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Group Vibrational Mode Assignments as a Broadly Applicable Tool for Characterizing Ionomer Membrane Structure as a Function of Degree of Hydration

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ABSTRACT

Infrared spectra of Nafion, Aquivion, and the 3M membrane were acquired during total dehydration of fully hydrated samples. Fully hydrated exchange sites are in a sulfonate form with a C_{3V} local symmetry. The mechanical coupling of the exchange site to a side chain ether link gives rise to vibrational group modes that are classified as C_{3V} modes. These mode intensities diminish concertedly with dehydration. When totally dehydrated, the sulfonic acid form of the exchange site is

mechanically coupled to an ether link with no local symmetry. This gives rise to C_1 group modes that emerge at the expense of C_{3V} modes during dehydration. Membrane IR spectra feature a total absence of C_{3V} modes when totally dehydrated, overlapping C_1 and C_{3V} modes when partially hydrated, and a total absence of C_1 modes when fully hydrated. DFT calculated normal mode analyses complemented with molecular dynamics simulations of Nafion with overall λ (λ_{Avg}) values of 1, 3, 10, 15 and 20 waters/exchange site, were sectioned into sub-cubes to enable the manual counting of the distribution of λ_{local} values that integrate to λ_{Avg} values. This work suggests that at any state of hydration, IR spectra are a consequence of a distribution of λ_{local} values. Bond distances and the threshold value of λ_{local} , for exchange site dissociation, were determined by DFT modelling and used to correlate spectra to manually counted λ_{local} distributions.

1. Introduction

In 2012, the United Nations General Assembly¹ set forth initiatives to meet sustainable energy objectives by 2030. Next generation fuel cells, electrolyzers and desalination reactors required to meet these objectives require proton exchange membranes (PEMS) as reactant and product separators, electrocatalytic layer supports and for proton conduction.²⁻¹¹ Perfluorinated sulfonated ionomers (PFSIs) are hydrophobic backbones (e.g., tetrafluoroethylene) with sulfonate terminated side chains.¹² PFSI conjugate base structures (Fig. 1) with stoichiometric values (x, m and n) for commercial PFSIs (y is proprietary) are classified by the side chain structure (e.g., long side chain (LSC), short side chain (SSC), etc.) in Table 1.

Figure 1. Conjugate base structures of perfluorinated sulfonated ionomer (PFSI).

Table 1. PFSI structural composition by company and membrane name. Long Side Chain, LSC; Short Side Chain, SSC. Data obtained from references a,¹³ b,¹⁴ c,¹⁵ d,¹⁶ e¹⁷ and f.¹⁸

Company	Membrane	LSC/SSC	x	m	n
Dupont	Nafion	LSC	6-10, ^a 6 or 14, ^b 6.6 ^c	1	2
Ashi Glass	Flemion	LSC	3-10 ^b	1	2
Fumatech	Fumion F	LSC	5 or 8 ^d	1	2
Asahi Chemical	Aciplex	LSC	1.5-14, ^a 2-14 ^a	1	3
Chlorine Engineers Corp.	Membrane C	LSC	4 ^c	1	2
3M	3M	LSC	6 or 12, ^b 4.7 ^c	0	4
DOW	DOW	SSC	3.6-10, ^f 3-10, ^a 8 or 14 ^b	0	2
Solvay Solexis	Hyflon	SSC	8 or 14 ^b	0	2
Solvay Solexis	Aquivion	SSC	5.5 ^c	0	2

The SSC that outperformed Nafion as a PEM¹⁹ was renamed Hyflon, structurally improved and commercialized as Aquivion.²⁰⁻²¹ Nafion, 3M, and Aquivion are used as PEMs, or solubilized in lower alcohols for dispersing catalysts in ink formulations. The preparation of the membrane electrode assembly (MEA) requires direct casting of inks upon PEM surfaces (Fig. 2). Porous carbon diffusion layers uniformly distribute reactant gases, delivered from flow field grooves, over electrocatalytic surfaces concomitant with electron transport to the external circuit.

