

# Dynamics of Water in Nafion Fuel Cell Membranes: the Effects of Confinement and Structural Changes on the Hydrogen Bonding Network

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## ABSTRACT

The complex environment experienced by water molecules in the hydrophilic channels of Nafion fuel cell membranes is studied by ultrafast infrared pump-probe spectroscopy. A wavelength dependent study of the vibrational lifetime of the O-D stretch of dilute HOD in H<sub>2</sub>O confined in Nafion membranes provides evidence of two distinct ensembles of water molecules. While only two ensembles are present at each level of membrane hydration studied, the characteristics of the two ensembles change as the water content of the membrane changes. Anisotropy measurements show that the orientational motions of water molecules in Nafion membranes are significantly slower than in bulk water and that lower hydration levels result in slower orientational relaxation.

**Keywords:** Nafion, water, confinement, dynamics, fuel cells

## 1 INTRODUCTION

Nafion is the most common membrane separator used in polymer electrolyte membrane fuel cells (PEMFCs) due to its chemical and thermal stability and its high proton conductivity. It is a polymer, consisting of a long chain fluorocarbon backbone with pendant, sulfonic acid terminated, polyether side chains. The extreme difference in the polarity of the fluorocarbon backbone and the sulfonic acid side chains causes segregation of the membrane into hydrophobic and hydrophilic aggregates.[1]

The importance of the hydrophilic regions of Nafion for proton conduction has inspired a great deal of research over the past three decades since its development in the early 1970s. One of the first experiments to look directly at the water inside Nafion membranes was presented by Falk, who used steady state IR spectroscopy of H<sub>2</sub>O, D<sub>2</sub>O and HOD to study the properties of water in Nafion.[2] IR spectra show that water experiences a range of environments in Nafion and that the hydrogen bonding network in Nafion is weaker than in bulk water.[2, 3] Often, the properties of Nafion are studied at various degrees of hydration from dry to fully hydrated. Scattering experiments show that the hydrophilic domains swell with increased hydration. NMR[4, 5], IR[3], and MD simulations[6, 7] show that the pendant side chains in the hydrophilic domains can rearrange as the hydration increases. Ultimately, the practical question in terms of fuel cell operation is: how does the swelling and

rearrangement of the hydrophilic domains affect the mechanism for proton transport through Nafion?

Here, we present an IR pump-probe study of the dynamics of water absorbed in Nafion membranes at four hydration levels. IR spectroscopy of dilute HOD in H<sub>2</sub>O or D<sub>2</sub>O provides a direct probe of the hydrogen bonding network and dynamics of water. The local environment of an HOD molecule is reported by its linear IR spectrum[8] and its vibrational lifetime. Vibrational relaxation is sensitive to both local fluctuating forces acting upon an excited vibrational mode and the availability of lower frequency accepting modes to dissipate the energy. Changes in the local environment can alter the fluctuating forces and shift the energy levels of the accepting modes, altering the vibrational lifetime. Although it is difficult to pinpoint the cause of a change in the vibrational lifetime, the fact that it is sensitive to local effects allows the identification of multiple ensembles based on differences in the vibrational lifetime at different frequencies.

Global rearrangements of the hydrogen bonding network are reflected in the time dependent orientational anisotropy, which is a measure of the reorientational motions of the water molecules. Reorientation requires the concerted motion of several water molecules and involves the reorganization of the hydrogen bonding network through the breaking and forming of hydrogen bonds. This requirement causes the anisotropy to be sensitive to the characteristics of the hydrogen bonding network as a whole rather than the local environment of an O-D oscillator. The detailed wavelength dependent study of the vibrational lifetime and orientational relaxation presented below provides insights into both the local and long range dynamics of water contained in the hydrophilic domains of Nafion. A detailed description of the experimental setup can be found in the recent work by Moilanen et. al.[9] Samples of Nafion were prepared at several different hydration levels,  $\lambda$ . We define  $\lambda$  as the number of water molecules per sulfonate group.

## 2 RESULTS AND DISCUSSION

### 2.1 Vibrational Lifetimes

Recently, the vibrational lifetime of dilute HOD in H<sub>2</sub>O absorbed in Nafion was measured for the first time.[3] The measurement of the vibrational lifetime as well as the IR spectrum of water in Nafion provided evidence for multiple ensembles of water molecules in Nafion. While the IR

spectra at all hydration levels could be fit using a weighted sum of two fixed spectral components, the vibrational lifetime showed evidence that the characteristics of the two ensembles was changing with hydration. The vibrational lifetime measurements in this earlier study were conducted only at the peak of the absorption spectrum for each sample.

