Journal of Physics: Conference Series

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To cite this article: F L Pratt *et al* 2023 *J. Phys.: Conf. Ser.* **2462** 012044

The 15th International Conference on Muon Spin Rotation, Relaxation and Resonance IOP Publishing
Journal of Physics: Conference Series **2462** (2023) 012044 doi:10.1088/1742-6596/2462/1/012044

Muon studies of the proton conducting polymer Nafion

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Abstract. The fluorinated ionomer Nafion, first discovered by the Du Pont company, is a material that provides efficient proton conducting membranes for application in important technological areas such as hydrogen fuel cells. Although many aspects of the polymer have been studied in relation to these applications, the microscopic mechanisms for proton transport in this polymer are still only poorly understood. We have therefore applied implanted muon techniques to the study of Nafion, aiming to gain information about these mechanisms via the muon acting as a local spin probe. Our results indicate that the muon is highly sensitive to the hydration state of the polymer and to the dynamical processes of the various sub-phases within the material. A three component model is found to describe the data well. This model has one F-μ-F component, reflecting muons in the PTFE-like polymer matrix, a second component representing quasi-static environments dominated by a single close proton and a third component encompassing highly dynamic proton-coupled environments. The properties have been studied within this modelling framework as a function of temperature for both dehydrated and fully hydrated samples.

1. Introduction

Nafion is a form of solid polymer electrolyte developed by the DuPont company that is particularly efficient and selective in transporting protons. As a result of this it finds technological application in many areas of electrochemistry and, in particular, Nafion membranes can provide a vital component in the design of the hydrogen fuel cell, which can be used to deliver clean zero carbon emission options for transport applications. Nafion is also the first member of a whole family of perfluorinated sulphonic acid ionomers (PFSA) [1].

The material can be viewed as a copolymer between polytetrafluoroetheylene (PTFE) and a sulphonic acid ionomer (Fig.1a). Although it has been carefully studied in the 20 years or so since first being discovered, clarifying some aspects of the structure and properties, the system is rather complex and the precise details of the transport mechanism in particular remain rather uncertain [2, 1]. In the generally accepted structural model of Nafion the sulphonic acid groups of the dry polymer aggregate and form ionic islands within the PTFE supporting matrix [3] (Fig.1b). Local proton mobility is expected to be high in these regions at high enough temperatures to unbind the ions. As water is introduced into the system these ionic regions swell and above a critical hydration level, percolation of diffusion paths across these ionic domains will occur (Fig.1c) [2], leading to efficient bulk proton transport.

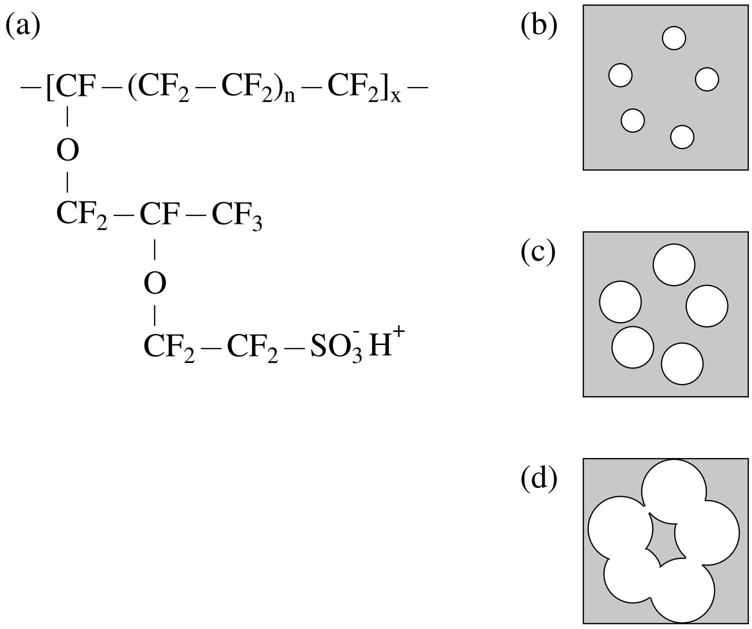

Figure 1. (a) The chemical form of the proton conducting ionomer Nafion. (b)-(d) Model for proton conduction in Nafion. (b) In the dry polymer the ionic parts of the side chains cluster to form ionic islands within the PTFE matrix . (c) Hydration leads to swelling of the ionic islands. (d) High proton conductivity through the bulk material occurs once there is percolation between these swollen ionic domains.