Figure 2. Scanning electron microscope image: Unsupported platinum catalyst coated Nafion with carbon cloth current collectors. This MEA was subsequently used for direct methanol fuel cell lifetime studies.²²

Infrared (IR) and Raman spectroscopy, correlated to density functional theory (DFT) calculated normal mode analyses facilitate characterization of the PFSI exchange site environment vs. state of hydration.^{11, 23-30} DFT, a quantum mechanical description of electronic, structural, and vibrational properties of molecular and crystalline systems, is based on the Hohenberg and Kohn theorems.³¹⁻³³ The total system energy is a functional of electron density. The exact ground state may be obtained if this functional is known. Observed IR bands are correlated to vibrational group modes obtained from normal mode analyses that provide eigenfrequencies and eigenvectors through the diagonalization of a Hessian matrix that accounts for the partial second derivatives of the potential relative to mass-weighted displacements.

Visualization of eigenvector animations (e.g., using Maestro 9.6) enabled assignment of normal modes having internal coordinates of mechanically coupled functional groups.³⁰ While it is not practical to consider the contribution of every oscillating fragment in a normal mode assignment, single-functional-group assignments, such as the Nafion 1060 cm^{-1} assignment to the sulfonate group,³⁴⁻³⁸ have been a source of decades of confusion.³⁹⁻⁴¹ Warren and McQuillan,⁴² Cable et al.,⁴⁰ and Smotkin et al.^{11, 24-25, 29-30} noted the importance of considering vibrational contributions from mechanically coupled functional groups.

Figure 3 recapitulates our work on group mode assignments for dehydrated (blue) and hydrated Nafion (red) transmission spectra.²³ Prior to our work, the 970 cm⁻¹ (red) was attributed to the COC ether link closest to the sulfonate group and the 1061 cm⁻¹ (red) was attributed to an SO₃⁻¹ symmetric stretch.^{12, 35-37, 39-41, 43}

Figure 3. The transmission IR spectra of Nafion-H: (a) Totally dehydrated membrane (blue); fully hydrated membrane (red). Hydration dependent spectra (b-e): (b) Totally dehydrated membrane showing exclusively C₁ bands shaded blue. (c & d) Partially hydrated membrane showing coexistent C₁ bands (blue) and C_{3v} bands (red). (e) Fully hydrated membrane showing exclusively C_{3v} bands. Adapted with permission from Doan et al.²³ Copyright 2015 Elsevier.

However, visualization of eigenvector animations³⁰ established that the 970 cm⁻¹ and 1061 cm⁻¹ peaks of Nafion are both group modes arising from mechanically coupled internal coordinates of both the COC and SO₃⁻¹ groups. The animations further showed that *COC motions dominate* the 1061 cm⁻¹ mode (COC-A u_{as}, SO₃⁻¹ u_s) and -SO₃⁻¹ motions dominate the 970 cm⁻¹ mode (SO₃⁻¹ u_s, COC-A u_{as}), contrary to the emphasis of the single functional group assignments.³⁰ During dehydration, sulfonate exchange sites gradually associate with protons to form the sulfonic acid form of the exchange site.

The 970 cm^{-1} and 1061 cm^{-1} band intensities concertedly diminish with emergence of the 1414 cm^{-1} , 999 cm^{-1} , and 910 cm^{-1} bands (Fig. 3e – b). At partial states of hydration (Fig. 3c and 3d) sulfonate and sulfonic acid forms of the exchange site coexist. The sulfonate group possesses a local 3-fold axis of symmetry. Group modes derived from sulfonate internal coordinates are C_{3V} modes. The $-\text{SO}_3\text{H}$ form of the exchange site has no local symmetry. Group modes with sulfonic acid internal coordinates are C_1 modes. The relative intensities of the C_{3V} and C_1 modes depend on the degree of hydration (Fig. 3b – e), which can be monitored by vibrational spectroscopy using sample compartments that accommodate the full MEA structure and function (i.e., operando). This work focuses on group modes with substantial internal coordinate contributions from the mechanically coupled COC and SO_3^- and/or SO_3H forms of the exchange site. Figure 3 emphasizes a high and low frequency C_{3V} mode, and 3 C_1 modes where HF, MF and LF designate high frequency, middle frequency and low frequency respectively. The observed band at 973 cm^{-1} does not shift or change in intensity with degree of hydration because the internal coordinates are those of the distant COC group (at the backbone) and practically uncoupled from the exchange site. Other than our reported transmission spectra,^{23, 25, 30} we are aware of no reports of Nafion spectra exhibiting a total absence of the 970 cm^{-1} and 1061 cm^{-1} C_{3V} modes. The challenge to acquiring spectra of totally dehydrated PFSIs by attenuated total reflectance (ATR) spectroscopy is schematized (Fig. 4).

