

## REVIEW

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## Infrared spectroscopy for understanding the structure of Nafion and its associated properties

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Significant effort has been invested previously to understand the effect of temperature and humidity on water uptake, water transport, structure, and proton conductivity of perfluorosulfonic acid (PFSA) ionomer membranes. One of the significant factors influencing the performance and durability of Nafion is its ability to retain and transport water. Water transport in Nafion is a strong function of sorption, ion exchange capacity, and transport properties of the membrane, which in turn, are functions of its structure and morphology. In addition to the operating conditions, pre-treatment conditions, additives, and the presence of cations significantly affect Nafion's morphology. Infrared spectroscopy (IR) is a powerful tool to gain insight into the properties of Nafion structure and properties. FTIR can monitor real-time changes in chemical interactions, molecular motions, and connectivity of ionic channels under varying operating conditions. FTIR has also been used to validate models developed to explain the dynamic behavior of polymer electrolyte membrane fuel cells. The potential of infrared spectroscopy to understand the impact of environmental changes on Nafion structure is immense but remains underutilized. This review provides a comprehensive summary of the assignment of vibrational modes of Nafion in various regions of the spectrum and sheds light on discrepancies concerning the allocation of vibrational modes to specific interactions.

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## 1 Introduction

Nafion is a perfluorosulfonic acid (PFSA) polymer developed by DuPont in 1966.<sup>1</sup> The cation transport properties of Nafion are central to its use in diverse applications. The biggest application for Nafion is in the chlor-alkali industry, but it also finds applications in fuel cells, electrolysis, catalysis, selective removal of various cations, batteries, sensors, and stimuli-responsive materials. Relevant to this review paper, Nafion is widely used as the polymer electrolyte membrane (PEM) in fuel cells and electrolyzers.

As shown in Fig. 1, Nafion consists of a polytetrafluoroethylene (PTFE) backbone with ionic side chains terminating in a sulfonic acid group. The hydrophobic PTFE backbone provides mechanical and chemical strength, while the sulfonic acid side chain is responsible for Nafion's proton transport properties. This combination of a hydrophobic backbone with a hydrophilic side chain results in a phase-separated morphology that is responsible for the unique transport properties of Nafion.<sup>2</sup> Other perfluorosulfonic acid polymers investigated in the literature include Aquivion,<sup>3</sup> Flemion,<sup>4</sup> Fumion,<sup>5</sup>

Aciplex,<sup>6</sup> 3M perfluorosulfonimide (PFIA) membrane terminated in sulfonic acid like other PFSA,<sup>7</sup> and PFSA from DOW chemicals.<sup>6</sup> The general structure of all these membranes is shown in Fig. 1, where  $m$ ,  $n$ ,  $x$ , and  $y$  vary depending on the supplier. PFSA's are usually characterized in terms of its equivalent weight (EW) and ion exchange capacity (IEC). EW is a measure of the concentration of sulfonic acid sites within the membrane, with higher EW indicating a lower degree of sulfonation. The presence of water results in the dissociation of sulfonic acid groups in the side chains, which enables proton transport. Water content in PFSA is usually described in terms of  $\lambda$  which is defined as the moles of water per mole of sulfonic

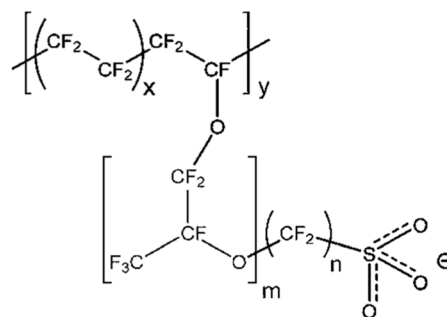


Fig. 1 Molecular structure of Nafion.

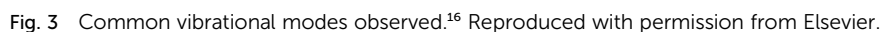
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Nafion was the first PFSA discovered which is also why it has been a topic of intensive research for more than 40 years. The use of Fourier Transform Infrared Spectroscopy (FTIR) to investigate the properties of perfluorosulfonate ionomers dates to the 1980s when Lowry and Mauritz<sup>10</sup> used it to study the effects of hydration. Dynamic water sorption, Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), water uptake studies, and proton conductivity changes have been used in the literature to understand the dynamics of water sorption and structure–property relationships in PFSA, as well as to understand the degradation mechanisms as a function of changing environmental factors for PFSA. Several other characterization tools that are periodically used for structural investigations of PFSA include X-ray Diffraction (XRD), Small

FTIR is a powerful tool to gain fundamental insights into the molecular level interactions within PFSA in a non-destructive manner and to relate them to its macroscale properties. FTIR can deduce local changes in the chemical environment of PFSA from changes in the vibrational frequency of the various bonds. Commonly observed vibrational modes in molecules is shown in Fig. 3. FTIR operates by measuring the interaction between matter and an applied electromagnetic field in the infrared region. When infrared radiation is incident on a sample, the incident energy is absorbed if the frequency of the photons coincides with the vibrational energy level of the molecule. When the environment around the molecule is changed, the vibrational frequencies of the various bonds change and so does the energy of the photon absorbed. These changes are recorded in the form of an FTIR spectra. A shift in the vibrational modes, changes in intensities, or the appearance and disappearance of peaks are accurate indicators of changes at the molecular scale in the vicinity of specific groups. Hence, FTIR represents a sensitive technique for measuring molecular level changes. Some of the common vibrational modes observed for a molecule are shown in Fig. 3.

The FTIR technique provides advantages such as ease of use and universality of applications. It is powerful because it offers unparalleled measurement speed with the ability to measure relevant frequencies within seconds. The short measurement time ensures that the sample measurement can be repeated to reduce noise in a matter of minutes. It also employs very



sensitive detectors with high optical throughput. FTIR is a self-calibrating instrument containing few moving parts which minimizes mechanical breakdown and errors induced by human intervention. It can measure a variety of samples and detect even the smallest amount of contamination which makes it a valuable tool.<sup>17</sup>

To fully utilize the potential of FTIR, it is critical to precisely assign the vibrational modes to specific interactions. Changes in those interactions can then be correlated to changes in the macroscale properties.<sup>3</sup> FTIR spectroscopy of a system like PFSA is, however, not easy. FTIR of protonated species is complicated because of the overlapping presence of various peaks corresponding to different functional groups and vibrational states.<sup>18</sup> This makes the study of hydrated Nafion a challenge leading to several unanswered questions and conflicting findings.<sup>19,20</sup> This is also the reason that most of the work on Nafion is addressed towards lower wavenumber region, below 2000 cm<sup>-1</sup> of the spectrum. Understanding the structure of Nafion has helped in the design of other types of membranes catering to various applications. It has also resulted in the development of new analytical techniques. Therefore, PFSA can continue to offer new possibilities when its chemistry is more completely understood.

## 2 Previous reviews

Several excellent reviews have been published on the structure–property relationship of Nafion. Mauritz and Moore<sup>21</sup> published a comprehensive review aimed at understanding the morphology of Nafion, the structure of its ionic clusters, and how SAXS, WAXS, and other characterization data come together to support the various models suggested in the literature. These authors found no model that could predict the behavior of Nafion in various environments and attributed it to the challenging nature of its structure. A recent review discussed advanced methods for understanding molecular ordering and features of conducting channels in Nafion membranes.<sup>22</sup> Hickner *et al.*<sup>23</sup> highlighted the problems associated with using different ionomers in the electrodes while using Nafion as the electrolyte membrane, and also comprehensively discussed past work aimed at understanding the properties of Nafion. Duncan *et al.*<sup>24</sup> published an elaborate review on the application of Nafion in ionic polymer transducers (IPT) and how the systematic investigation of its properties has helped design new polymers to improve IPT performance over time. Kusoglu *et al.*<sup>9</sup> compiled an extensive dataset from various studies to understand the structure–property correlation of Nafion. In a recent review, Choi *et al.*<sup>25</sup> highlighted the influence of structure on the crystalline domains of PFSA and the influence of the nanostructure on PFSA mechanical properties. Okonkwo *et al.*<sup>26</sup> comprehensively reviewed the degradation studies on Nafion. Yan *et al.*<sup>27</sup> examined the properties of Nafion thin films as opposed to membranes, and investigated aggregate structures in catalyst layers and film structure in detail.

