined water, sharing key anomalous properties such as reduced viscosity, lower dielectric permittivity, decreased electrical conductivity, and altered diffusion coefficients. [4] Electrochemical impedance spectroscopy (EIS) data on MRET-activated water demonstrate a larger dynamic range of ionic activity both before and after transition points compared to untreated control bulk water samples. Experimental and theoretical evaluations classify MRET-treated water as a functional equivalent or special case of nanoconfined water.

INTRODUCTION

Water is essential for almost every aspect of life on our planet and, unsurprisingly, its properties have been studied in great detail. However, disproportionately little remains known about the electrical properties of interfacial and strongly confined water, in which the structure deviates from that of bulk water, becoming distinctly layered. The structural change is expected to affect the conductivity of water and particularly its polarizability, which in turn modifies inter-molecular forces that play a crucial role in many physical and chemical processes [1].

Bulk water can exhibit properties typically associated with nanoconfinement when subjected to extreme thermodynamic conditions or specific molecular environments that disrupt its normal 3D hydrogen-bonding network.

Specific molecular environments with disrupt water normal hydrogen-bonding network:

molecular relaxation times in bulk water increase dramatically, mirroring the restricted mobility (immobilization) seen in water molecules trapped in sub-nanometer slits.

The correlation between NMR proton peak widening (increased FWHM), increased proton dispersion (chemical shift anisotropy/range), and reduced electrical conductivity in nanoconfined water is primarily driven by the disruption of the tetrahedral hydrogen-bond (H-bond) network and increased dipolar interactions. When water is confined to <2 nm, its properties change from bulk-like to highly ordered or restricted, often leading to slower proton transfer, although extreme, quasi-2D confinement can paradoxically lead to high proton conductivity. An increase in the width of the proton peak (full width at half maximum, FWHM) and increased proton dispersion (broadening/splitting) in ^{1}H NMR spectra of nanoconfined water indicate a transition from bulk-like liquid behavior to a highly ordered or restricted interfacial state. This spectral behavior strongly correlates with a reduction in the overall self-diffusion coefficient (*D*) of water, a decrease in the rate of proton hopping (Grotthuss mechanism), and modified ionic activity.

Under nanoconfinement, water molecules near surfaces lose their rotational mobility, leading to longer correlation times, decreased proton exchange rates, and increased intermolecular dipolar coupling. This restriction appears as significant broadening in the ^{1}H NMR spectrum. The confined water experiences a variety of different local environments (surface-bonded vs. free-like water), which causes a wide dispersion of chemical shifts rather than a single sharp peak. The disruption of the H-bond network (the "water wire" required for proton tunneling) causes a slowing of aqueous proton transfer rates, sometimes by several orders of magnitude compared to bulk water. The inability of protons to move cooperatively through the disrupted, rigidified H-bond network reduces the overall DC ionic conductivity.

Key Findings on Confined Water Dynamics:

- Slow Proton Transfer: Nanoconfinement, particularly in cationic reverse micelles, leads to a significant slowing of proton transfer rates.
- H-bond Disruption: Nanoconfinement increases the energy barrier to hydrogen exchange.
- Phase Transition: Confined water often shows continuous liquid-to-solid transitions, resulting in broadening (solid-like NMR signals).
- Exceptions in Conductivity: While generally, increased constraint reduces conductivity, very specific 2D geometries (<1.5 nm) can paradoxically enhance proton conductivity, reaching superionic values due to strongly disordered hydrogen bonding that facilitates fast proton exchange, a trend which only decreases at the absolute lowest confinement levels.

In bulk solutions, rapid Brownian molecular diffusion modulates dipolar interactions between a spin pair from different molecules, resulting in very weak intermolecular relaxations. We show that in fluids confined in nanospace or nanopores (nanoconfined fluids) the correlation of dipolar coupling between spin pairs of different molecules is greatly enhanced by the nanopore constraint boundaries on the molecular diffusion, giving rise to an enhanced correlation for the spin pair. As a result, the intermolecular dipolar interaction behaves cooperatively, which leads to a large intermolecular dipolar relaxation rate and opposite in sign to the bulk solution. We found that the classical NMR relaxation theory fails to capture these observations in a nanoconfined fluid environment. Hence, we developed a formal theory and experimentally confirmed that enhanced correlation and cooperated relaxation are ubiquitous in nanoconfined fluids [2].