Here we report a complete wavelength dependent study of the vibrational lifetime at each hydration. Figure 1 shows normalized plots of the vibrational lifetime of  $\lambda = 3$  Nafion at four frequencies in the 0-1 absorption region.

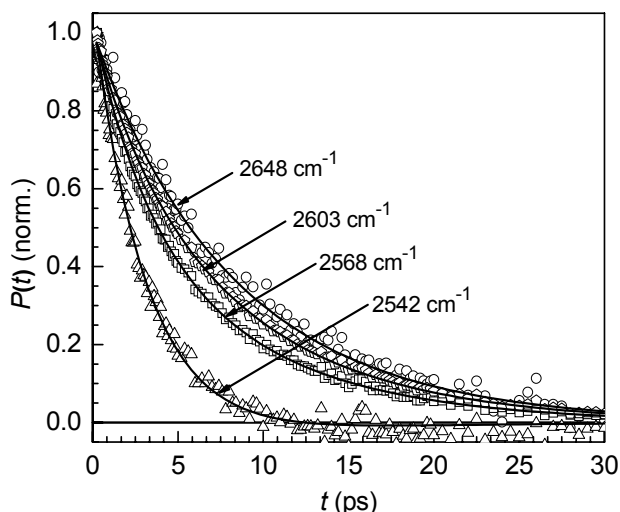


Figure 1: Population dynamics (vibrational lifetimes) at four different frequencies in the 0-1. The solid lines are biexponential fits to the data at each frequency with the time constants fixed at  $\tau_1 = 3.2$  ps and  $\tau_2 = 8.6$  ps.

It is clear that the vibrational lifetime decay is much faster on the red (low frequency) side of the 0-1 region than it is on the blue (high frequency) side. The vibrational lifetime increases monotonically from the red side to the blue side across the 0-1 transition and is fit well by a biexponential at all wavelengths. Interestingly, the vibrational lifetime can be fit at all wavelengths in the 0-1 (and also in the 1-2) using two fixed time constants. This is strong evidence that water in  $\lambda = 3$  Nafion experiences two very different environments. The relative amount of water in each environment can be extracted from the amplitudes of the two exponentials. For normalized population decays we have:

$$P(t) = ae^{-t/\tau_1} + (1-a)e^{-t/\tau_2} \quad (1)$$

where  $a$  is the fraction of water molecules in environment 1 with vibrational lifetime  $\tau_1$  and  $(1-a)$  is the fraction of water molecules in environment 2 with vibrational lifetime  $\tau_2$ . In  $\lambda = 3$  Nafion,  $\tau_1 = 3.2$  ps and  $\tau_2 = 8.6$  ps. The solid lines in figure 1 are fits to the data using these two time constants.

Evidence for multiple hydrogen bonding environments has been observed in several other systems including AOT

reverse micelles,[10] and mixtures of water and acetonitrile.[11] Nafion is similar in many ways to AOT reverse micelles. In fact, early models of Nafion invoked a reverse micellar structure for the hydrophilic regions. However, recent experiments have shown that the two environments in AOT reverse micelles, a core type region with bulk water characteristics, and a shell type region are preserved at all reverse micelle sizes studied.[10] In Nafion, both components of the vibrational lifetime change as the hydration level is increased. Table 1 contains the results of global fits to the vibrational lifetime data of the four different hydration levels of Nafion studied. At each hydration level, the relative amount of each component at a given wavelength follows a similar trend to the results for  $\lambda = 3$  Nafion shown in figure 1.

	$\tau_1$ (ps)	$\tau_2$ (ps)
$\lambda = 1$	5.1	11
$\lambda = 3$	3.2	8.6
$\lambda = 5$	2.3	6.5
$\lambda = 7.5$	2.0	5.9

Table 1: Population relaxation times for the two components of the vibrational lifetime at different hydrations.

The change in both components of the vibrational lifetime as the hydration level of the membrane increases bears some resemblance to the results for acetonitrile/water mixtures, yet it is clear that the hydrophilic regions of Nafion cannot be viewed as a simple binary solution due to the fluorocarbon backbone of the polymer which restricts the mobility of the sulfonate terminated side chains. While the hydrophilic domains of Nafion may seem similar to AOT reverse micelles in many respects, the change in the vibrational lifetime with changing water content indicates that the hydrophilic domains restructure, in contrast to the interfacial region of AOT. The sulfonate groups in AOT reverse micelles have very little mobility because they are constrained by the close packing of the surfactant molecules. In Nafion, the side chains are clearly not constrained to the extent that they are in AOT and are therefore able to rearrange to some degree. Acetonitrile molecules in binary mixtures of acetonitrile/water have essentially complete mobility to rearrange in order to form the most stable water cluster possible. Clearly, the ability of the sulfonate terminated side chains in Nafion to rearrange is intermediate between the fixed structure of the headgroups in AOT reverse micelles and the free reorganization that is possible in a binary acetonitrile/water solution. The side chains in Nafion have some ability to reorganize to produce more thermodynamically stable water clusters but this restructuring is constrained by the structure of the fluorocarbon backbone and the packing of the polymer's hydrophobic aggregates.