This review collects and organizes the various FTIR investigations on Nafion to elucidate how this tool has helped to gain

fundamental insights into Nafion as it exists today, unfold its complex structure, and explain the observed property changes with various environmental changes. It aims to stimulate the use of FTIR for additional investigations of Nafion. This review also aims to highlight the discrepancies between FTIR assignments of Nafion and how its resolution would further help in understanding PFSA.

The review is organized as follows:

(1) We first examine how the understanding of vibrational modes of Nafion's sidechains has evolved over time. This includes determination of vibrational modes attributed to sulfonic acid groups in Section 3.1.1, ether group modes in Section 3.1.2, and C–S vibrational mode in Section 3.1.3. Vibrational modes under dry conditions for the side chain of Nafion are discussed in Section 3.2. The effects of annealing and aging (Section 3.3) on Nafion's properties by examining changes in the Nafion sidechain vibrational modes are henceforth discussed in Section 3.3. We also evaluate the reasons for discrepancies in the assignment of vibrational modes to the sidechains in each section and identify areas that need further work. This section discusses side chain vibrational modes that have laid the foundation for explaining Nafion transport properties over time.

(2) We review the influence of cations on the vibrational modes of Nafion's sulfonic acid groups and water environment in Section 3.4. This section highlights the complex nature of Nafion environment as a function of changing molecular environment of Nafion.

(3) Section 4 discusses studies relating to the assignment of vibrational modes to the polymer backbone of Nafion.

(4) Studies relating to the vibrational modes of Nafion due to the presence of water are discussed in Section 5. This section highlights how FTIR alone could explain complex transport properties of Nafion by closely following vibrational modes of water as a function of environmental changes, in conjunction with the changes in side chain vibrational modes.

## 3 Ionic vibrational region

Nafion is interesting for various applications because of its proton transport properties. Accordingly, we first consider the ionic vibrational region associated with the proton transport properties of the membrane. This region consists of vibrational modes associated with the Nafion side chain. The vibrational modes in this region belong to the stretching, bending and wagging vibrations from C–F, C–O–C, C–S, and SO<sub>3</sub><sup>-</sup>. The FTIR spectrum for as-received Nafion 212 under ambient conditions of 25 °C, 30% RH conditions is shown in Fig. 4, and the major vibrational modes observed for it along with their assignments are presented in Table 1. The region below 800 cm<sup>-1</sup> consists of overlapped peaks from bending, and wagging modes of side chain functional groups and represents the fingerprint for a given polymer. Changes in the fingerprint region are indicative of changes in the structure of the polymer.

Single functional group assignments have caused a lot of confusion for decades and are still a topic of debate. For example, some groups<sup>28,32</sup> assigned the peak at 512 cm<sup>-1</sup> to



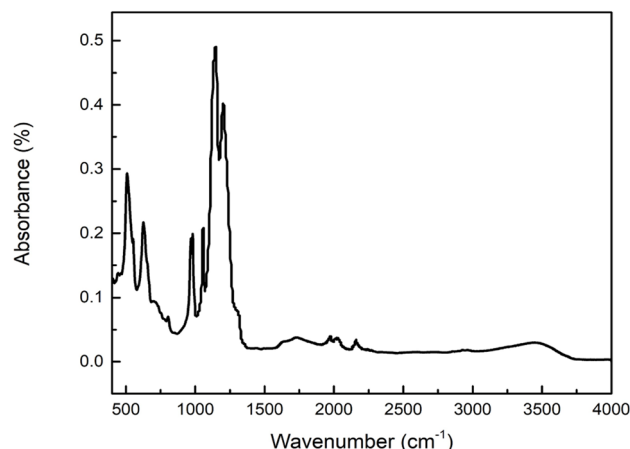


Fig. 4 FTIR spectra of Nafion 212 recorded at ambient conditions in our lab.

Table 1 Major vibrational modes of a Nafion side chain

Wavenumber (cm <sup>-1</sup> )	Assignment
513 <sup>28</sup>	Symmetric O-S-O stretching
553 <sup>28</sup>	Asymmetric C-F bending
629 <sup>29</sup>	CF <sub>2</sub> wagging
808 <sup>30</sup>	C-S stretching
970 <sup>18</sup>	C-O-C stretching
982 <sup>31</sup>	Asymmetric C-O-C stretching
1060 <sup>2</sup>	Symmetric SO <sub>3</sub> <sup>-</sup> stretching
1150 <sup>29</sup>	Asymmetric CF <sub>2</sub> stretching
1210 <sup>30</sup>	Symmetric CF <sub>2</sub> stretching
1315 <sup>18</sup>	Asymmetric SO <sub>3</sub> <sup>-</sup> stretching

asymmetric O-S-O stretching while others<sup>29</sup> assigned this peak to CF<sub>2</sub> rocking and wagging vibrations by comparing with the spectrum of polytetrafluoroethylene (PTFE) as shown in Fig. 5. The small peak observed at 731 cm<sup>-1</sup> was assigned to C-C stretching by some groups<sup>30</sup> while others<sup>29,33</sup> assigned it to CF<sub>2</sub> symmetric stretching. The accurate assignment of peaks in the FTIR spectra to specific vibrational modes is non-trivial, and therefore, still a matter of investigation in the research community. These issues will be explored in the following subsections.

### 3.1 Assignment of vibrational modes to Nafion side chains

A typical spectrum for the Nafion sidechain vibrational region is as shown in Fig. 6. The first known FTIR spectrum for Nafion was recorded in 1976 by Lopez *et al.*<sup>34</sup> who observed three major peaks for the Na<sup>+</sup> form of Nafion. OH stretching of water was observed at 3530 cm<sup>-1</sup>, C-F stretching at 2350 cm<sup>-1</sup>, and water scissoring at 1630 cm<sup>-1</sup>. The region between 500 cm<sup>-1</sup> and 1350 cm<sup>-1</sup> was opaque and could not be recorded. This problem was solved by Heitnerwurgin<sup>32</sup> by collecting reflectance spectra along with the absorbance spectra for Nafion. Assignments of vibrational modes for the Nafion-like system could be simplified by comparing its spectra with the spectra of simpler

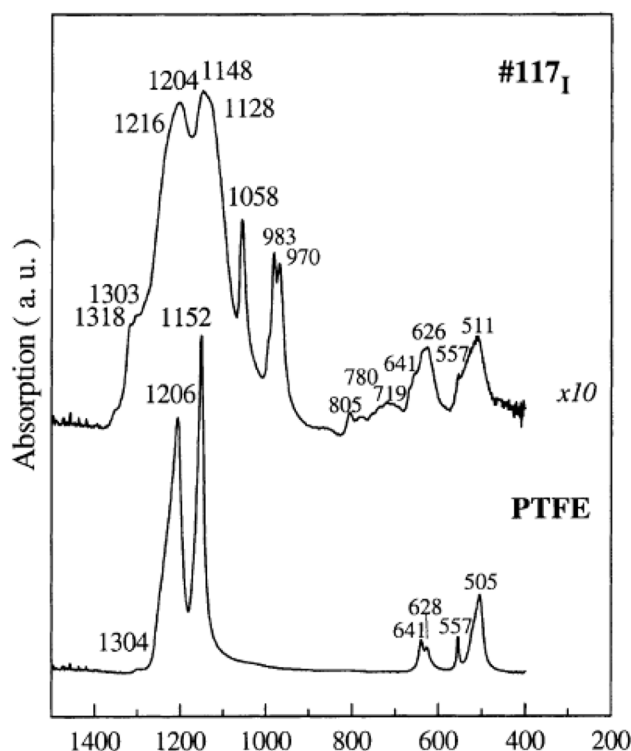


Fig. 5 Vibrational modes of Nafion 117 compared to PTFE vibrational modes.<sup>29</sup> Reproduced with permission from Elsevier.

