Tracking Water's Response to Structural Changes in Nafion Membranes

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As the water content of Nafion membranes increases, the local environments of water molecules change due to reorganization of the pendant side chains in the hydrophilic domains. Changes in local structure as a function of water content are studied by measuring the IR spectra and the vibrational lifetimes of the hydroxyl stretch of dilute HOD in H_2O. The main features of the IR spectra are fit well by a weighted sum of the spectra of bulk water and almost dry Nafion, suggesting a two-environment model. An additional small peak on the high frequency side of the main band associated with non-hydrogen-bonded water embedded in the polymer near the interface is analyzed quantitatively as a function of the membrane water content. The spectra of this peak show that a significant reorganization of the interfacial region occurs when the water content of the membrane exceeds the threshold for ion conduction. Vibrational excited state population relaxation times (lifetimes) of the main band lengthen substantially as the water content of the membrane is decreased. The population decays are not single exponentials and indicate that multiple ensembles of water molecules exist, and the characteristics of the individual ensembles change with water content. This is in contrast to the spectra of the main water absorption band, which is only sensitive to two classes of water molecules.

I. Introduction

Nafion membranes have attracted a great deal of experimental and theoretical attention since their development in 1972 because of their importance in chlor-alkali technologies, as superacid catalysts,[1] and recently their use as polymer electrolyte fuel cell membranes. In fuel cells, the membranes act as gas impermeable barriers to separate the reactant gases while allowing protons to diffuse from the anode to the cathode of the fuel cell to complete the electrochemical circuit. Nafion is a perfluorosulfonate ionomer which consists of a long chain fluorinated backbone with sulfonate terminated polyether side chains (see Figure 1).

Proton transport, both in bulk water and in Nafion membranes is intimately related to the structural dynamics of water's hydrogen bond network. Hydrogen bond network dynamics have a substantial effect on the translational and rotational motions of water. Recent experiments probing water confined in AOT reverse micelles of various sizes[2−6] have shown that the dynamics of water in confined environments slows considerably compared to bulk water and the slowing of the dynamics depends on the size of the reverse micelle. AOT (sodium bis-2-ethylhexyl sulfosuccinate) has a sulfonate headgroup with a sodium counterion and forms well characterized spherical reverse micelles whose size varies regularly with water content. The hydrophilic domains of Nafion also consist of sulfonate headgroups that may have hydrogen, sodium, or other cations as counterions. Early models for the internal structure of Nafion membranes described the hydrophilic domains as reverse micellar structures, so a comparison to AOT reverse micelles is informative to determine how well a reverse micelle model describes the structure of the hydrated regions.

Water absorbed in Nafion membranes also experiences a high degree of confinement. Neutron and X-ray scattering experiments indicate that the hydrophilic domains in Nafion have sizes on the nanometer length scale which grow with increased water content.[7−12] These scattering experiments as well as atomic force microscopy[13] and NMR[14] experiments show that structural changes occur in the membrane as the water content increases. Most of the structural changes take place in the ionic domains with reorganization and plasticization of the sulfonate terminated ether side chains[14] to allow the hydrophilic domains to swell. NMR[15] and quasi-elastic neutron scattering[16] have also been used to study the diffusion of water in Nafion membranes and FT-IR absorption experiments have monitored changes in the absorption spectrum of the water and the fluorinated backbone with changing water content[17−20]

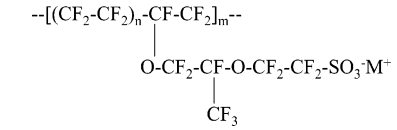

Figure 1. Repeat structure of Nafion. *n* can vary between 5 and 14. and *m* is typically on the order of 1000.