Figure 4. ATR vs. transmission IR spectroscopy of hydrated, protonated, and lithiated Nafion.³²

Values for the in-plane and perpendicular polarization refractive indices of dry and wet Nafion were calculated using equations from Leis et al.⁴⁴ and used to calculate the effective evanescent wave depths-of-penetration⁴⁵ for dry and wet Nafion. Details of the calculations are provided (SI Calculations). The penetration depth (inset: downward red triangle) into hydrated Nafion layered onto a ZnSe ATR crystal (orange) is $\sim 2.2\text{--}2.3\text{ }\mu\text{m}$ ⁴⁶ corresponding to about 4.5% of Nafion 212 thickness. Figure 4 includes spectra from our study of metal ion exchanged Nafion.²³ The spectra of fully hydrated Nafion-[H] shows the 970 cm^{-1} $\text{C}_{3\text{V},\text{LF}}$ peak in both transmission (Fig. 3a, red) and ATR modes (Fig. 4, blue). However, the transmission spectrum of fully hydrated Nafion-[Li] shows the 970 cm^{-1} band (Fig. 4, dashed black) diminished to a slight shoulder *even* at full hydration: Li ions occupy the inner solvation sphere of the exchange site at all states-of-hydration. Consider this in the context of previously reported ATR spectra showing an undiminished band at 970 cm^{-1} ^{41, 47} for fully hydrated Nafion-[Li]. We acquired both ATR and transmission spectra of Nafion-[Li] to address the dilemma. The ATR spectra of Nafion-[Li] and Nafion-[H] feature near perfect overlap of $\text{C}_{3\text{V},\text{LF}}$ peak (Fig. 4 solid lines spectra). Matic et al.⁴⁸ used operando Raman spectroscopy to study water profiles across Nafion 117 in a PEM fuel cell and found it to be an inverted U shape for their given parameters. Weiss et al.⁴⁹ used polarization extinction ratios and the index of refraction measurements and concluded that Nafion surface hydration can change rapidly and reversibly. The key point of Weiss,⁴⁹ Matic,⁴⁸ and Doan,²³ is that ATR spectroscopy of Nafion-[Li], or any ion exchanged ionomer, can be misleading because the surface region of the PFSI can be substantially different from the bulk structure, primarily when attempting to acquire spectra of dehydrated membranes that are extremely hygroscopic.

The bulk ratio of water molecules to exchange sites is λ_{Avg} .⁵⁰ Our DFT modelling requires use of a per site λ_{local} where λ_{Avg} is an integral over a distribution of λ_{local} . Local hydration of PFSI exchange sites had been modelled using triflic acid and the PFSI full side chain structure from λ_{local} values from 0 up to 10.²⁹⁻³⁰ Our prior work showed that the build-up of the solvation environment is similar for triflic acid and the full side chain structures.³⁰ In either case, our calculations showed proton dissociation at $\lambda_{\text{local}} = 4$. Paddison et al. showed proton dissociation at $\lambda_{\text{local}} = 3$. We believe that the use of an all electron and diffuse basis set, and a functional optimized for hydrogen bonding (X3LYP) yielded our more reasonable threshold λ_{local} of 4. A diffuse basis set prevents abrupt loss of orbital overlap as the oxygen-proton distance increases and thus mitigates predictions of premature proton dissociation.