## 2.2 Orientational Relaxation

Unlike the vibrational lifetime, orientational relaxation, which is measured through the time resolved anisotropy, has a concrete physical connection to the motions of water molecules. The breaking and forming of hydrogen bonds, which is central to the reorientation of a water molecule, is an important step in both translational diffusion and proton transfer. In Nafion, both translational motion and proton transfer are critical for fuel cell performance, and understanding how the orientational motions of water molecules change as the amount of water in the membrane varies is fundamental in modeling these processes.

Anisotropy decays collected at the peak of the absorbance spectrum for each sample are shown in figure 2 along with the anisotropy decay of bulk water for comparison. Clearly, the anisotropy decays become significantly slower as the hydration level of the membrane decreases, and none of the curves (except water) can be fit by a single exponential decay.

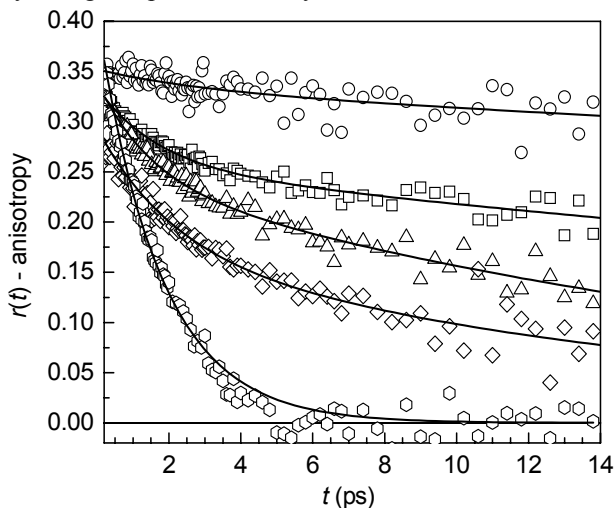


Figure 2: Anisotropy decays at the peak of the absorption spectrum for  $\lambda = 1$  (circles), 3 (squares), 5 (triangles), and 7.5 (diamonds). The anisotropy decay of bulk water (hexagons) is shown for comparison.

While several groups have measured the anisotropy decays of bulk water[12-14] and confined water,[10, 15-18] only recently has an MD simulation provided a physically meaningful interpretation of the anisotropy decay for bulk water.[19] Often, the single exponential decay of the experimentally measured anisotropy of bulk water is modeled by the Debye-Stokes-Einstein (DSE) equation. The DSE equation is based on the reorienting molecule taking random, infinitesimal steps. While the data may be fit with this model, infinitesimal diffusion does not take into account an important property of water: its tetrahedral hydrogen bonding network. The directionality of the interactions between water molecules within the tetrahedral framework of the hydrogen bonding network means that

hydrogen bonds must be broken and new bonds formed for complete reorientation to occur.

The biexponential decay of the anisotropy observed for water in AOT has been described using a model based on restricted orientational diffusion or “wobbling in a cone.”[10, 17] In the wobbling in a cone model, the motions of the molecules are restricted at short times to lie within a cone of half-angle  $\theta_c$ . This motion is diffusive in nature, but rather than proceeding to sample the entire sphere, it is restricted by the hard boundary conditions of the cone. After this initial wobbling period, the slow, long time decay of the anisotropy is attributed to full sampling of the rest of orientational space. The final exponential decay constant was interpreted using the DSE equation. However, recent MD simulations have provided evidence for a different interpretation of the long time component of the anisotropy.[19]

The MD simulation of Laage et. al. highlighted the well established tetrahedral nature of the hydrogen bonding network of water.[19] Based on this physical picture for the microscopic structure of water, Laage et. al. found that the orientational motions of water molecules are better described by a jump diffusion model, in which the jumps correspond to the rearrangement of hydrogen bonds among water molecules.[19] From a physical point of view, this description makes sense; the breaking and forming of hydrogen bonds, which changes the orientation of the hydroxyl transition dipole, cannot involve many infinitesimal random steps. Likewise, it is energetically unrealistic to imagine a water molecule breaking a hydrogen bond without being able to immediately form a new hydrogen bond.[20]