Various mechanisms for transport within the ionic regions have been proposed [4] involving protons interacting with different numbers of water molecules, along with the involvement of translational and/or rotational degrees of freedom of the clusters. Muon studies can provide further informaton on the nature of dynamics of the system, that can be used to test the various models. These results are complementary to the existing NMR data on Nafion [5, 6, 7]. We have previously made some systematic studies of the behavior of muons in various fluorinated polymers [8, 9], where a key feature of the relaxation is the characteristic precession signal reflecting dipolar interaction between the muon and one or more fluorine atoms. In Nafion this allows the signal from the PTFE matrix and the ionic regions to be separately identified and studied as a function of temperature and hydration level.

2. Experimental details

Nafion 115 was obtained from Sigma-Aldrich in the form of membrane sheets of thickness 125 μm. The equivalent molecular weight of the monomer is 1100 g mol^{-1}, corresponding to n=6.5 in the structural unit (Fig.1a). Stacks of 3-4 sheets measuring 3×3 cm^2 were used for the muon measurements on the EMU and ARGUS spectrometers at the ISIS Neutron and Muon Source. Ag foil degraders were placed in front of the stack to ensure that the muons stop in the sample. The highly hydrated sample was placed in a sealed cell with a mylar window directly after a long period of soaking in deionized water. A CCR cryostat was used to control the temperature in EMU and a helium flow cryostat was used for temperature control for the measurements that were made on ARGUS.

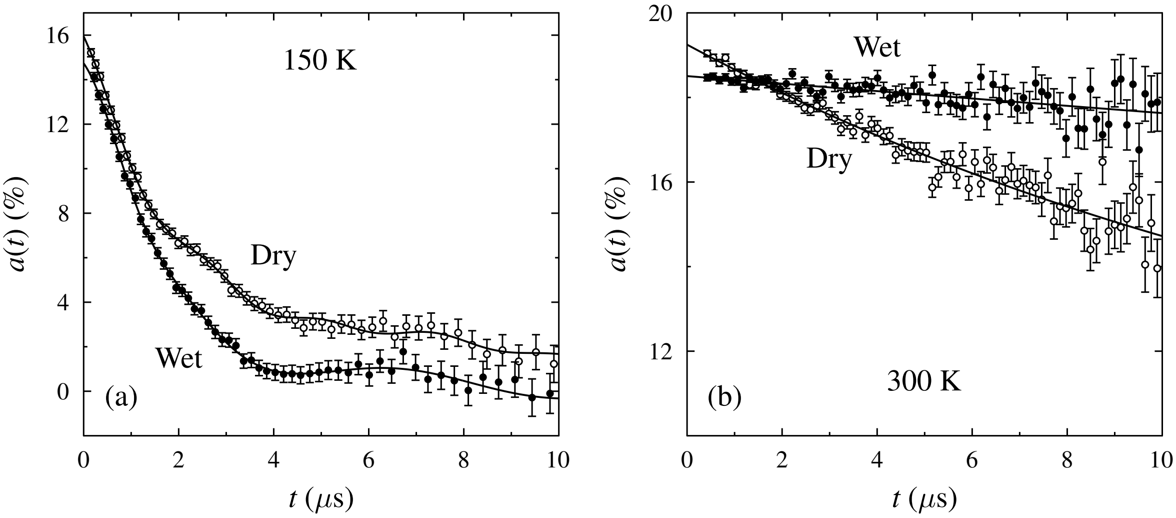

Figure 2. Comparison between the ZF relaxation signals of wet and dry samples at (a) 150 K and (b) 300 K. Note the different vertical scale for each panel. The solid lines in (a) represent fits to the three component model described in the main text. The solid lines in (b) represent a single component relaxation fit.