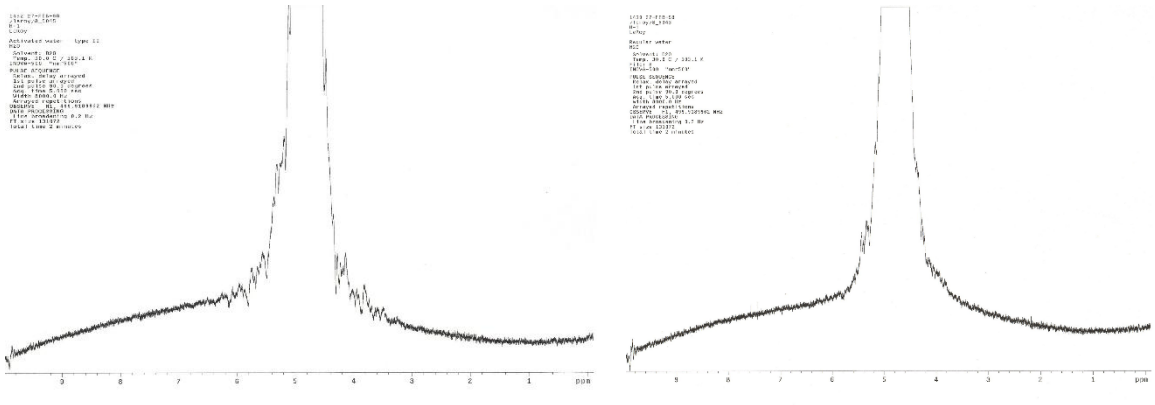
Comparable NMR testing of nanoconfined and bulk water reveals significant differences in proton peak diagrams, primarily driven by restricted molecular motion, hydrogen bond disruption, and surface interactions. The proton NMR spectrum of nanoconfined water typically exhibits broader peaks, shifted chemical shifts (usually downfield), and distinct low-temperature behavior (e.g., lower freezing points) compared to the sharp peak of bulk water at 4.7 ppm.

DISCUSSION

Nuclear Magnetic Resonance tests were conducted at the laboratory of Department of Chemistry of San Diego State University by Dr. Leroy Lafferty. The experimental data were

recorded on INOVA-500 spectrometer. Each sample of MRET activated and regular water was inserted into 10-ml NMR test tube, and a 5-ml NMR tube filled with D_2O was then inserted into the 10-ml test tube to provide a lock signal for the NMR. A 90° second pulse was used for the experiment. Acquisition time was set to 5.000 sec with one second delay, and a spectral width of 8000.0 Hz was employed. Line broadening was utilized and set to 0.2 Hz. Fourier transformation was performed on each spec following the scanning. Signal peak was observed for all samples, indicating that both MRET Activated and regular water samples are free of detectable organics.

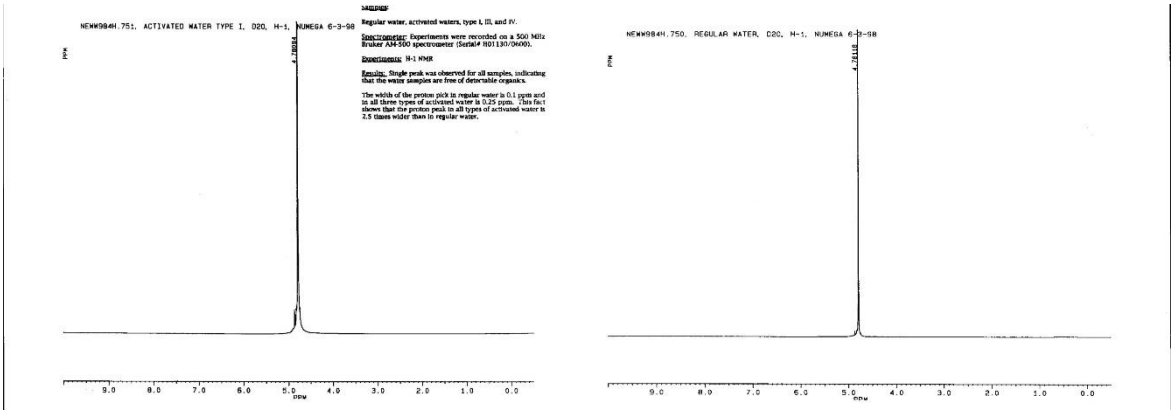
The experimental data revealed a consistent **2.1** times increase in the width of proton peak in the line of ^1H NMR absorption for the samples of MRET activated water in comparison with a sample of regular water from the same source Fig.1.



(a) **(b)**

Fig. 1: Proton peak in the line of NMR absorption for sample of MRET treated water (a) and regular water (b). Test conducted at the lab of San Diego State University by Dr. Leroy, USA.