This work correlates hydration dependent transmission spectra of Nafion, 3M, and Aquivion to the DFT modelling of λ_{local} from 0-20 waters, and MD simulations of Nafion at a variety of λ_{Avg} values. For λ_{Avg} of 1, 3, 10, 15, and 20, a distribution of λ_{local} values are manually counted by examining atom coordinates about each exchange site in the simulation.

2. Experimental

2.1 Membrane Preparation

Membranes were cleaned as previously reported.²³ Briefly, Nafion 212 (EW=1100, 2.15 mil, Ion Power Inc., New Castle, DE), Aquivion (EW=980, 2.00 mil, Solvay, Bollate MI, Italy) and 3M PFSI (EW=825, 1.35 mil, 3M, St Paul, MN) membranes were immersed boiling in 8 M HNO_3 at 80°C (1h) followed by rinsing in water 6 times and finally immersing in boiling Nanopure™ water (hereafter “water”) for 1 hour, allowed to cool and then stored in water.

2.2 Membrane Transmission IR spectroscopy

Spectra were obtained with the Vertex 70 IR spectrometer (Bruker, Billerica, MA) and signal averaged (40 scans, 4 cm^{-1} resolution, 0.01 cm^{-1} accuracy) using a DLaTGS detector. Spectra were baseline corrected (Concave rubber band correction: 10 interactions; 64 baseline points) and cut (600 – 4000 cm^{-1}). Data processing was completed using Bruker™ OPUS 6.5™ software.

2.2.1 Fully hydrated (saturated) membrane spectra

Membranes were removed from water and placed in the Vertex 70 IR spectrometer (Bruker, Billerica, MA) to obtain the spectra of the fully hydrated membrane at 25 °C. During collection of the fully hydrated membrane spectra, the following precautions were taken to minimize sample dehydration risk: the sample chamber

door was opened and remained open, the sample holder purge flow was turned off at the instrument, the membranes were secured in a sample holder, and spectra were collected the moment samples were secured before returning samples to the solution container.

2.2.2 Totally dehydrated membrane spectra

Samples were placed in a high temperature (90 °C) high pressure (30 psig) cell (SPECAC, United Kingdom) equipped with a Welch 1402 DuoSeal vacuum pump for time dependent spectra.²⁷ Spectra were obtained every ten minutes for one full hour, and then every two hours until a steady state condition was attained (Nafion-H: 19 h, Aquivion-H: 49 h, 3M-H: 75 h). Final spectra were then obtained at 25 °C.

2.3 DFT Calculations

DFT output files were converted to eigenvector animations using the Maestro graphical user interface (Schrodinger Inc., New York, NY). Jaguar calculations were carried out on the high-performance computing clusters at the University of Texas Rio Grande and Northeastern University. The calculated 3N-6 normal modes, for the PFSI repeat units, were used to assign IR bands. Maestro animations for normal modes with normalized intensity above 1% of the largest line were selected for viewing.

2.3.1 X3LYP functional DFT of PFSIs and side chain fragments

Unrestricted DFT^{32, 51-52} with the X3LYP⁵³ functional was used for geometry optimizations and calculations of the normal mode frequencies of (a) Nafion, (b) Aquivion, (c) 3M PFSI, (d) perfluorinated (4-methoxybutane) sulfonate (PFMBS), (e) perfluorinated (2-methoxyethane) sulfonate (PFMES), (f) triflate, and (g) perfluorinated methyl ether (PFME) as well as the associated acid forms, not shown in Fig. 5: dehydrated Nafion-H, Aquivion-H, 3M PFSI, perfluoro(4-methoxybutane) sulfonic acid (PFMBSA), perfluoro(2-methoxyethane) sulfonic acid (PFMESA) and triflic acid. The Teflon like backbone of the Nafion, Aquivion and 3M PFSI repeat units were capped with CH₃ groups for consistency and to prevent computational overlap with the Nafion side chain CF₃ group.⁵⁴ The X3LYP is an extension to the hybrid B3LYP⁵⁵ semiempirical functional providing more accurate heats of formation. Jaguar 8.7- 2017-3 (Schrodinger Inc., Portland, OR) was used with the all-electron 6-311G**++ Pople triple- ζ basis set (“**” and “++” denote polarization³² and diffuse⁵¹ basis set functions, respectively).