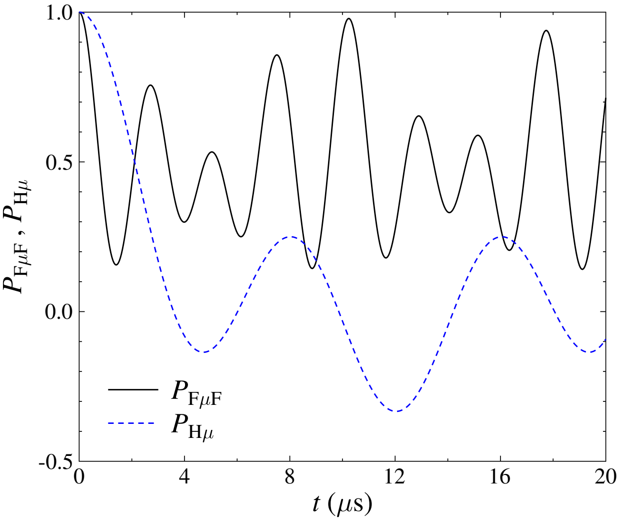

Figure 3. Illustration of the general form of the polarization functions $P_{\mathrm{F}\mu\mathrm{F}}$ and $P_{\mathrm{H}\mu}$.

3. Experimental results

Fig.2 shows a comparison of the raw relaxation data for dry and wet (i.e. highly hydrated) samples at 150 K and 300 K. The marked effect of the presence of the additional protons is clearly seen in the case of the wet sample for both temperatures. At 150 K the non-oscillatory part of the overall relaxation is faster for the wet sample, whereas it is slower for the wet sample at 300 K. This indicates a crossover from a slow fluctuation regime to a fast fluctuation regime where the fluctuation rate ν is inversely proportional to the relaxation rate λ. The following three component model was used to fit the data

$$a(t) = a_0 \left[f_{\mathrm{F}\mu\mathrm{F}} P_{\mathrm{F}\mu\mathrm{F}}(d_{\mathrm{F}\mu\mathrm{F}}, t) e^{-(\sigma t)^2} + f_{\mathrm{H}\mu} P_{\mathrm{H}\mu}(d_{\mathrm{H}\mu}, t) e^{-\lambda_{\mathrm{H}\mu} t} + f_{\mathrm{dyn}} e^{-\lambda_{\mathrm{dyn}} t} \right]. \quad (1)$$

The first term in Eq. 1 describes muons forming linear FμF states with dipolar polarization function $P_{\mathrm{F}\mu\mathrm{F}}$ and a Gaussian damping parameter σ to reflect a distribution of states as well as decoherence resulting from a transfer of polarization to more distant nuclear spins [10]. $P_{\mathrm{F}\mu\mathrm{F}}(d_{\mathrm{F}\mu\mathrm{F}}, t)$ is given by [11]

$$P_{\mathrm{F}\mu\mathrm{F}}(d_{\mathrm{F}\mu\mathrm{F}}, t) = \frac{1}{6}\left\{3 + \cos(\sqrt{3}\omega_{\mathrm{F}\mu\mathrm{F}}t) + \left(1 - \frac{1}{\sqrt{3}}\right)\cos\left[\left(\frac{3-\sqrt{3}}{2}\right)\omega_{\mathrm{F}\mu\mathrm{F}}t\right]\right.$$
$$\left. + \left(1 + \frac{1}{\sqrt{3}}\right)\cos\left[\left(\frac{3+\sqrt{3}}{2}\right)\omega_{\mathrm{F}\mu\mathrm{F}}t\right]\right\}, \tag{2}$$

where

$$\omega_{\mathrm{F}\mu\mathrm{F}} = \frac{\mu_0 \hbar \gamma_\mu \gamma_\mathrm{F}}{4\pi d^3_{\mathrm{F}\mu\mathrm{F}}}. \tag{3}$$