To confirm the repeatability of the experimental results another NMR testing was conducted at independent NuMega Resonanace Laboratory, San Diego, USA. The experiments were recorded on a 500 MHz Bruker AM500 spectrometer. Experiments: H-1 NMR. Single peak was observed for all samples of regular and MRET activated water, indicating that all water samples are free of detectable organics. The width of the proton peak in regular water is 0.1 ppm and in all three samples of MRET treated water is 0.25 ppm. (Fig.2)



(a) **(b)**

Fig.2: Proton peak in the line of NMR absorption for sample of MRET treated water (c) and regular water (d). Test conducted at NuMega Resonance Laboratory by Dr. Chiang, San Diego, USA.

When comparing two proton NMR (^{1}H NMR) spectra of water samples where the peak heights are identical, but one peak is significantly wider, it indicates that the total number of protons contributing to the wider peak is greater, but they are experiencing a faster decay of magnetization (shorter (T_2) relaxation time). The obvious key cause for the wider water proton peaks (considering the equal proton peaks heights) is the faster proton exchange. According to Nuclear Magnetic Resonance Theory there is a synonymous correlation between the form of the line of ^{1}H NMR absorption in the homogeneous magnetic field and the characteristics of molecular motions and dispersion in the liquids being tested. Thus, the increase of proton pick width and proton dispersion could occur only as a result of proton recombination in the lattice of hydrogen bonding of water molecules that leads to deviation of stochiomentric composition in MRET activated water. An increase in the width and proton dispersion (chemical shift range) of the water peak in ^{1}H NMR spectroscopy typically indicates altered hydrogen bonding, fast chemical exchange, or interactions with paramagnetic species. An increase in the width of the water proton ^{1}H NMR peak, often accompanied by increased dispersion (chemical shift changes) and a decrease in the self-diffusion coefficient (*D*), is a direct indication of reduced water mobility and heightened ion-water interaction, typical of high ionic activity or low hydration environments. In summary, the widening of the water proton peak is a "fingerprint" of decreased water activity resulting from its coordination with ions, which concurrently restricts water translation, leading to lower diffusion coefficients. The decrease of (*D*) diffusion coefficient of bulk water after MRET treatment was observed during the experimental measurements of (*D*) at Moscow State University, Department of Physics. The process of activation renders a much stronger influence on the dynamics of the mechanical fluctuation motion of stable global structural elements in the water bulk. The formation and the long-term existence of such structural elements depend on the activation of water and confirm the possibility for the memory of water to exist. With the purpose to discover the presence of such structural elements in the water bulk, we carried out additional study of the optical characteristics of activated water with the use of a laser correlation analyzer AKVA-01. The principle of action of this device is based on the analysis of the characteristics of a mutual temporal coherence function of the laser emission scattered in the volume of the studied water in the direction

perpendicular to the initial laser beam. In the study, we used the emission with a wavelength of $\lambda = 0.63\mu m$ generated by a He–Ne laser. The longitudinal coherence length of such an emission prior to its scattering is very large and, in any case, exceeds hundreds of meters. The width of the spectrum of this emission is very small. The spectrum of the scattered emission is calculated with the help of the Wiener–Khinchin formula:

$$S_E(\vec{k}, \theta, R, \omega) = 1/2\pi \int_{-\infty}^{\infty} K_E(\vec{k}, \theta, R, \tau)\, e^{-i\omega\tau}\, d\tau = \{ | f(\vec{k}, \theta) |^2 \}\, NE^2_0 / \pi R^2 \cdot k^2 D / (\omega-\omega_0)^2 + (k^2 D)^2 ; \quad (1)$$

where E_0 is the amplitude of an incident wave, $f_i(\vec{k}, \theta)$ is the scattering amplitude of the emission with the wave vector $\vec{k}$ scattered by an angle θ, R is the distance from the region center in the water bulk, where the objects scattering the light are positioned, to detectors which registered the scattered light, and D is the diffusion coefficient.It is seen from formula (1) that the spectrum of the scattered emission depends on the coefficient of diffusion D defining the mean characteristics of the motion of scattering objects. This coefficient, in turn, depends on the size and mass of these objects. Thus, the study of the correlation spectrum allows us to determine the mean characteristics of the motion of scattering objects in the water bulk and, on this basis, to perform the qualitative analysis of the spatial structure of water. In addition, such studies allow one to determine the dependence of these characteristics on the activation of water [3].