Several experiments have studied the fluorinated ether side chains to predict how their motions and interactions may affect the environment of the water,[14] but the majority have focused directly on the water. Water is a very sensitive probe of its local environment. For example, the frequency of a water hydroxyl stretch in gas-phase water peaks ∼200 cm^{-1} to higher energy than the corresponding peak in liquid water. Early work by Falk[20] indicated that water in Nafion membranes experiences a range of environments, which led to a proposed model of an irregular network of interconnected water channels. The interconnected channel model is in contrast to early neutron and X-ray scattering models, which hypothesized water exists in isolated spherical cavities.[12] Falk's studies of H_2O, D_2O and HOD absorption spectra in the sodium form of Nafion showed peaks shifting and the appearance of additional peaks relative to bulk water. Other groups have presented IR spectra of Nafion

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membranes, both in the sodium form[18] and the acid form[19] and have seen similar shifts in the water absorption bands.

Here, we present a detailed study of water in Nafion membranes ranging from essentially dry to fully hydrated Nafion using both linear and nonlinear-IR spectroscopy of the OD stretching mode of dilute HOD in H_2O. The O−D stretch has been shown to be an excellent probe of the hydrogen bonding network of liquid H_2O.[21] Probing the OD stretch mode of dilute HOD simplifies the spectrum because it does not have the complicated spectral contributions from the symmetric and antisymmetric stretching modes and Fermi resonances present in H_2O. Studying the OD stretch of HOD permits a more straightforward interpretation of the spectra. At the same time, the absorption spectrum of the OD stretch of HOD depends strongly on the hydrogen bonding and local environment experienced by the water molecule.[22] Therefore, the OD stretch reports on the changing structural morphology of the Nafion membrane as the water content of the membrane changes.

The OD stretch vibrational lifetime is strongly influenced by the local water environment. For an excited OD stretch to relax, the energy must be dissipated into a collection of intra- and intermolecular modes. Changes in the local structure of both the water and the membrane can shift the energy gaps between the OD stretch and lower energy accepting modes. This changes the density of states of the quasicontinuum of low frequency intermolecular modes, one or more of which is generally necessary to conserve energy.[23,24] Although it is difficult to identify the particular environmental change responsible for a change in the vibrational lifetime, the sensitivity of the lifetime to environment makes it a useful tool for detecting structural changes and the presence of multiple subensembles of water molecules that may not be evident in the infrared spectrum.

II. Experimental Procedures

Nafion-117 samples were purchased from Fuelcellstore.com in the acid form. Samples were converted to the sodium form by soaking in 1 M sodium chloride solution for 24 h followed by a deionized water rinse and were used without further purification. A home-built humidity control system was used to equilibrate the samples under constant relative humidity conditions. Relative humidity on a scale of 0 to 1 is equivalent to the activity of water, which is defined as the ratio of the partial pressure of water in the air to the partial pressure of water-saturated air at a given temperature. The humidity system consists of a water reservoir containing dilute (<5%) HOD in H_2O. The reservoir is maintained at various constant temperatures to produce relative humidities ranging from 0 to 100% (activities from 0 to 1). Dry air (dewpoint −100 °C) is bubbled through the water reservoir to produce the humidified air. The humidified air purges a Plexiglas box with a humidity meter to monitor the relative humidity and glove ports for sample manipulation and preparation. The number of water molecules per sulfonate group, λ, was determined by measuring the mass uptake of a Nafion membrane as a function of water activity. Mass uptake measurements were made with a balance placed inside the Plexiglas humidity box. IR spectra were collected using an FT-IR spectrometer. Samples were prepared at water contents varying from 1 to 9 water molecules per sulfonate group ($\lambda = 1$ to 9) for FT-IR experiments and $\lambda = 1$ to 7.5 for pump−probe experiments. Samples equilibrated under 0% relative humidity still contained approximately one water per sulfonate, ($\lambda = 1$). These samples will be referred to as "dry" Nafion. All samples prepared in the humidity system were sealed in sample cells between 3 mm thick CaF_2 windows separated by a 200 μm Teflon spacer. The stability of the samples was monitored by FT-IR spectroscopy to ensure that the cells were airtight.