The second term in Eq. 1 describes muons having a dominant dipolar interaction with a single H atom and an additional Lorentzian relaxation reflecting decoherence via interaction with more distant spins and the presence of molecular dynamics. An attempt to model this term with a Kubo-Toyabe term produced a worse quality fit, indicating that the interaction with one close spin is dominant and corresponding polarization function $P_{\mathrm{H}\mu}(d_{\mathrm{H}\mu}, t)$ is given by [12]

$$P_{\mathrm{H}\mu}(d_{\mathrm{H}\mu}, t) = \frac{1}{6}\left[1 + \cos(\omega_{\mathrm{H}\mu}t) + 2\cos(3\omega_{\mathrm{H}\mu}t/2) + 2\cos(\omega_{\mathrm{H}\mu}t/2)\right], \tag{4}$$

where

$$\omega_{\mathrm{H}\mu} = \frac{\mu_0 \hbar \gamma_\mu \gamma_\mathrm{H}}{4\pi d^3_{\mathrm{H}\mu}}. \tag{5}$$

The polarization functions described by Eq. 2 and Eq. 4 are illustrated in Fig. 3. The final term in Eq. 1 is a slowly relaxing Lorenztian term reflecting muons that experience a highly dynamic environment. The sum of the three component fractions $f_{\mathrm{F}\mu\mathrm{F}} + f_{\mathrm{H}\mu} + f_{\mathrm{dyn}}$ is equal to 1. The temperature dependences of some of the relaxation parameters derived from fitting our data to Eq. 1 are shown in Fig.4.

The FμF fraction is always found to be less than 20% (Fig. 4a,e), indicating that the majority of the muons stop in the ionic regions. The F-F distance for the FμF state is not sensitive to the hydration level and only starts to increase a little at higher temperatures (Fig. 4b,f). The FμF damping parameter σ is essentially independent of temperature for the dry sample, but increases substantially at 150 K for the hydrated sample (Fig. 4c,g). For the second component, the Hμ distance does not vary significantly with temperature, but become a little shorter on hydration (Fig. 4b,f). The relaxation parameters for the second and third components have opposite temperature dependences, with the temperature dependences of both becoming more rapid in the hydrated sample (Fig. 4e,h).

In the hydrated sample the relaxation becomes very slow at higher temperatures, so in order to follow the relaxation self-consistently over a wider range of temperature, a single component model was used to fit the data. Some transverse field (TF) measurements taken for the hydrated sample in a field of 2 mT are shown in Fig. 5. The relaxation of the TF oscillations was fitted with a stretched exponential where the stretch exponent was close to 1. The relaxation rate is shown in Fig. 5a and shows a rapid fall near 175 K. The equivalent increase in the fluctuation rate is shown in Fig. 5b. This increase in fluctuation rate is accompanied by a significant downward shift in the rotation frequency (Fig. 5c). Such a correlation between the fluctuation rate and rotation frequency is the signature of a pseudo-diamagnetic signal resulting from a paramagnetic muonium state that is subject to rapid spin exchange [13]. We believe that a