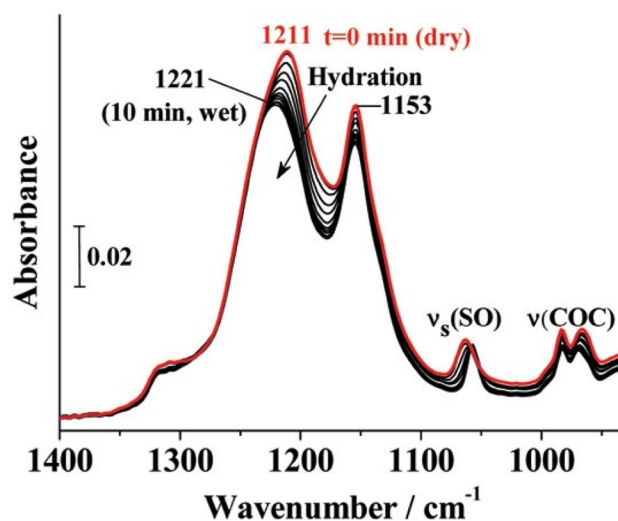


Fig. 6 Ionic vibrational region of Nafion.<sup>35</sup> Reproduced with permission from ACS Publications.

molecules containing the target functional group. Therefore, sulfonic acid group assignments for Nafion were made by comparing with the FTIR spectra of polystyrene sulfonic acid.<sup>32</sup> Similarly, C-O-C assignments were made by comparing with the spectra of polyoxymethylene,<sup>32</sup> and vibrational mode assignments of the Nafion backbone were made by comparing with the FTIR spectra of PTFE as shown in Fig. 5.

**3.1.1 Sulfonic acid vibrational modes.** Buzzoni *et al.*<sup>18</sup> studied the FTIR and Raman spectra of H<sub>2</sub>SO<sub>4</sub> and CF<sub>3</sub>SO<sub>3</sub>H





(triflic acid), because their acidic character is analogous to Nafion. Comparing the peak assignments for these acids with those of Nafion can help resolve its spectrum. They found that the spectra for aqueous concentrated acids were different from those of pure acids, likely resulting from the transfer of protons to the water species. Concentrated  $\text{CF}_3\text{SO}_3^-$  shows a strong absorption at  $1040\text{ cm}^{-1}$ ,  $\text{HSO}_4^-$  at  $982\text{ cm}^{-1}$ , and  $\text{SO}_4^{2-}$  at  $1050\text{ cm}^{-1}$ .  $1060\text{ cm}^{-1}$  was therefore assigned to  $\text{SO}_3^-$  stretching in Nafion. Later, Danilczuk *et al.*<sup>19</sup> compared the FTIR spectrum of Nafion with Aquivion,<sup>3</sup> perfluoroimide acid (PFIA) made by 3M,<sup>7</sup> and other PFSA<sup>6</sup> polymers with sulfonic acid side chains like Nafion. They claimed  $1060\text{ cm}^{-1}$  as the  $\text{SO}_3^-$  stretching mode after comparing the calculated assignments with the experimental results in agreement with Buzzoni *et al.*<sup>18</sup> Density Functional Theory (DFT) calculations performed using X3LYP exchange correlation functional taking  $\lambda = 3$  show that  $1060\text{ cm}^{-1}$  is dominated by the asymmetric stretching of the side chain ether group coupled to  $\text{SO}_3^-$  symmetric stretching in agreement with findings of other groups.<sup>36,37</sup> A similar result was obtained with DFT calculations when using the B3LYP exchange–correlation functional.<sup>38</sup> Loupe *et al.*<sup>39</sup> found  $1060\text{ cm}^{-1}$  to be dominated by the C–O–C mode based on their DFT calculations for  $\lambda = 4$ . These findings suggest that  $1060\text{ cm}^{-1}$  mode is not a single functional mode corresponding to  $\text{CF}_3\text{SO}_3^-$  as initially speculated but is rather a group mode of ether stretching and sulfonic acid stretching mode.

Additional peaks are observed for Nafion in a dehydrated state. Two vibrational modes at  $1420\text{ cm}^{-1}$  and  $910\text{ cm}^{-1}$  are observed along with the absence of peak at  $1060\text{ cm}^{-1}$ . These modes were resolved by comparing Nafion spectra to that of undissociated  $\text{CF}_3\text{SO}_3\text{H}$ .  $1420\text{ cm}^{-1}$  was assigned to S=O stretching in Nafion and  $910\text{ cm}^{-1}$  to S–OH stretching.<sup>18</sup> Two additional modes observed at  $1150\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  were ascribed to the  $\text{SO}_3^-$  asymmetric stretching by comparing Nafion with the spectrum of Perfluoro(2-ethoxyethane)sulfonic acid (PES) where these modes are observed at  $1134\text{ cm}^{-1}$  and

$1289\text{ cm}^{-1}$ .  $\text{SO}_3^-$  is a symmetric structure and shows a doubly degenerate asymmetric stretching mode. But the strong polarization of the hydronium ion could disturb this symmetry and result in a split peak as was observed at  $1150\text{ cm}^{-1}$  and  $1200\text{ cm}^{-1}$  in Nafion.<sup>20,40</sup> The asymmetric stretching peak of sulfonic acid at  $1150\text{ cm}^{-1}$  was found to be a strong function of hydration.<sup>20</sup> For a partially hydrated membrane, this peak was spread over  $1000\text{--}1100\text{ cm}^{-1}$ , blue shifting (increase in wave-number) by  $40\text{--}60\text{ cm}^{-1}$  with increasing hydration.<sup>20</sup>

**3.1.2 Vibrational modes of the C–O–C group.** The modes observed at  $970\text{ cm}^{-1}$  and  $980\text{ cm}^{-1}$  in the Nafion spectrum were assigned to C–O–C stretching.<sup>32</sup> The peak observed in Nafion at  $980\text{ cm}^{-1}$  was not observed for Aquivion. Aquivion lacks a C–O–C side group, which supports the assignment of  $980\text{ cm}^{-1}$  mode in Nafion to the C–O–C backbone group.<sup>19</sup> Aquivion shows a peak at  $970\text{ cm}^{-1}$  and it has a C–O–C group closer to the  $-\text{SO}_3\text{H}$  group, which supports the assignment of  $970\text{ cm}^{-1}$  to the C–O–C side chain group of Nafion.<sup>19</sup> Two model compounds, PFMHSA, and PFEESA shown in Fig. 7 were investigated by FTIR which help understand mode assignments. PFEESA lacks the backbone C–O–C group and it also did not show the peak at  $980\text{ cm}^{-1}$  which further supports these assignments.<sup>19</sup> This was further confirmed by the FTIR recorded for the 3M membrane which also lacks a C–O–C group close to its sidechain, and therefore did not show any mode at  $970\text{ cm}^{-1}$ .<sup>39</sup>