TABLE 1: Spectral Characteristics, Absorption Maxima, Full Width at Half Maximum (Fwhm), and Two Component Fits to the Absorption Spectra, Percent Dry Nafion and Percent Water, Area of the High Frequency Shoulder, and Number of Water Molecules per Sulfonate Group, λ, in the High Frequency Embedded Environment

	$\lambda = 1$	$\lambda = 3$	$\lambda = 5$	$\lambda = 7.5$	$\lambda = 9$	water
peak (cm^{-1})	2590	2585	2570	2565	2553	2509
fwhm (cm^{-1})	122	151	174	184	188	170
percent "dry"	100	82	72	64	55	0
percent bulk	0	18	28	36	45	100
area shoulder	7.7	7.2	7.5	2.9	2.5	
$\lambda_{shoulder}$	0.2	0.1	0.1	0.05	0.04	

The laser system used in these experiments has been described in detail elsewhere[2] Briefly, a home-built Ti:sapphire oscillator and regenerative amplifier operating at 1 kHz pump an OPA and difference frequency stage to produce ~70 fs, ~4 μm IR pulses. Pulses are split into pump and probe pulses with the probe's polarization set to ~45° relative to the pump. After the sample, the components of the probe with polarization parallel and perpendicular to the pump are selected to avoid depolarization effects due to optics in the beam path[25] and the perpendicular component is rotated back to parallel by a half wave plate to eliminate differences in diffraction efficiency of the monochromator grating. The spectrally resolved pump−probe signal is detected by a HgCdTe detector. Vibrational population relaxation, $P(t)$ (lifetime) is obtained using,[3]

$$P(t) = I_{\parallel} + 2I_{\perp} \quad (1)$$

III. Results and Discussion

A. IR Spectra. Although several groups have published IR spectra of H_2O in Nafion[17−20] the interpretation of these spectra is complicated by the overlapping symmetric and antisymmetric stretching modes making it very difficult to extract information about the underlying subensembles of water molecules. Early infrared experiments by Falk[20] included two spectra of the OD stretch of HOD in H_2O absorbed in Nafion but this work explored only a small range of water content and discussion of the local environment of the absorbed water was limited to peak positions relative to bulk water and gas-phase water. Infrared spectra of the OD stretching region are shown in Figure 2, parts A and B, and characteristics of the spectra from fits are listed in Table 1. Figure 2A shows the background subtracted spectra without normalization. The spectra consist of a main broad peak with a small shoulder on the high-frequency side. This shoulder was also observed by Falk and was attributed to HOD molecules interacting with the fluorocarbon backbone.[20] The normalized spectra are shown in Figure 2B making differences between the spectra more obvious. As the water content increases, the peak positions of the spectra shift to lower frequencies and the peak widths increase. A shift toward lower frequency is often attributed to increased hydrogen bonding between water molecules. Broadening of the peak indicates a more heterogeneous environment. Table 1 shows that the full width at half-maximum of the spectra of water absorbed in Nafion changes from values smaller than that of bulk water at $\lambda = 1$ to values larger than bulk water at $\lambda = 5$.

Recent work on water confined in AOT reverse micelles, which also have sulfonate headgroups, has demonstrated that the IR spectra of the confined water can be described well by a strict core−shell model involving a two-component fit. The