Figure 6. Nafion molecular dynamic simulation specifications.

3. Results and Discussion

3.1 Experimental and DFT calculated IR spectroscopy

Figure 7 shows PFSI anion structures and their fully hydrated (red) and dehydrated (blue) transmission spectra, and sum of bond lengths (green) between the exchange site and nearest neighbor ether oxygen.

Figure 7. Anion structures with bond length sum (green) and spectra of dry (blue) and hydrated (red) membranes with local-symmetry-based assignments (drop lines) for (a) Aquivion (2.00 mil), (b) Nafion (2.15 mil) and (c) 3M (1.35 mil) plotted as normalized absorbance.

We focus on the $C_{1, HF}$, $C_{1, MF}$, and $C_{1, LF}$ group modes (blue) of dehydrated PFSIs ($\sim 1400\text{ cm}^{-1}$, $\sim 1000\text{ cm}^{-1}$ and $\sim 900\text{ cm}^{-1}$) and $C_{3V, HF}$ and $C_{3V, LF}$ group modes (red) of fully hydrated PFSIs ($\sim 1060\text{ cm}^{-1}$ and $\sim 970\text{ cm}^{-1}$).

The assignment of vibrational group modes makes use of eigenvector animations of the ionomer repeat units, side chain molecular fragments and small molecules (Fig. 5). Small molecule vibrational modes are called “pure modes”. Examination of the full side chain normal mode animations in the context of pure modes contributions enables ranking of functional group contributions to observed IR bands. Snapshots of the dominant contributors are highlighted by solid lines and circles. Secondary and tertiary contributors are highlighted by dotted lines and circles that are color coded as:

Red line:	Triflic acid	ν_{as}
Blue line:	PFME	ν_{as}
Purple line:	PFME	ν_s

Orange line: Triflic acid ν_s

Orange line: Triflate ν_s

3.1.1 Dehydrated PFSI-H: C_1 modes

$C_{1, HF}$ modes: Background. Eigenvector animations (reference^{25, 29} and SI video 9) of calculated peaks at 1396* cm^{-1} , 1405* cm^{-1} , and 1395* cm^{-1} (Aquivion, Nafion and 3M respectively)^a correspond to observed bands at 1414 cm^{-1} , 1414 cm^{-1} , and 1412 cm^{-1} , respectively (Fig. 7). Figure 8 are extrema animation snapshots of small molecule pure modes (Col. 1) and side chain group modes (Col. 2) used to schematize derivation of the $C_{1, HF}$ ionomer group modes (Col. 3). The -O-(CF₂)₂-SO₃H side chain (Col. 2, top) pertains to the Aquivion and Nafion side chains (Col. 3, top and middle). The -O-(CF₂)₄-SO₃H side chain (Col. 2 bottom) pertains to the 3M side chain. The Nafion side chain has two ethers groups (Fig. 5a and 7b): COC (A) is mechanically coupled to the exchange site; COC (B) is connected to the backbone and thus less coupled to the exchange site. The Nafion COC (A) and the Aquivion COC are both 1.56 Å from the exchange site (Fig.7). The 3M COC group, 4.69 Å from the exchange site, is essentially not mechanically coupled to the exchange site. The Triflate and PFME pure modes are at 1398 cm^{-1} and 1136 cm^{-1} respectively (Fig. 8, Col. 1). The side chain group modes are approximately mechanically coupled small molecule pure modes.

$C_{1, HF}$ modes: Aquivion and Nafion. The side chain mode (Col. 2 top) shows that both the triflic acid and the PFME contribute to the side chain mode. The extreme snapshots show that the triflic acid pure mode dominates. Thus, a solid red line connects the triflic acid mode (Col. 1 bottom) to the side

^a Wavenumbers superscripted with * are DFT calculated eigenvalues.

chain mode (Col. 2 top) to indicate that the triflic acid pure mode is the dominant contributor to the side chain mode. The dotted blue line shows that PFME is a contributor to the side chain group mode, but it is not a dominant contributor to the Aquivion and Nafion side chain group modes. The calculated Aquivion and Nafion ionomer group modes are within a few wavenumbers of the side chain group modes (Col. 2, top) supporting $C_{1, HF}$ assignment as predominantly a sulfonic acid mode.