Webber *et al.*<sup>36</sup> claimed from their DFT calculations performed using X3LYP functional for  $\lambda = 0$  to 10, that the groups at  $983\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$  were dominated by  $-\text{SO}_3^-$  symmetric stretching coupled to the ether group mode. Okamoto *et al.*<sup>38</sup> also found from their DFT calculations that the experimentally observed peak at  $980\text{ cm}^{-1}$  is dominated by symmetric vibrations of  $-\text{SO}_3^-$  in agreement with Webber *et al.*<sup>36</sup> Loupe *et al.*<sup>39</sup> used DFT calculations using X3LYP functional and molecular dynamic calculations performed using LAMMPS for  $\lambda = 0$  to 20, and found that the  $970\text{ cm}^{-1}$  mode is also dominated by the –

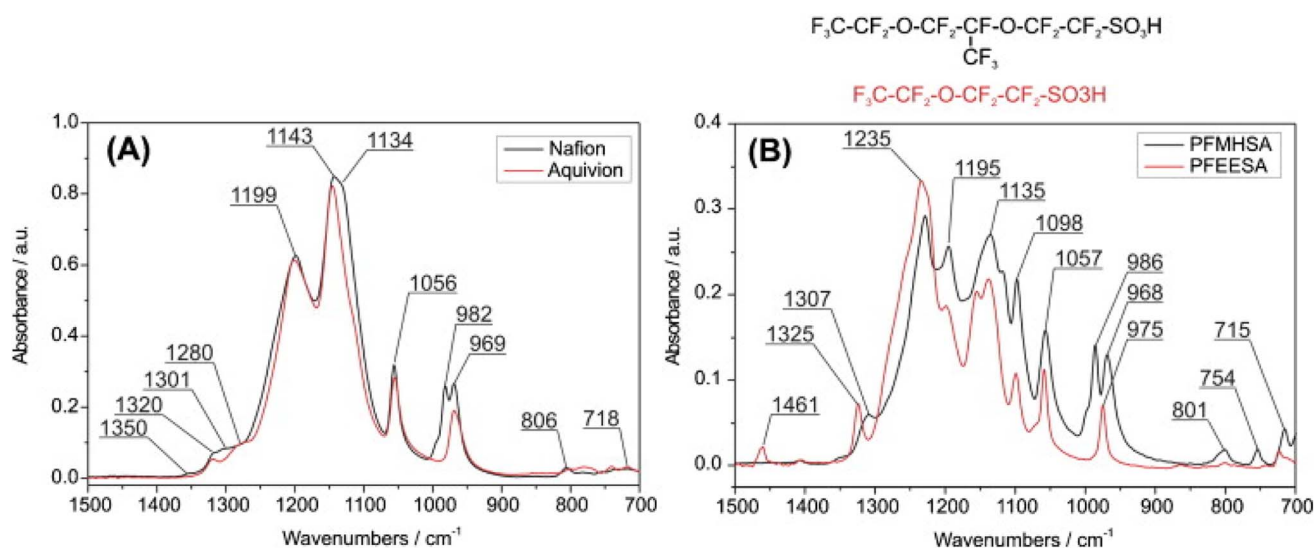


Fig. 7 (a) Spectra of Nafion compared to Aquivion (A) and other model compounds (B).<sup>19</sup> Reproduced with permission from Elsevier.



$\text{CF}_3\text{SO}_3^-$  stretching mode. In marked contrast to all the above studies, Danilczuk *et al.*<sup>19</sup> calculated C–O–C stretching modes to be in the  $800\text{ cm}^{-1}$  region suggesting none of the modes in the  $900\text{--}1000\text{ cm}^{-1}$  could come from the C–O–C mode. They claimed this based on the investigation of the model compounds and correlating the FTIR of model compounds to Nafion and Aquivion. They assigned  $980\text{ cm}^{-1}$  to the stretching mode of  $-\text{CF}_2$  groups in the side chain in agreement with Ferrari *et al.*<sup>41,42</sup> who assigned this mode to the stretching of  $-\text{CF}$  in the  $(-\text{CF}_2-\text{CF}(\text{R})-\text{CF}_3-)$  groups of the sidechains that is absent in Aquivion.

The above studies suggest that  $980\text{ cm}^{-1}$  and  $970\text{ cm}^{-1}$  modes have contributions from C–O–C stretching mode, C–S stretching mode,  $-\text{SO}_3^-$  symmetric stretching mode and possibly C–F stretching modes that are strongly coupled to each other. Different modes could dominate at different hydration numbers and measurement conditions which could explain the discrepancy observed between the studies.

Another peak at  $910\text{ cm}^{-1}$  is observed in the vibrational spectra of Nafion. This peak at  $910\text{ cm}^{-1}$  was assigned to  $-\text{SO}_3\text{H}$  symmetric stretching with C–O–C symmetric stretching as the secondary contributor.<sup>39</sup> The modes at  $910\text{ cm}^{-1}$ , and  $970\text{ cm}^{-1}$ , were found to be a strong function of hydration with  $C_1$  (single functional group mode) dominating below  $\lambda = 3$  and  $C_{3v}$  (three-fold symmetry) dominating above it.<sup>39</sup> The  $980\text{ cm}^{-1}$  mode was not found to change much with hydration.<sup>36</sup> This indicates that the  $980\text{ cm}^{-1}$  mode might not be dominated by  $-\text{SO}_3^-$  symmetric stretching as calculated by Webber *et al.*<sup>36</sup> and others.<sup>38</sup>  $980\text{ cm}^{-1}$  assignment to C–O–C stretching mode in the backbone or to the  $-\text{CF}$  stretching mode of the Nafion side chain follows the experimental observation that this mode is independent of hydration. However, further studies are needed to validate these findings. The peak at  $970\text{ cm}^{-1}$  is likely a group mode of C–O–C stretching and  $-\text{SO}_3^-$  stretching, with the dominating mode being a function of hydration. Further experimental studies could help validate these assignments further.

**3.1.3 Vibrational modes of the C–S group.** DFT calculations for dissociated PES in the gas phase showed  $967\text{ cm}^{-1}$  as the

C–S symmetric stretching mode. This mode shifted to  $952\text{ cm}^{-1}$  for undissociated PES.<sup>20</sup> The C–S stretching mode for Nafion was calculated at  $974\text{ cm}^{-1}$  for the undissociated form and at  $1019\text{ cm}^{-1}$  for the dissociated form.<sup>20</sup> Etheve *et al.*<sup>43</sup> assigned the peak at  $798\text{ cm}^{-1}$  to the C–S mode in agreement with Lage *et al.*<sup>30</sup> Danilczuk *et al.*<sup>19</sup> calculated that the C–O–C stretching mode should be observed in the  $800\text{ cm}^{-1}$  vibrational region while other authors believe that  $970\text{ cm}^{-1}$  is dominated by stretching modes of C–O–C and  $-\text{SO}_3^-$  as discussed in the previous section. Aquino *et al.*<sup>40</sup> calculated that the C–S mode has a main peak at  $1066\text{ cm}^{-1}$  with side modes at  $897\text{ cm}^{-1}$  and  $1180\text{ cm}^{-1}$  for Nafion in sodium form. However, the peak at  $1066\text{ cm}^{-1}$  is ascribed to the group mode of  $\text{SO}_3^-$  and C–O–C stretching as mentioned in the previous section.<sup>19,39</sup>

Since C–S vibrations are strongly coupled to the vibrational modes of C–O–C and  $\text{SO}_3^-$ , their vibrational modes span the range of  $800\text{--}1300\text{ cm}^{-1}$ .<sup>40</sup> Various groups have tried to decouple C–S stretching mode from the ether and sulfonic acid stretching modes in the side chain, and assign the observed peaks to a single vibrational mode which is a reason for controversies in the assignment of C–S modes. DFT calculations also vary widely in terms of the hydration level and the solvation model used for calculations. Peak assignment of  $800\text{ cm}^{-1}$  mode remains unresolved and no clear agreement of its assignment to a specific vibrational mode exists in the literature.