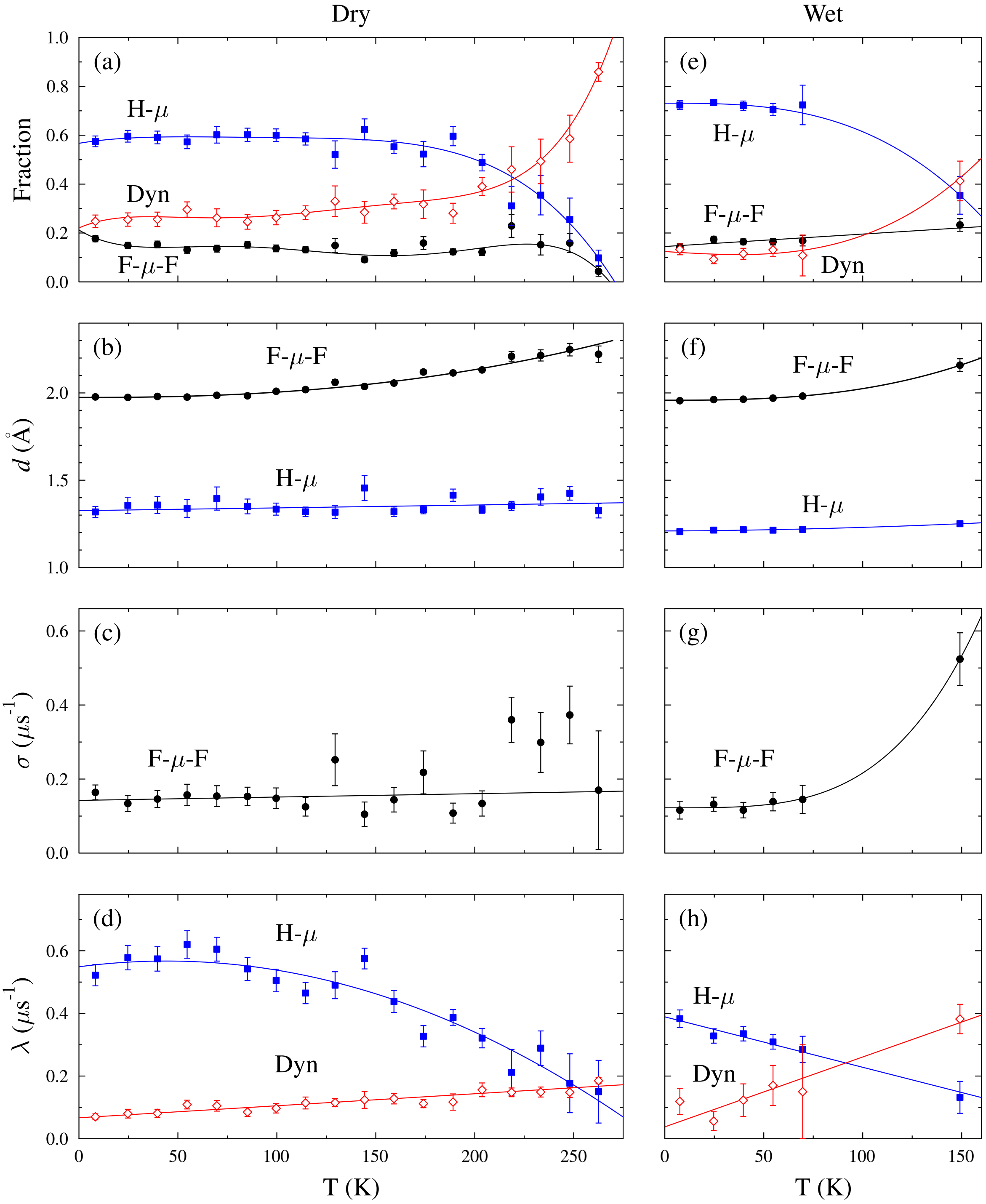

Figure 4. (a)-(d) Temperature dependence of the model parameters for the dehydrated sample. (e)-(h) Temperature dependent model parameters for the hydrated sample. The solid lines provide a guide to the eye.