$C_{1, HF}$ mode: 3M. The 3M side chain mode (Col. 2 bottom) has an eigenfrequency identical to the triflic acid pure mode. Because there is negligible contribution of the PFME pure mode to the 3M side chain mode, the 3M side chain mode (Col. 2, bottom) has a solid line contribution (red) only from the triflic acid pure mode (Col. 1 bottom). The calculated eigenfrequency of the 3M-H ionomer (1395^* cm^{-1}) suggests that the mode is essentially the triflic acid pure mode.

In summary, the solid red lines indicate that the dominant contributor to both side chain group modes is the triflic acid pure mode. The secondary contributor (dotted blue line) contributes only to the $-O-(CF_2)_2-SO_3H$ side chain mode. In the case of the 3M membrane, where the COC group is $4.69 \text{ \AA}$ from the exchange site, there is no secondary contributor. Column 3 results from normal mode analysis of the entire ionomer repeat unit.

Figure 8. Eigenvector animation snapshots of pure modes (Col. 1) and side chain group modes (Col. 2) that schematize derivation of the C_{1, HF} group modes for Aquivion, Nafion and the 3M membranes (Col. 3). Small molecules: PFME (perfluoro-dimethyl ether); Triflate-H (triflic acid). Side chain molecules: -O-(CF₂)₂-SO₃H (perfluorodimethyl ether sulfonic acid); -O-(CF₂)₄-SO₃H (perfluoro-methyl butyl ether sulfonic acid). Dominant and secondary contributions identified by solid and dotted arrows respectively. Wavenumbers superscripted with * are DFT calculated eigenvalues.

C_{1, MF} modes: Aquivion, Nafion and 3M. Eigenvector animations (SI videos 2, 5 and 11) of calculated peaks at 960* cm⁻¹, 986* cm⁻¹, and 1009* cm⁻¹ (Aquivion, Nafion and 3M respectively) correspond to bands (Fig. 7) at 1001 cm⁻¹, 999 cm⁻¹, and 1031 cm⁻¹. Figure 9 are extrema animation snapshots used to schematize derivation of the C_{1, MF} ionomer group modes. The side chain derivatives (i.e., -O-(CF₂)₂-SO₃H and -O-(CF₂)₄-SO₃H) C_{1, MF} modes are both dominated by the PFME pure mode (solid purple lines). The triflic acid pure mode is a secondary contributor (dashed red lines). The Nafion C_{1, MF} mode (Col. 3) is dominated by CF₃ δ_u with minor coupling to COC B δ_s, COC A ρ_r, and SO₃H v_{as}. We suggest viewing of SI videos 2, 5, and 11.

Figure 9. $C_{1, MF}$ ionomer group mode derivation (column 3) from small molecule pure modes (Col. 1) and side chain group modes (Col. 2). Same pure mode small molecules and side chain molecules as in figure 8. Wavenumbers superscripted with * are DFT calculated eigenvalues.

$C_{1, LF}$ mode: Aquivion, Nafion, and 3M. Eigenvector animations (reference^{25, 29} and SI video 13) show $C_{1, LF}$ group modes at 777^* cm^{-1} , 786^* cm^{-1} , and 791^* cm^{-1} for dehydrated Aquivion, Nafion, and 3M, respectively. The $C_{1, LF}$ group modes are correlated to bands (Fig. 7) at 905 cm^{-1} , 910 cm^{-1} , and 926 cm^{-1} for dehydrated Aquivion, Nafion, and 3M respectively. The calculated $C_{1, LF}$ lines are lower than the observed $C_{1, LF}$ by $\sim 14\%$. We found that systematic errors in eigenfrequency calculations can be remedied by modification of the selected basis set.⁵⁹ Work is in progress to reconcile calculated $C_{1, LF}$ mode values.