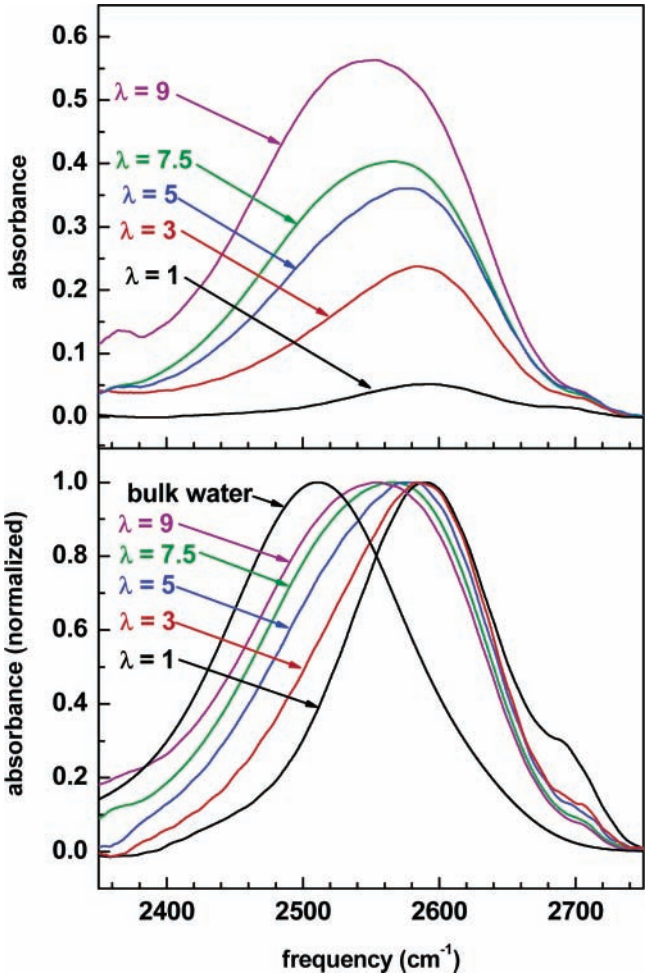

Figure 2. (A) Background subtracted spectra of ~5% HOD in H_2O in Nafion membranes at various water content, λ. λ is the number of water molecules per headgroup. (B) Normalized spectra of water absorbed in Nafion membranes at various water content, λ, and the spectrum of bulk water for comparison. Note the relative amplitude of the high frequency shoulder tends to decrease with increased water content.

core spectrum is modeled as that of bulk water, and the spectrum of the surrounding shell of water molecules, which are water molecules associated with the headgroups, is modeled as that of the lowest water content reverse micelle.[3] The lowest water content reverse micelle has essentially all water molecules associated with the headgroups. This same approach gives good results for fitting the IR spectra of water in Nafion. The main peak of the spectrum (ignoring the small shoulder at ~2708 cm^{-1}) is fit using a weighted sum of the experimental spectra of bulk water and the main peak of dry ($\lambda = 1$) Nafion. The high frequency shoulder is fit with an additional Gaussian function to extract information about the amount of water in the embedded environment. On the basis of its frequency, the shoulder is associated with water molecules that are most likely not hydrogen bonded and that are removed from both interfacial water that is associated with the headgroups and with the more bulk like water in the channels. The results of the fit are listed in Table 1 and a representative fit is shown in Figure 3. The two-component fit using eq 2 for fitting the main peak reproduces the data extremely well.

$$\Gamma(\lambda) = N[a\Gamma(\lambda = 1) + (1 - a)\Gamma(H_2O)] \qquad (2)$$

Γ is the absorption spectrum of a particular sample. There is

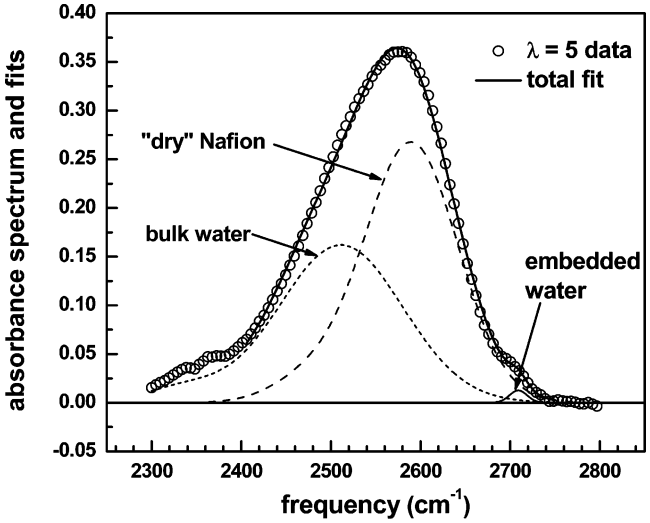

Figure 3. Example of fitting the absorption spectrum using a fit based on the spectra of "dry" Nafion and bulk water. A third Gaussian peak is used to fit the high frequency shoulder associated with embedded water molecules.

essentially one important adjustable parameter, *a*, the relative contribution of the spectrum of dry Nafion to the total observed spectrum, and *N* the overall scaling constant.