In Nafion, the anisotropy decay does not fit to a single exponential. Unlike the vibrational lifetime, biexponential behavior does not imply that the anisotropy is produced by two subensembles.[10] Here the time scales of the two components of the anisotropy decay differ by a large enough amount that it is possible to propose a reasonable physical underpinning for the different mechanisms that give rise to the decays. At short times, the motions of water molecules are restricted by the attractive potential of the hydrogen bond (wobbling in a cone). At later times, large amplitude fluctuations in the orientation occur through a rearrangement of the hydrogen bond network by breaking and forming new hydrogen bonds.

With this physical picture in mind it is possible to combine the wobbling in a cone model applied previously (short time dynamics) with the jump diffusion model (long time dynamics) for water reorientation. A detailed description of this analysis can be found in the recent paper by Moilanen et. al.[9]

There are several trends in the anisotropy parameters reported in Table 2. First, the amplitude of the short time component,  $A_S$ , increases with increased hydration leading to larger cone angles for higher hydration levels. This means that the water molecules are able to sample more of

	$A_S$	$\tau_w$ (ps)	$\theta_c$	$A_L$	$\tau$ (ps)
$\lambda = 1$	$0.02 \pm 0.02$	$3 \pm 3$	$20^\circ \pm 4^\circ$	$0.33 \pm 0.02$	$\infty$
$\lambda = 3$	$0.08 \pm 0.01$	$1.8 \pm 0.2$	$31^\circ \pm 2^\circ$	$0.25 \pm 0.01$	$63 \pm 10$
$\lambda = 5$	$0.10 \pm 0.01$	$1.3 \pm 0.2$	$33^\circ \pm 2^\circ$	$0.24 \pm 0.01$	$22 \pm 2$
$\lambda = 7.5$	$0.12 \pm 0.02$	$1.9 \pm 0.4$	$42^\circ \pm 3^\circ$	$0.17 \pm 0.02$	$17 \pm 3$
water				$0.34 \pm 0.01$	$2.6 \pm 0.1$

Table 2: Orientational relaxation parameters:  $A_S$  is the short component amplitude,  $\tau_w$  is the wobbling time constant,  $\theta_c$  is the cone angle,  $A_L$  is the long component amplitude, and  $\tau$  is the jump diffusion time constant.

their orientational space on a fast time scale. At the lowest hydration level,  $\lambda = 1$ , virtually no reorientation occurs after the small amplitude short time component. While the time constant for the fast component is similar for all four samples, the long time component,  $\tau$ , becomes significantly faster for the higher hydration levels. If the reorientational angular displacements that water molecules make during a jump are similar at each of the hydrations, the increase in the decay of the long component indicates that the jump rate is increasing with increased hydration. In the case of  $\lambda = 1$ , so little water is present in the membrane that it is never possible to find a new hydrogen bond acceptor, so no jumps occur on the time scale of the experiment.

It is clear that within this model, the orientational motions of water molecules are not local phenomena. Complete reorientation requires the breaking and forming of a hydrogen bond, which depends on the concerted motion of several water molecules to lower the energy barrier of the hydrogen bond transition state. Although the local reorientational event requires the participation of water molecules in the first and second solvation shells of the reorienting molecule, the ability of these two molecules to accept a hydrogen bond depends on the dynamics of their own solvation shells. The necessity for cooperative motion means that the anisotropy is sensitive to the hydrogen bond dynamics of the entire cluster of water molecules, not the local environment of a single water molecule. The short time scale wobbling in a cone motion is also determined by the nature of the hydrogen bond network bonded to the wobbling OD hydroxyl group under observation.

### 3 CONCLUSIONS

Wavelength dependent studies of the vibrational lifetime at four different hydration levels show evidence for two ensembles of water molecules that have characteristics which change with the amount of water in the membrane due to a restructuring of the sulfonate terminated side chains. Unlike the vibrational lifetime, the anisotropy is sensitive to the global structural rearrangements of the changing hydrogen bond network. The orientational motions of water molecules in Nafion membranes are strongly restricted with virtually no reorientation possible at the lowest hydration levels. In fuel cells, the performance of polymer electrolyte membranes like Nafion depends on the dynamical properties of the water inside the membranes. Understanding how the changing environment

of the water molecules affects their ability to reorient provides a key tool for unraveling the mechanisms for the transfer and transport of protons in fuel cell membranes.

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