Figure 10 shows the DFT generated normal mode animation extrema snapshots of the $C_{1, LF}$ modes along with relevant pure mode, side chain, and ionomer repeat unit modes. Aquivion, Nafion, 3M, and side chain derivatives (i.e., $-\text{O}-(\text{CF}_2)_2-\text{SO}_3\text{H}$ and $-\text{O}-(\text{CF}_2)_4-\text{SO}_3\text{H}$) $C_{1, LF}$ modes are dominated by

SO₃H ν_s mechanically coupled to a COC ν_s secondary contributor. While the 3M assignment is the same (i.e., functional group contribution and their dominance ranking) as those of Aquivion and Nafion, the 3M PFSI C_{1,LF} band relative intensity is substantially less than those of Aquivion and Nafion. The intensity is *inversely correlated* to the bond distance between the mechanically coupled SO₃H and the distant COC (Fig. 7, 4.69 Å). It is noteworthy that the 3M C_{1,LF} intensity is less than that of the 3M C_{1,HF} band (Fig. 7): The C_{1,HF} band is essentially an SO₃H ν_{as} mode that is not coupled to a COC pure mode. However, the C_{1,LF} mode is an SO₃H ν_s coupled to a distant COC pure mode. That extended distance (4.69 Å) drastically diminishes the intensity. The similarities of C_{1,LF} group mode components (Col. 3 top to bottom) is remarkable (Fig. 10). The salient point is that all three C_{1,LF} ionomer group mode frequencies (~785 cm⁻¹) track back to the triflic acid pure mode with calculated peak at 795 cm⁻¹ (vs. 1256 cm⁻¹ PFME pure mode), thus validating this methodology for group mode assignments. The relationships between the pure modes and the ionomer group modes are more explicit by visualization of the video animations. A key point is that the C_{1,HF}, C_{1,MF}, and C_{1,LF} bands are attributed to the same pair of functional groups (SO₃H and COC).

Figure 10. Pure modes (Col. 1) and side chain group modes (Col. 2) to schematize derivation of the $C_{1, LF}$ ionomer group mode (Col. 3). Wavenumbers superscripted with * are DFT calculated eigenvalues.

3.1.2 Fully hydrated PFSI-H

$C_{3V, HF}$ modes: Background. These modes arise from the sulfonate form of the exchange site with a local three-fold axis of symmetry. Eigenvector animations (reference^{25, 29-30} and SI video 15) show calculated peaks at 1051* cm^{-1} , 1059* cm^{-1} , and 1014* cm^{-1} (Aquivion, Nafion and 3M respectively) that correlate to observed bands (Fig. 7) at 1057 cm^{-1} , 1061 cm^{-1} , and 1060 cm^{-1} . Figure 11 shows animation extrema snapshots of the pure modes and side chain modes used to schematically derive the ionomer $C_{3V, HF}$ modes. This differs from the previous ionomer group mode derivations: There are *three* pure modes to consider.

$C_{3V, HF}$ modes: Aquivion and Nafion. The side chain derivative (i.e., $-\text{O}-(\text{CF}_2)_2-\text{SO}_3^{-1}$) pure mode contributors are dominated by $\text{COC } \nu_{\text{as}}$ (i.e. PFME pure mode, blue line) with a secondary contribution from the triflate pure mode (dotted orange line). The ionomer modes of both Aquivion and Nafion are dominated by COC pure modes, with secondary contributions from the sulfonate group. This contrasts with decades of literature ascribing the 1060 cm^{-1} bands to the triflate pure mode,³⁹⁻⁴¹ when in fact it is due to both the triflate and PFME pure modes with the dominant contributor being the PFME mode, not the triflate mode.