Determining the relative concentrations of bulk water and headgroup water (water with the spectrum of dry Nafion) that contribute to the spectrum of a sample for a particular water content is complicated by the fact that the transition dipole moment, μ, of the OD stretch varies with frequency. Using mixed molecular dynamics/quantum mechanics calculations, Skinner and co-workers found that the transition dipole varies linearly with frequency for bulk water.[26] This has been supported by experimental measurements on bulk water and the smallest AOT reverse micelles.[3] However, the linear-IR spectrum depends on μ^2 and the nonlinear pump probe experiment discussed below depends on μ^4 so the differences in the transition dipole moment become amplified. Using the published results,[26] at the peak of bulk water's spectrum, μ^2 is 1.6 times larger than it is at the peak of dry Nafion's spectrum and 4.8 times larger than at ~2708 cm^{-1}, the location of the high frequency shoulder. These differences become more important in the vibrational lifetime measurements, magnifying the contribution of bulklike water.

After correcting for the change in the transition dipole moment across the spectrum, it is possible to extract the percentage of water in Nafion experiencing bulklike conditions as opposed to dry Nafion-like conditions with reasonable accuracy; these percentages are given in Table 1. The percentage of bulklike water increases fairly linearly as the water content of the membrane increases indicating that there is no abrupt change in structure of the main part of the hydrophilic regions. This result agrees well with earlier predictions that the hydrophilic region has reverse micelle-like characteristics.[11,12]

Additional information can be extracted from the high-frequency feature in the IR spectrum that reflects the concentration of embedded water molecules. The results in Table 1 show that as the water content of the membrane increases there is an abrupt drop in the area of the high frequency shoulder above $\lambda = 5$. Studies measuring the ionic conductivity of Nafion membranes as a function of water content show that ion conduction is restricted below $\lambda = 5$.[27] Fluorine NMR studies have shown that water does not appreciably hydrate the pendant side chains,[14] yet IR and ionic conductivity[28] results indicate

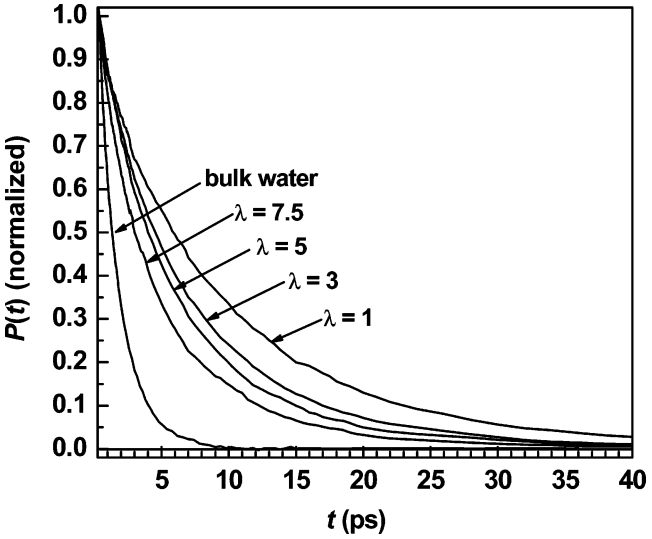

Figure 4. Vibrational lifetime decays at various water content, λ.

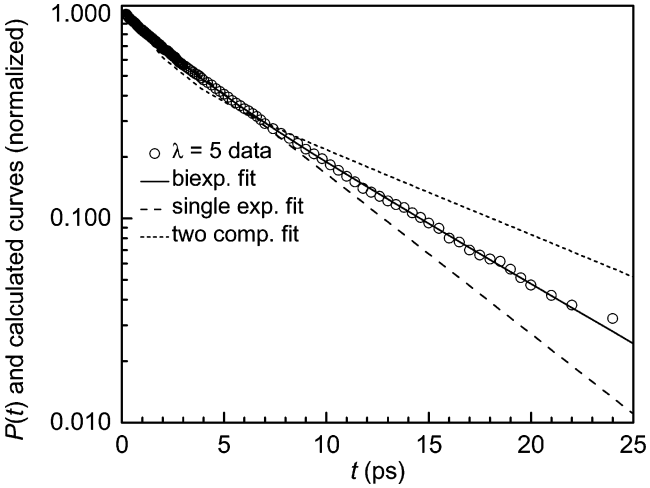

Figure 5. Example of fitting the lifetime with a single exponential, a biexponential, and a two-component fit based on a weighted sum of the lifetimes of "dry" Nafion and bulk water.