It is pertinent to study C–S, C–O–C and  $-\text{SO}_3^-$  as group modes rather than single functional modes. A detailed investigation on changes in spectra with hydration and subsequent dehydration in the  $800\text{--}1300\text{ cm}^{-1}$  would also provide helpful insights to accurately assign each of these peaks observed to specific vibrational modes.

### 3.2 Sulfonic acid group modes for dry Nafion

The vibrational spectrum of dry protonated form of Nafion was compared with the  $\text{Na}^+$  form of dry Nafion by Negro *et al.*<sup>44</sup> The peak at  $1410\text{ cm}^{-1}$  was absent in dry Nafion- $\text{Na}^+$  but was present in dry Nafion- $\text{H}^+$ . This peak was therefore assigned to the antisymmetric stretching mode of  $-\text{SO}_3\text{H}$  in the undissociated

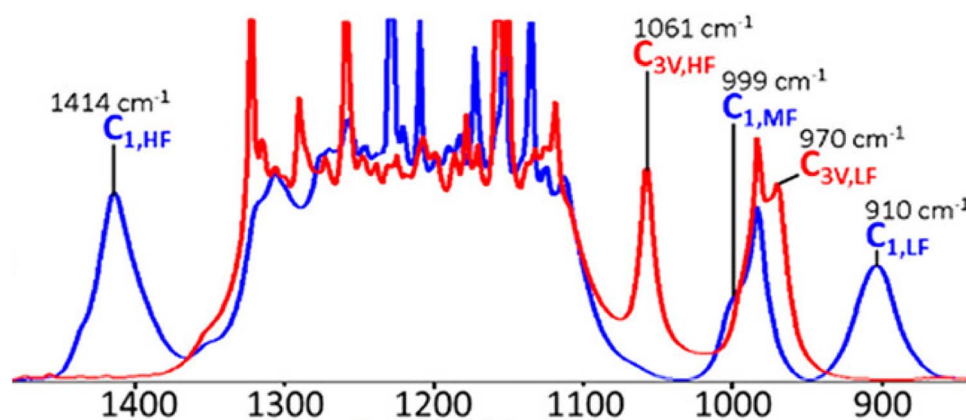


Fig. 8 DFT calculated spectra for fully dehydrated (blue) and fully hydrated membrane (red).<sup>39</sup> Reproduced with permission from ACS Publications.



form of Nafion.<sup>44</sup> This assignment was further supported by the disappearance of the sulfonic acid symmetric stretching mode at  $1060\text{ cm}^{-1}$  on dehydration and simultaneous appearance of a peak at  $1410\text{ cm}^{-1}$ <sup>18,51,53</sup> as shown in Fig. 8.  $C_1$  stands for single functional modes while  $C_{3v}$  indicates coupled vibrational modes. DFT calculations also corroborated the assignment of  $1414\text{ cm}^{-1}$  to the undissociated sulfonic acid.<sup>34</sup> The growth of the  $1440\text{ cm}^{-1}$  band in treated membranes was accompanied by decreases in the intensities of water stretching and bending bands which are associated with the water molecules, which further supports this mode to be associated with dehydration of Nafion, anhydride formation.<sup>45</sup>

Contrary to the above studies, Los Alamos National Lab (LANL) did extensive investigation on the source of  $1400\text{ cm}^{-1}$  mode observed in the FTIR of Nafion. Researchers at LANL could not see peaks at  $1400\text{ cm}^{-1}$  irrespective of the membrane aging protocol followed.<sup>46</sup> Interestingly enough, LANL was able to reproduce this peak when they used Nylon as their material in their conditioning chamber. However, when using a 100% Teflon in the conditioning chamber, the peak was not present.<sup>46</sup>

Coms *et al.*,<sup>47</sup> in agreement with LANL, did not agree with the assignment of the  $1440\text{ cm}^{-1}$  peak to undissociated  $-\text{SO}_3\text{H}$  acid stretching mode and argued that if it was indeed anhydride, a peak near  $750\text{ cm}^{-1}$  should have been observed. They found a blue shift in the  $1440\text{ cm}^{-1}$  mode when Nafion was deuterated or exchanged with ammonium ions containing N14 and N15 isotopes. They argued that the  $1440\text{ cm}^{-1}$  mode is a bending mode of water significantly red shifted due to a complex change in the structure of water channels on dehydration. LANL also ascribed this peak to the impurities in the system.<sup>46</sup>

Another peak at  $2720\text{ cm}^{-1}$  is observed in Nafion. Since this peak shows a monotonic decrease with increasing hydration, it was ascribed to undissociated  $-\text{SO}_3\text{H}$  by some groups.<sup>42,48</sup> Other groups assign at  $2720\text{ cm}^{-1}$  mode to the Evans window (a local minimum resulting from various resonances) from overtones of bending modes and Fermi resonances.<sup>18</sup> Ferrari *et al.*<sup>41</sup> did not observe peaks at  $1410\text{ cm}^{-1}$  mode, which is typical of  $-\text{SO}_3\text{H}$ , alongside  $2720\text{ cm}^{-1}$  peak and therefore disfavored assignment of the  $2720\text{ cm}^{-1}$  peak to the  $-\text{SO}_3\text{H}$  mode.

The above studies indicate that the mode at  $1400\text{ cm}^{-1}$  is likely not associated to anhydride formation as speculated. This peak also does not appear when Nafion is exchanged with sodium ions, but appears when exchanged with ammonium ions or deuterated water molecules. This implies that this mode could be related to the water molecules associating with the sulfonic acid groups. However, the limited number of studies performed on this subject makes it difficult to draw conclusions. Nevertheless, it seems like this mode is more complex than anhydride formation on Nafion drying speculated in the literature and needs to be further studied.

### 3.3 Changes in sidechain vibrational modes as a function of hydration

Proton transport in Nafion is widely accepted to occur *via* two mechanisms, vehicular and proton hopping. The proton hopping mechanism is prevalent under medium and lower

levels of hydration when the protons are able to hop from one sulfonic site to the other. On the other hand, the vehicular or Grotthuss mechanism prevails under high levels of hydration and involves the transfer of protons by successive breaking and forming of covalent bonds across a chain of water molecules much like the transport of protons in bulk water.<sup>9</sup> The water transport mechanism in Nafion can be well interpreted by following the changes in the stretching modes of sulfonic acids and ether groups in the side chain as a function of hydration. The vibrational modes of the backbone are found to be unchanged with hydration.  $-\text{CF}_2$  bending modes at  $511\text{ cm}^{-1}$  and  $626\text{ cm}^{-1}$  were found to be unaffected by hydration as also the mode at  $983\text{ cm}^{-1}$ .<sup>2,29</sup>

Nafion FTIR spectra show two distinct peaks at  $1740\text{ cm}^{-1}$  and  $1630\text{ cm}^{-1}$ , which exhibit different behaviors during hydration/dehydration.  $1650\text{ cm}^{-1}$  mode was assigned to water hydrogen bonding with other water molecules and sulfonic acid sites.<sup>29</sup> The  $1720\text{ cm}^{-1}$  mode was assigned to water bound to protons.<sup>35</sup>

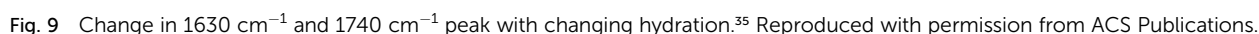
The mode at  $1650\text{ cm}^{-1}$  is assigned to the highly confined hydronium ion for  $3 \leq \lambda \leq 6$  which was found to shift to  $1635\text{ cm}^{-1}$ , representing bulk water, as  $\lambda$  was further increased beyond 6. It was observed that sulfonic acid groups are completely dissociated for  $1 \leq \lambda \leq 2$ , which corresponds to 19% RH<sup>49</sup> in agreement with Ferrari *et al.*<sup>41</sup> who found complete dissociation of sulfonic acid groups for  $\lambda$  between 1.5 to 2. Leuchs and Zundel<sup>50</sup> also found that at sulfonic acid sites are completely dissociated  $\lambda = 1.6$ .