The experiments were carried out on the basis of four different samples of the initial water:

1. Natural Mineral Water “AVIAN” (produced in France);
2. Fresh Water Life “JINBO/Seok Su” (produced in the Republic of Korea);
3. Natural Mineral Water “HAITAI/Gangwondo/Pyeong Chang” (produced in the Republic of Korea);
4. Natural Mineral Water “JEJU/Sa Da Soo” (produced in Iceland).

As a quantitative characteristic, we used the integral index of the molecular dynamics of water W which is inversely proportional to the coefficient of diffusion D of the scattering objects, includes the normalizing factor (in order to make W dimensionless), and is directly related to the parameters of the auto-correlation function. An increase of the index W corresponds to a decrease of the coefficient of diffusion and characterizes uniquely the increase of the mass and size of a stiffly bound molecular complex which is present in the water bulk and scatters the laser emission.

After the completion of the whole cycle of measurements, the values of the index (W) for all samples of water (except for water specimen 3) turned out on a level somewhat exceeding the initial value (W_0) (prior to the first activation). The characteristics of water specimen 3 after the completion of all actions and all measurements turned out to be equal to the initial values of the index (W_0) which were determined prior to the beginning of the cycle of measurements and were anomalously great. Based on the results of the analysis of the performed cycle of measurements, we can made some conclusions.

First of all, it should be noted that, upon the activation of water, there occur both a very significant increase of the degree of correlation of the scattered emission and a decrease of the coefficient of diffusion of scattering complexes in water, which testifies unambiguously the formation of very large and stable clusters in water after the activation.

The second important conclusion consists in that the processes of formation and change of these clusters do not cease after the termination of the activation but continue for many hours and days. Such an effect can occur in the case where the activation of water induces such **a** change of the properties of separate water molecules and strongly-bound molecular groups, at which their further joining in great clusters becomes energy-gained [3].

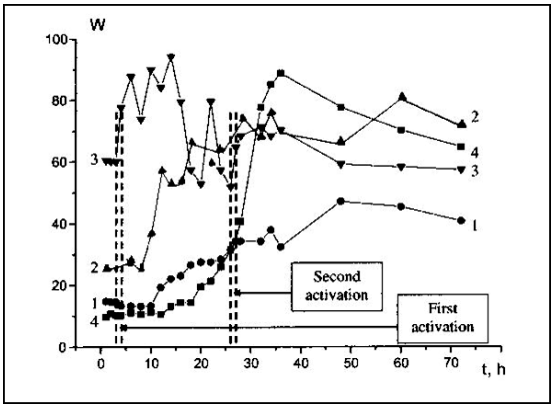


Fig.3: Integral index *W* of the molecular dynamics of MRET activated water of different types versus time. The numbers stand for the types of water given in the text above.

NMR Peak Broadening and Dispersion Analysis

- Increased FWHM (Width): Water confined in nanopores (e.g., in zeolites, carbon nanotubes, or membranes) shows significant peak broadening, often with a FWHM increasing from a few Hz in bulk to ppm-level width (e.g., 1–2 ppm). This indicates shorter transverse relaxation times (T_2), resulting from slower rotational and translational motion near the pore surfaces.
- Proton Dispersion: The appearance of multiple peaks or broadened, complex signals indicates the coexistence of different water populations: "bulk-like" water in the pore center and "bound/interfacial" water closer to the walls.
- Temperature Sensitivity: As temperature decreases, the peak broadens significantly, suggesting a transition toward a solid-like or frozen state, even above the bulk freezing point.

Correlation with Diffusion Coefficient Behavior

- Reduced Self-Diffusion (*D*): The broad NMR peak correlates with a decreased diffusion coefficient, often 1–3 orders of magnitude lower than bulk water ($D_{bulk} \approx 2.3 \times 10^{-9}$ m^2/s).
- Surface Mobility: In very small, restricted channels (sub-nm), the confinement reduces translational freedom, leading to "trapped" water molecules with very low mobility.
- Non-Monotonicity: While generally lower, in specific cases like hydrophobic carbon nanotubes with diameter ≈ 8 Å), water can exhibit accelerated transport, yet still show broad NMR spectra due to specialized ordering.

Correlation with Ion Activity and Proton Hopping

- Slower Proton Transfer (Grotthuss Mechanism): The structural restrictions that widen the ^{1}H NMR peak hinder the rearrangement of hydrogen bonds needed for proton hopping. In small droplets (<4 nm), this transfer is over 10 times slower than in bulk water.
- Ion Activity Modification: The increased ordering (high dispersion) near the surface often lowers the dielectric constant of water, increasing the ion-dipole interaction and trapping ions. This leads to reduced ion mobility, even if local water mobility seems high, as the "vehicles" (water clusters) for transport are less efficient.
- Anomalous Conduction: Contrary to the general decrease, in specific interfacial cases, proton conduction can be extremely high (up to 0.02 S/cm) due to ordered interfacial networks.