TABLE 2: Single Exponential and Biexponential Fit Parameters for the Vibrational Lifetime

	$\lambda = 1$	$\lambda = 3$	$\lambda = 5$	$\lambda = 7.5$	water
		Single Exponential Fits			
τ (ps)	9.5	6.9	5.9	3.8	1.7
		Biexponential Fits			
A_1	0.17	0.34	0.32	0.36	
τ_1 (ps)	1.5	3.2	2.4	1.6	
A_2	0.83	0.66	0.68	0.64	
τ_2 (ps)	10.5	8.8	7.4	6.2	

that some water is still in contact with fluorocarbon. Molecular dynamics simulations show that the orientations of adjacent side chains are anticorrelated at low water content allowing the chains to sandwich water molecules between them or trap water molecules against the fluorocarbon backbone.[29] At higher water content, the side chains tend to orient in the same direction reducing the likelihood of trapped water. These previous results are consistent with our experimental findings which show that an abrupt structural change occurs in the membrane above $\lambda = 5$, which dramatically reduces the number of embedded water molecules in close proximity to the fluorocarbon. The IR spectroscopic results also quantify the concentration of the embedded water molecules. As discussed above, the area of the shoulder alone is insufficient to determine the concentration of the water associated with this peak. The wavelength dependence of the transition dipole matrix element, which determines the extinction coefficient, must be taken into consideration in the analysis.

B. Vibrational Lifetimes. As discussed above, the vibrational lifetime of the OD stretch is sensitive to its local environment.[3] Figure 4 shows the vibrational lifetime decays collected at the peak of the absorption spectrum for each sample. In Nafion, the vibrational lifetime increases significantly as the water content of the membrane decreases. Vibrational relaxation causes a small, <1 K, transient temperature increase in the sample that is long-lived compared to the time scale of the measurements.[3,21] The temperature increase following vibrational relaxation results in a long-lived bleach at the peak of the spectra. The bleach occurs because the change in temperature shifts the equilibrium distribution of hydrogen bonds to fewer bonds, resulting in an overall shift of the spectrum to higher frequency.[3,21] These data were corrected for this small heating contribution using a standard procedure that has been employed for both bulk water and reverse micelles.[3,21,30] Following the removal of the small heating contribution, population decays, $P(t)$, are not single exponential, in contrast to bulk water.[3] Although a single exponential does not fit the data perfectly, an initial single exponential analysis is useful for identifying trends. Table 2 lists the parameters for both single and biexponential fits to the data. On the basis of a single-exponential fit, the vibrational lifetime is more than 5 times longer in $\lambda = 1$ Nafion than bulk water.

Water in the hydrophilic domains of Nafion not only experiences a high degree of confinement, but also a high concentration of ions and strong, local electric fields. On the basis of experiments in bulk water, it has been suggested that water hydrogen bonded to anions has a longer vibrational lifetime than bulk water.[31,32] Cations do not have a large effect on the vibrational lifetime.

The ionic environment in Nafion and AOT reverse micelles is quite different than a bulk water solution of ions. In Nafion and AOT the anions are confined to a relatively limited region on the surface of the water channel or water pool, rather than an isotropic distribution of cations and anions. Molecular dynamics simulations of AOT[33] as well as considerations based on the Onsager length[34] show that the localization of anions at the interface causes a commensurate localization of cations at the interfacial region. Therefore, the nature of the ionic environment and the interactions of water with ions in confined systems of Nafion and AOT are very different from those in a bulk water ionic solution. In AOT, it has been demonstrated that water molecules (HOD) outside of a thin shell at the interface with the headgroups have the vibrational lifetime measured in bulk water.[3]