The mode at  $1650\text{ cm}^{-1}$  disappears slowly on dehydration as shown in Fig. 9. When the membrane is completely dehydrated at  $100^\circ\text{C}$ , no peaks are observed in the  $1600\text{ cm}^{-1}$  region.<sup>47</sup> Peaks around  $1600\text{ cm}^{-1}$  are the first to disappear on dehydration which is associated with the solvation sphere of water.<sup>18</sup> This implies that as the membrane is dehydrated, the non-hydrogen bonded free water reduces while the water tightly bonded to sulfonic acid remains even at low  $\lambda$ .

At 20% RH, surface diffusion of water is dominant. Water is tightly bound to  $-\text{SO}_3^-$  up to 54% RH and the proton hopping is the dominant proton transport mode while Grotthuss diffusion is not present.<sup>49</sup> This was rationalized by the consistent presence of the  $1720\text{ cm}^{-1}$  peak. Beyond 54% RH, water transitions to the bulk phase and can no longer exist as  $\text{H}_3\text{O}^+$  and Grotthuss diffusion commences evident by the rise in intensity of the bulk water mode at  $1635\text{ cm}^{-1}$ <sup>49</sup> as shown in Fig. 9.

In a completely dehydrated membrane, a peak is observed at  $1440\text{ cm}^{-1}$ .<sup>51</sup> Lage *et al.*<sup>30</sup> observed peak broadening at  $1060\text{ cm}^{-1}$  on drying which is attributed to internal dipole relaxation of  $-\text{S}-\text{O}$  as water is slowly removed. The mode at  $1060\text{ cm}^{-1}$  vanishes in a completely dehydrated membrane with the simultaneous growth of the  $1440\text{ cm}^{-1}$  mode.<sup>18</sup> The intensity of the asymmetric  $\text{S}-\text{O}$  stretching mode at  $1210\text{ cm}^{-1}$  was found to increase with dehydration along with the simultaneous decrease in the symmetric  $-\text{S}-\text{O}$  stretching mode intensity at  $1060\text{ cm}^{-1}$ , blue shifted to higher wavenumbers as hydration decreased.<sup>52</sup> Nuclear Magnetic Resonance (NMR) confirmed a strong correlation between membrane water content and  $-\text{SO}_3^-$  symmetric stretching mode shifting.<sup>30</sup> The





Aging decreased the proton conductivity for various membranes owing to dehydration and subsequent loss in proton conductive sites ultimately leading to decreased water content. Changes in dissociated and undissociated sulfonic acid stretching mode at  $1060\text{ cm}^{-1}$ ,  $1440\text{ cm}^{-1}$  respectively, and the peaks assigned to water stretching modes at  $1630\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$  have been used to explain the changes in the water uptake and proton transport of Nafion when subjected to aging. The next section reviews studies of Nafion exchanged with cations to explore the effect of differing environment on Nafion vibrational modes and gain a deeper understanding of Nafion structure and transport properties.



Sulfonic acid symmetric stretching is found to be strongly influenced by the counterion as shown in Fig. 11. The interactions between cations and the sulfonate groups in the fully hydrated Nafion membranes follow the order  $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$  for the alkali metal cations, and  $\text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$  for the alkaline earth metal cations.<sup>56</sup> The  $\text{SO}_3^-$  symmetric stretching mode at  $1060\text{ cm}^{-1}$  was found to shift to higher wavenumbers as the alkaline metal ion radius increased due to reduced hydrogen bonding.<sup>30</sup> Li showed the strongest shift for the  $\text{SO}_3^-$  symmetric stretching mode,  $1073\text{ cm}^{-1}$  for the dry sample and  $1058\text{ cm}^{-1}$  for the wet sample<sup>10</sup> due to strong polarization of the  $\text{S-O}$  group. Peak shifting of the  $\text{SO}_3^-$  mode also starts at lower mole fractions of cations for smaller cations compared to heavier cations.<sup>10</sup> Little or no shift for  $\text{SO}_3^-$  stretching vibrational mode was observed for large sized cations due to weak polarization.<sup>10</sup> For the 3M PFIA, symmetric stretching of the

Species	Wavelength $\lambda$	Frequency $\nu_{\text{SO}_3^-} / \text{cm}^{-1}$
Cs <sup>+</sup>	8.5	1055
Rb <sup>+</sup>	9.5	1058
K <sup>+</sup>	10.5	1060
Ba <sup>2+</sup>	14.5	1064
Sr <sup>2+</sup>	16.5	1069
Ca <sup>2+</sup>	17.5	1073
Na <sup>+</sup>	17.5	1065
Mg <sup>2+</sup>	17.5	1059
Li <sup>+</sup>	19.5	1071
H <sup>+</sup>	23.5	1058

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organic vs. inorganic cations and could result from the varying polarizability of the cation to  $-\text{SO}_3^-$  or its preferential localization in hydrophobic regions of the membrane.<sup>10</sup>

Water permeability was found to be lower for membranes exchanged with metal ions because of their tendency to complex with  $-\text{SO}_3\text{H}$  groups causing cross-linking of channels.<sup>58</sup> However, the effective water content of the membrane is a function of the cation type with higher charge density cations holding more water. For  $\text{Li}^+$  and  $\text{La}^{3+}$  forms of Nafion, the bending mode for water at  $1600\text{ cm}^{-1}$  in Nafion could be resolved into two distinct components as shown in Fig. 12. These split peaks were not observed for other cations.<sup>59</sup> These split bands indicate two distinct water environments for Nafion exchanged with these cations showing strong polarization effect resulting in a low frequency mode around  $1616\text{ cm}^{-1}$  and a high frequency mode around  $1629\text{ cm}^{-1}$ .<sup>59</sup>

The bending vibrational mode of water around  $1650\text{ cm}^{-1}$  blue shifted with the decrease in cation radius due to increased H bonding.<sup>30</sup> The frequencies of the water stretching peak around  $3690\text{ cm}^{-1}$  and  $3500\text{ cm}^{-1}$  decrease with a decrease in cation radius. This was attributed to polymer contraction causing increased interaction with the  $-\text{C}-\text{F}$  backbone, and stronger interaction of the cation with water by hydrogen bonding, respectively.<sup>30</sup>

For the  $-\text{O}-\text{H}$  stretching region of Nafion, two vibrational peaks (A and B) were observed for cation exchanged membranes as shown in Fig. 13.<sup>59,60</sup>