Summary Table of Correlations

NMR Feature	Structural Change	Diffusion (D)	Ion/Proton Activity
Increased Peak Width (FWHM)	Reduced rotational freedom	Significant Decrease	Decreased Mobility
Increased Dispersion/Splitting	Distinct interfacial vs. bulk-like zones	Lower average (D)	Lower Activity/Binding
Decreased (T2)	Enhanced interaction with surface	Lower mobility	Slower Exchange

This behavior is crucial in understanding the functionality of proton-exchange membranes (e.g., Nafion), where high water content allows rapid, bulk-like transport (narrow peaks, high \(D), while dehydration forces tight confinement, broadening the peak and crippling ion transport.

Results of Increased Water Proton Peak Width (Broadening):

- Fast Chemical Exchange: The proton peak broadening is most commonly due to rapid exchange of water protons with acidic or basic protons (e.g., OH, NH, COOH) in the sample. This causes the signal to represent an average of multiple chemical environments.
- Hydrogen Bonding Changes: Increased inter-molecular hydrogen bonding (e.g., higher concentration of water or interaction with a polar solvent like DMSO) results in a wider, more downfield signal.

Results of Increased Proton Dispersion (Shift in Chemical Shift):

- Solvent Dependent Shifts: The chemical shift of water is highly dependent on the solvent's ability to form hydrogen bonds. Increased dispersion of water protons in different environments (or different solvents) is often seen, with peaks observed at 0.4ppm in benzene-d6, 1.5 ppm in chloroform-d, and 3.3 ppm in DMSO-d6.

- Temperature Dependence: Increased temperature reduces hydrogen bonding, typically shifting the water peak upfield (lower ppm) and sometimes narrowing it, while cooling can broaden it.
- Interaction with Interfaces: In biological or heterogeneous samples, surface interactions (e.g., with proteins) can cause a subset of water molecules to experience restricted motion, increasing the effective dispersion of the water signal.
- Bulk Water: Displays a single, sharp isotropic peak around 4.7 ppm at room temperature due to fast, isotropic molecular tumbling and rapid hydrogen exchange.
- Nanoconfined Water: Often shows a composite spectrum due to heterogeneous environments (surface-bound water vs. center-pore water).
- Surface/Bound Water: The 1H NMR signal frequently exhibits a downfield shift (higher ppm), sometimes appearing around 5-7 ppm due to strong hydrogen bonding with the confining surface (e.g., Si-OH groups in zeolites).
- Confined Center Water: Can show a second, less-shifted peak (around 2.7 ppm in zeolite MOR-P) representing water with fewer or different hydrogen bonds compared to bulk.
- Peak Broadening: The line width of the 1H MAS NMR signal broadens significantly with a decrease in pore size (R) due to inhibited molecular motion and reduced exchange rates.

Key NMR Differences

- Chemical Shift (Δ): Nanoconfined water shows greater sensitivity to temperature, with the shift increasing (downfield) upon cooling as hydrogen bonds develop differently than in bulk.
- Relaxation Times (T1, T2): Nanoconfined water displays substantially shorter spin-lattice (T1) and spin-spin (T2) relaxation times compared to bulk, indicating faster relaxation due to confined, slower rotation.
- Low-Temperature Phase Behavior: While bulk water freezes at 0°C, nanoconfined water (e.g., in silica pores) often remains liquid at much lower temperatures, resulting in a persistent, albeit broadened, NMR peak below 273° K.

This contrast in peak position and width, especially at low temperatures, serves as a direct, comparable measure of the structural and dynamic changes within nanoconfined spaces compared to bulk water.

CONCLUSION

MRET (Molecular Resonance Effect Technology) activated water exhibits a direct physical and functional correlation with nanoconfined water, sharing key anomalous properties such as reduced viscosity, lower dielectric permittivity, decreased electrical conductivity, and altered diffusion coefficients [4]. True nanoconfined water requires tight physical boundaries (e.g., narrow silica pores, carbon nanotubes, or biological protein cavities) to

alter its hydrogen-bond network and molecular freedom. Conversely, MRET treatment imposes a long-range dynamic structuring of water molecules at normal room temperature and atmospheric pressure via a low-frequency resonant electromagnetic field without needing physical nanoscale constraints.Experimental and theoretical evaluations (such as NMR analysis and diffusion coeffisient measurements) classify MRET-treated water as a functional equivalent or special case of nanoconfined water.

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