If water only existed in two environments in Nafion (bulklike water and $\lambda = 1$ like water) it should be possible to fit the population decays using a two-component model similar the one used to fit the IR spectra. In the vibrational lifetime measurement, there is no contribution from water in the high frequency shoulder because the data are collected at the peak of the spectra, more than 100 cm^{-1} from the shoulder and the μ^4 dependence of the pump−probe signals means that signals arising from the shoulder would be insignificant at the detection wavelength. Figure 5 displays a semilog plot showing the results from three different methods for fitting the vibrational lifetime decay of $\lambda = 5$: a single exponential, a biexponential, and a two-component fit using the lifetimes of bulk water and $\lambda = 1$ with the relative amplitude of the two components as the only

adjustable parameter. Clearly, neither a single exponential decay nor the two-component model fits the data well at all times. Of the three, only a biexponential function fits the data well. The nonexponential decay that does not fit the two-component model indicates that multiple ensembles of water molecules are present in Nafion, but as the water content of the membrane changes the population relaxation is not a weighted sum of decays arising from bulklike water and water in nominally dry Nafion. Rather, the characteristics of the two ensembles themselves change. This may be due to the structural changes occurring at the interface between the hydrophilic and hydrophobic domains leading to irregularly shaped channels and nonuniform swelling. An indication of a reorganization at the interface is also manifested in the IR spectra of the embedded water shoulder.

In contrast, recent work on AOT reverse micelles showed that the vibrational lifetimes could be fit quite well using a strict, two-component core−shell model (although orientational relaxation and spectral diffusion could not be fit with this model).[3] AOT reverse micelles are spherical in shape and increase regularly in diameter with increased water content. The interfacial region in an AOT reverse micelle does not change structure significantly at different water contents. Although the hydrophilic regions of Nafion also increase in size with increased water content, the vibrational lifetime results indicate that the detailed structures of the domains do not remain constant. The fact that the linear-IR spectra could be fit to the two subensemble model suggests that the vibrational population relaxation is more sensitive to subtle variations in the local environment than the almost featureless absorption spectrum.

Both Nafion membranes and AOT reverse micelles have sulfonate headgroups with sodium counterions, but vibrational relaxation in these two systems is quite different. If vibrational relaxation only depended on the identity and concentration of ions, one might expect that the vibrational lifetime in Nafion and AOT reverse micelles would be the same. In fact, the longest vibrational lifetime in AOT reverse micelles is 5.2 ps in a reverse micelle containing two water molecules per sulfonate headgroup.[3] Nafion membranes with comparable water content ($\lambda = 1$ and $\lambda = 3$) had vibrational lifetimes of 9.5 and 6.9 ps respectively based on single-exponential fits. This indicates that the vibrational lifetime is sensitive to the topology of the confined region even when the headgroup and counterion are the same.

IV. Concluding Remarks

The internal structural morphology of Nafion is complicated by the irregularity of the polymer backbone which restricts the locations and orientations of the pendant side chains. This constraint makes it impossible for the side chains to form highly spherical cavities similar to those found in AOT reverse micelles. Infrared spectroscopy of water in a Nafion membrane allows a direct probe of the changing environment experienced by water in its hydrophilic domains. FT-IR spectroscopy shows that in addition to the swelling of the hydrophilic domains a structural change occurs above $\lambda = 5$ leading to fewer embedded water molecules in direct contact with the fluorocarbon backbone. Measurements of the vibrational lifetime demonstrate the presence of multiple subensembles of water molecules in Nafion. However, the subensembles cannot be broken down into bulklike and $\lambda = 1$ like water as they can in analyzing the IR spectra.

Ongoing experiments are examining the wavelength dependence of the vibrational lifetimes and measurements of orientational relaxation of water in Nafion membranes, also as a function of wavelength. As the application of Nafion membranes in fuel cells depends on the internal water for proton conduction, understanding the dynamics of water in Nafion membranes is an important part of optimizing their function in these applications. These measurements will provide detailed insights into the changing nature of water in Nafion membranes as the water content is varied.

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