Two distinct kinds of proton environments are possible in Nafion  $\text{OH}\cdots\text{F}$  and  $\text{OH}\cdots\text{O}$ , resulting in three different kinds of water environments, assigned as AA, BB, and AB. Peak A was ascribed to protons associated with the fluorocarbon backbone while peak B was ascribed to protons involved in hydrogen bonding. Therefore, AA refers to  $-\text{O}-\text{H}$  involved in hydrogen bonding with water molecules in the fluorocarbon phase  $\text{A}\cdots\text{OH}\cdots\text{A}$ , AB refers to  $-\text{O}-\text{H}$  involved in hydrogen bonding with

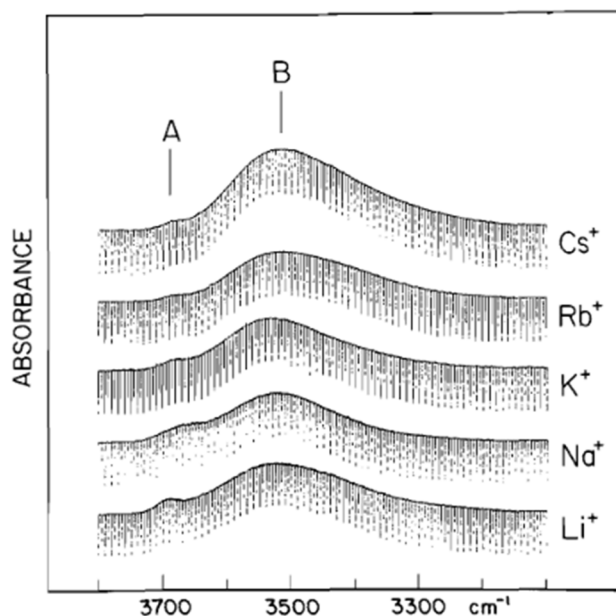


Fig. 13 Vibrational peaks for the  $-\text{O}-\text{H}$  stretching region of Nafion.<sup>59</sup> Reproduced with permission from Copyright clearance.

water at the interface of the fluorocarbon and the bulk water and BB refers to  $-\text{O}-\text{H}$  hydrogen bonded to water in the bulk phase  $\text{B}\cdots\text{OH}\cdots\text{B}$  on both sides.<sup>56</sup> BB and AA peak formation was found to be correlated to the basic strength of the Lewis acid. AB is the predominant mode when the acid strength of the cation matches the acid strength of the sulfonate ion ( $=0.27$ ), otherwise BB is found to predominate.<sup>59</sup>

The above studies show that the type of counterion (*viz.* its radius and charge density) significantly influences the water environment of Nafion. The interaction of the sidechain with the backbone is also affected by the type of counterion present in Nafion. It is also curious to note that no simple rule can explain the behavior of Nafion for all cation types, which again highlights the complex behavior of Nafion. For example,  $\text{Mg}^{2+}$  does not follow the expected trend of peak shifting for the  $-\text{SO}_3^-$  symmetric stretching mode for which no explanation exists.<sup>56</sup> However, it is clear from the previous section that Nafion structural investigation becomes easier by exchanging Nafion with cations. For example, peak shifting of  $1060\text{ cm}^{-1}$  with different cations confirm this mode is associated to  $-\text{SO}_3^-$  stretching mode with contributions from  $-\text{C}-\text{O}-\text{C}-$  stretching possible. Further, the bending mode of water around  $1600\text{ cm}^{-1}$  ascribed to bulk water in previous section, showed blue shifting with cation radius. This attests to the fact this mode likely represents bulk water phase in agreement with previous studies.

## 4 Vibrational modes of the Nafion backbone

Vibrational modes for the Nafion backbone corresponding to  $-\text{CF}-\text{CF}-$  were assigned by comparing Nafion's FTIR spectra with

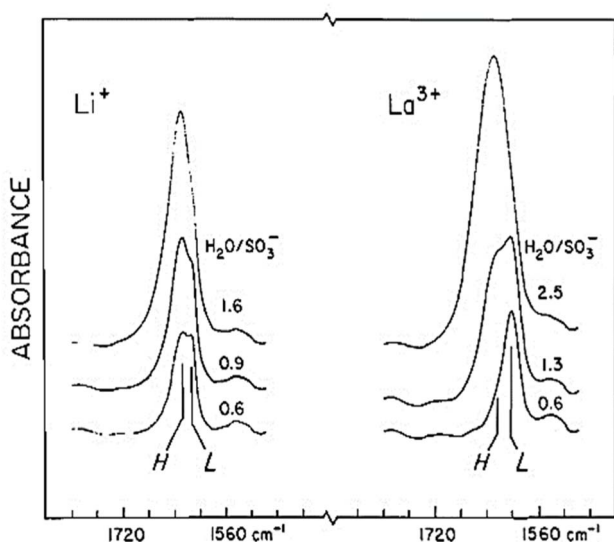


Fig. 12 Nafion spectrum for  $\text{Li}^+$  and  $\text{La}^{3+}$  forms of Nafion.<sup>59</sup> Reproduced with permission from Copyright clearance.

that of PTFE as shown in Fig. 4. Vibrational modes for PTFE were observed at 505  $\text{cm}^{-1}$ , 557  $\text{cm}^{-1}$ , 628  $\text{cm}^{-1}$ , 641  $\text{cm}^{-1}$ , 1152  $\text{cm}^{-1}$ , and 1206  $\text{cm}^{-1}$ .<sup>29</sup> Therefore, the peaks observed in Nafion at these wavenumbers were assigned to  $-\text{CF}-\text{CF}-$  stretching modes in Nafion. The peak observed at 1120  $\text{cm}^{-1}$  was assigned to  $-\text{C}-\text{C}$  symmetric stretching.<sup>40</sup> The peaks at 1108  $\text{cm}^{-1}$  was ascribed to  $-\text{C}-\text{F}$  stretching<sup>40</sup> while the peaks at 1156  $\text{cm}^{-1}$  and 1229  $\text{cm}^{-1}$  were assigned to the symmetric and asymmetric C-F stretching, respectively.<sup>29</sup> The assignment of vibrational modes to Nafion backbone is straightforward and not complicated by overlapping peaks and interference from other vibrational modes as discussed in the past section.

## 5 OH vibrational region of Nafion

Proton transport and preventing gases on the anode and cathode sides from mixing with each other are the two critical functions of the electrolyte in fuel cells and electrolyzers. Nafion exists as a phase-segregated structure comprising the main hydrophobic backbone and ionic sidechains. This has implications for proton transport which varies with the degree of hydration. IR pump probe spectroscopy indicated that the energy levels of the modes within Nafion are correlated with their vibrational lifetimes. Two vibrational lifetimes were observed for  $\lambda = 3$  at 3.2 ps and 8.6 ps strongly suggesting that Nafion has two different kind of water environments. The vibrational lifetimes were found to change with hydration suggesting that there is restructuring of the hydrophilic domain with hydration.<sup>61</sup> Therefore, understanding the changes in OH vibrational modes with hydration is instrumental in understanding the changes in the membrane's proton transport channels and proton transport mechanisms with varying  $\lambda$ .<sup>62</sup>

### 5.1 Assignment of frequencies

As the water content in the membrane changes, so do the interactions of water with the various functional groups in Nafion. This also modifies the  $-\text{OH}$  stretching modes observed in Nafion. Therefore, changes in the water bending and stretching modes can serve as effective probes for the effect of hydration on Nafion's transport properties. The vibrational spectra for  $-\text{OH}$  in Nafion is, however, not straightforward. It is complicated by the overlapping from overtones of lower frequency modes and Fermi resonances resulting from two vibrational modes appearing at the same frequency.<sup>18</sup> Studying the deuterium-substituted OD stretching is useful for deconvoluting the overlapped peaks observed in the spectra. The mass effect causes the hydroxyl stretching of the deuterium-substituted group, OD, to be red-shifted to around 2500  $\text{cm}^{-1}$  relative to the OH stretch which helps in data analysis.