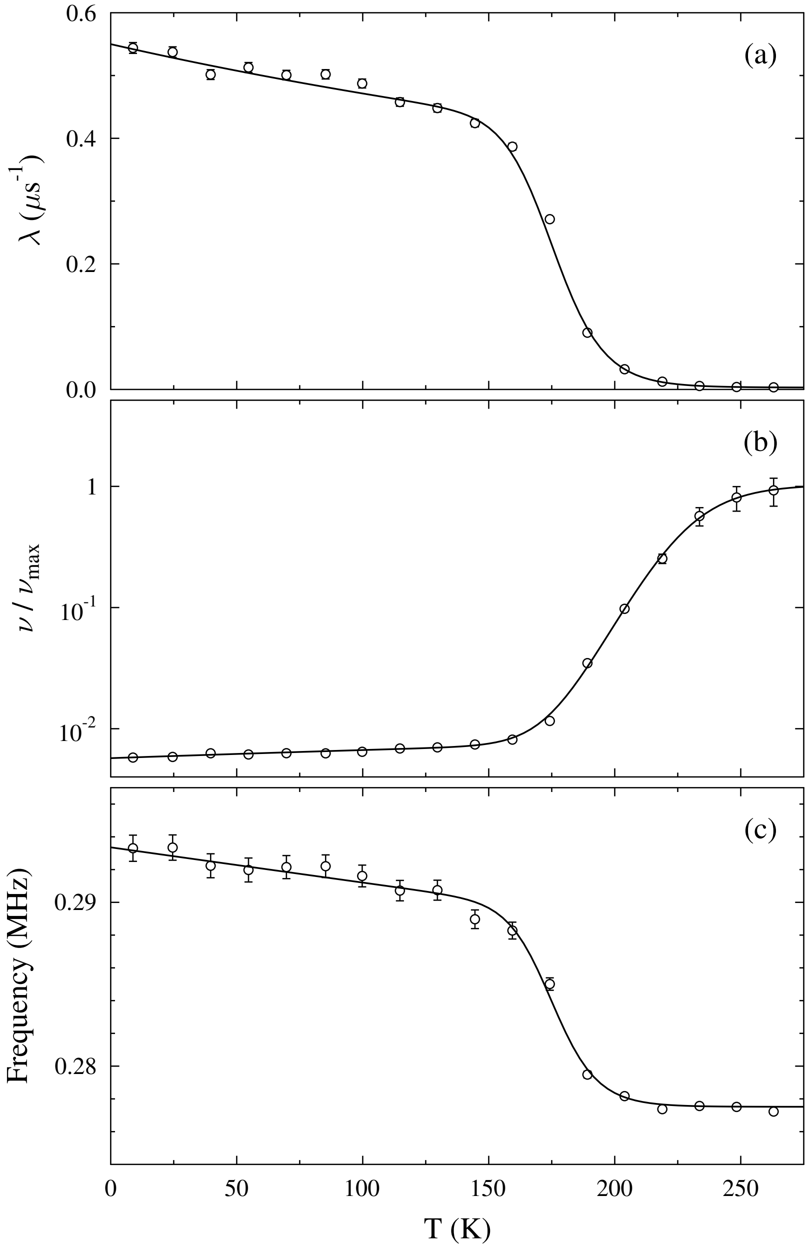

Figure 5. Temperature dependence of the parameters obtained from a single component fit to the asymmetry measured for a hydrated Nafion sample measured in a transverse field of 2 mT. (a) Relaxation rate showing a dramatic onset of motional narrowing above 175 K. (b) The corresponding fluctuation rate in a fast fluctuation regime, normalised to its value at the highest temperature in the measured range. (c) The frequency of the TF rotation signal, showing a shift that correlates with the fluctuation rate. This is the signature of a pseudo-diamagnetic signal orginating from a muonium state that is subject to rapid spin exchange [13]. The solid lines in each plot are a guide to the eye.

MuH_2O molecule that forms the muoniated version of the H_3O hydronium molecule would be a strong candidate for this pseudo-diamagnetic muonium state. A muon hyperfine coupling of order 200 MHz would be expected for such a radical on the basis of previous studies of the H_3O radical [14, 15].

4. Conclusion

Our muon measurements have demonstrated that implanted muons in Nafion predominantly stop in the ionic regions. The relaxation at temperatures above 150 K shows evidence of fast proton dynamics in hydrated samples. Correlation between the relaxation rate and the frequency shift observed for the TF rotation signal provides clear evidence that a pseudo-diamagnetic paramagnetic muon state is the dominant contributor to the muon spin relaxation signal in this higher temperature region. A MuH_2O analogue of the hydronium molecule was suggested to be a strong candidate for this paramagnetic state in a pseudo-diamagnetic regime. This poses a key question concerning the relationship between the dynamics of this molecule, as revealed by muons, and the mechanisms at play for the bulk transport of protons in hydrated Nafion. Diffusive transport of H_3O^+ hydronium ions, for example, has been suggested to be the dominant proton transport mechanism at lower levels of hydration [1], so the dynamical properties of MuH_2O molecules may indeed be relevant here. Further studies may be able to clarify this issue.

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