The infrared spectrum of HOD in liquid water was compared to Nafion. Two peaks were observed at 3660  $\text{cm}^{-1}$  (Peak A) and 3520  $\text{cm}^{-1}$  (Peak B) as shown in Fig. 13 suggesting two different kinds of water surroundings in Nafion.<sup>59,63,64</sup> This was also implied by the observation of two peaks at 1740  $\text{cm}^{-1}$  and 1630  $\text{cm}^{-1}$  in the sidechain vibrational region of Nafion.<sup>35</sup> HOD was impregnated in Nafion to verify the assignment of

frequencies in the 3000  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  range. Since HOD has distinct asymmetric and symmetric modes dominated by OD and OH stretching respectively, resolution of the peaks is easier. Using this strategy, it was found that the 3668  $\text{cm}^{-1}$  mode is the symmetric stretching mode of HOD with the OH bond directed towards the hydrophobic phase.<sup>65</sup> 3520  $\text{cm}^{-1}$  mode was assigned to water hydrogen bonding with other water molecules blue shifted from 3400  $\text{cm}^{-1}$  compared to bulk water due to weaker hydrogen bonding interactions.<sup>66</sup>

Ferrari *et al.*<sup>41</sup> observed two peaks at 3005  $\text{cm}^{-1}$  and 3280  $\text{cm}^{-1}$  for dehydrated Nafion. At 5% RH, a peak was observed at 3470  $\text{cm}^{-1}$  which was assigned to less strongly bonded water molecules. As the RH was increased to 40%, another peak at 3515  $\text{cm}^{-1}$  started appearing.<sup>41</sup> Peak at 3700  $\text{cm}^{-1}$  was assigned to the free OH group.<sup>64</sup> This mode was also observed by Falk *et al.*<sup>60</sup> and was ascribed to AA interactions referring to water primarily in the fluorocarbon phase and shown in Fig. 13. This peak was later assigned to the OH stretching mode for interfacial water by Hofmann *et al.*<sup>67</sup>

Several other peaks were observed in this region by various groups. Laporta *et al.*<sup>68</sup> assigned the peak at 3370  $\text{cm}^{-1}$  to the OH stretching of residual water in the membrane after dehydration. Peaks at 3414  $\text{cm}^{-1}$  and 3202  $\text{cm}^{-1}$  were assigned to the water-free  $\text{H}_3\text{O}^+$  mode, due to their presence with the peak at 1700  $\text{cm}^{-1}$  ascribed to hydronium ions strongly hydrogen bonded to sulfonate.<sup>29</sup> This aligns with the observations of Ferrari *et al.*<sup>41</sup> who observed peaks at 3280  $\text{cm}^{-1}$  and 3470  $\text{cm}^{-1}$  for a dehydrated Nafion. A peak at 3400  $\text{cm}^{-1}$  was observed for triflic acid associated with two water molecules.<sup>69</sup> This further attests that the peaks around 3400  $\text{cm}^{-1}$  in Nafion are indicative of low water content tightly bound to sulfonic acid sites. Basnayake *et al.*<sup>64</sup> observed that on dehydration, the peak at 3690  $\text{cm}^{-1}$  ascribed to interfacial OH stretching mode diminishes and a sharp peak at 2670  $\text{cm}^{-1}$  appears. This agrees with the results from Ren *et al.*<sup>69</sup> who observed a peak at 2800  $\text{cm}^{-1}$  for triflic acid with  $\lambda = 1$ , nearly dehydrated state.  $\text{H}_3\text{O}^+$  strongly H-bonded to sulfonate was assigned to 2980  $\text{cm}^{-1}$  mode in the previous section.<sup>29</sup> On complete dehydration, the peak at 2750  $\text{cm}^{-1}$  vanished and new modes at 3012  $\text{cm}^{-1}$  and 1410  $\text{cm}^{-1}$  appeared.<sup>64</sup> In another study by Ren *et al.*,<sup>69</sup> triflic acid was used for understanding the different water states of Nafion. The peak at 3000  $\text{cm}^{-1}$  present in dehydrated Nafion is indicative of regions with densely packed sulfonic acid groups<sup>18</sup> in alignment with the findings of other groups.<sup>67</sup>

Modes in the 3500  $\text{cm}^{-1}$  to 3700  $\text{cm}^{-1}$  region were also observed for thin films on hydration.<sup>70</sup> A rise in the peak intensities of A and B was observed as RH was increased, and when RH reached 100%, a broad peak at 3500  $\text{cm}^{-1}$  appeared which was assigned to bulk water. Intensity changes of the OH stretching modes for Nafion were recorded as a function of humidity.<sup>71,72</sup> Peaks at 3525  $\text{cm}^{-1}$  and 3674  $\text{cm}^{-1}$  were found to increase with humidity following similar trends which suggests that both these vibrational modes come from bulk water and water in both these modes rapidly equilibrate on hydration.<sup>64</sup>

A higher frequency peak observed at 3810  $\text{cm}^{-1}$  was ascribed to water molecules weakly hydrogen bonded to  $\text{SO}_3^-$  by Basnayake *et al.*<sup>64</sup> This seems to be an imprecise assignment since







## 7 Conclusions

There are, however, research gaps in terms of some of the assignments in Nafion FTIR spectrum. Despite extensive modeling and comparison studies with model compounds, the literature reveals a lack of consensus on the assignment of  $983\text{ cm}^{-1}$  and  $800\text{ cm}^{-1}$  mode.  $983\text{ cm}^{-1}$  is a humidity independent mode and has been assigned to  $-\text{CF}_2$  stretching mode or  $-\text{C}-\text{O}-\text{C}$  stretching mode in sidechain by differing groups. The C-S mode is spread between  $800\text{--}1200\text{ cm}^{-1}$  and strongly coupled to the sulfonic acid and ether modes. It has been associated to  $800\text{ cm}^{-1}$ ,  $980\text{ cm}^{-1}$  and  $1180\text{ cm}^{-1}$  with no accepted assignment to date. Effect of organic cations on Nafion side chain vibrational modes need to be investigated further. Much of the knowledge of sulfonic acid symmetric stretching mode shifting with alkali and alkaline metal ions exists but similar understanding is non-existent for organic cations. Organic cations are used to change processability of Nafion for varied applications and understanding their impact on Nafion properties and structure would advance those areas.

Disagreements still exists about the peak assignment of  $1440\text{ cm}^{-1}$  mode observed in FTIR. It is still widely believed to be due to anhydride formation. However, this mode was found to be absent when Nafion is investigated under conditions where impurities are eliminated. This raises questions about this assignment and needs further experimental and computational studies to identify the source of this vibrational mode.

However, there are modes that are observed by some groups but not by others like the  $3000\text{ cm}^{-1}$  and  $2800\text{ cm}^{-1}$  mode. This stems from inaccurate measurement of hydration for the membranes which could change observations between groups. More work is needed on the interfacial to bulk water dynamics in Nafion with hydration level which is fundamental to Nafion proton transport properties. Future work should also focus on modeling studies with experimental validation that would allow comparison between studies from different groups. Pretreatment and measurement conditions of Nafion should be reported clearly by researchers to enable accurate use of published information.

With the advancements in FTIR technology, one can anticipate using this technique for a host of other applications. The potential of infrared spectroscopy in applications like hydrogen fuel cells continues to remain strong considering the ease of use and availability that the technique offers as against other more demanding techniques like X-ray scattering or neutron scattering.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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