$C_{3V, HF}$ modes: 3M. The 3M PFSI and the $-\text{O}-(\text{CF}_2)_4-\text{SO}_3^{-1}$ side chain derivative $C_{3V, HF}$ modes are dominated by $\text{SO}_3^{-1} \nu_s$ (solid orange line) mechanically coupled to a $\text{COC } \nu_s$ pure mode as a secondary contributor (dashed purple). All three $C_{3V, HF}$ modes are a consequence of mechanically coupled sulfonate and ether groups, however in the case of the 3M membrane, the dominating contributor to the group modes is the triflate pure

mode. The relationships between pure modes and group modes are more easily seen by visualization of the full animations.

Figure 11. $C_{3V, HF}$ ionomer group mode (column 3) derivations from small molecule pure modes (column 1) and side chain group modes (column 2). PFME (perfluoro-dimethyl ether); $-O-(CF_2)_2-SO_3^{-1}$ (perfluorodimethyl ether sulfonate); $-O-(CF_2)_4-SO_3^{-1}$ (perfluoro-methyl butyl ether sulfonate). Wavenumbers superscripted with * are DFT calculated eigenvalues.

$C_{3V, LF}$ mode: Aquivion, Nafion and 3M. Eigenvector animations (reference^{25, 29-30} and SI video 17) correlate the calculated $C_{3V, LF}$ group modes at 923* cm^{-1} , 983* cm^{-1} , and 975* cm^{-1} (Aquivion, Nafion and 3M respectively) to observed bands at 970 cm^{-1} , 970 cm^{-1} , and 991 cm^{-1} (Fig. 7). Smotkin et al.^{22, 30} used experimental data, including the effects of ion exchange, to correlate the calculated Nafion 983* cm^{-1} line to the observed 970 cm^{-1} band rather than an observed band at 983 cm^{-1} that is insensitive to the state of hydration or ion exchange.³⁰ Figure 12 are extrema snapshots relevant to the $C_{3V, LF}$ modes. The pure modes are triflate and PFME small molecule modes (Col. 1). The $-O-(CF_2)_2-SO_3^{-1}$ and $-O-(CF_2)_4-SO_3^{-1}$ group modes are both dominated by the triflate pure mode (solid orange lines). The PFME pure mode is a secondary contributor to both side chain modes (dotted blue lines). The relative intensity of the 3M $C_{3V, LF}$ band is substantially lower than those of Aquivion and Nafion. This is likely due to the longer distance (4.69 Å) between the SO_3^{-1} group and the near neighbor COC (Fig. 7). The salient point is that the triflate pure mode is always the dominant contributor *in a group mode*, in contrast to decades of assignments attributing these bands to only a PFME pure mode (or single functional group mode).³⁴⁻³⁸ The relationships between the pure modes and the ionomer group modes are more easily captured by visualization of SI video 17.

Historically, Cable et al.⁴⁰ had assigned the hydrated Nafion 969 cm^{-1} band to COC-A alone because of its observed sensitivity to ion exchange. This sensitivity was attributed to concurrent solvation^{34, 41, 60-} of the COC-A ether group and the sulfonate group. The proximity of COC-A to the solvated sulfonate group has been used to rationalize exposure of the ether oxygen to waters of solvation. An

argument against COC-A solvation is based on the strong inductive withdrawing effects of neighboring fluorine atoms and the low surface free energy associated with CF_2 groups.⁶² Our state-of-hydration dependent spectroscopy combined with DFT normal mode analysis resolved similar such controversies^{25, 35, 40, 42, 63} by (1) use of normal mode eigenvector animations for IR band group mode assignment and (2) categorization side-chain group modes in terms of the exchange site local symmetry.^{11, 23-25, 29-30} A key point is that the $\text{C}_{1, \text{HF}}$, $\text{C}_{1, \text{MF}}$, $\text{C}_{1, \text{LF}}$, $\text{C}_{3\text{V}, \text{HF}}$, and $\text{C}_{3\text{V}, \text{LF}}$ bands are derivable from the mechanically coupled internal coordinates of the sulfonate/sulfonic acid exchange site and the nearest ether link. The assignments are summarized in Table 3.

Figure 12. $\text{C}_{3\text{V}, \text{LF}}$ group mode (Col. 3) derivations from small molecule pure modes (Col. 1) and side chain group modes (Col. 2). Same pure mode molecules and side chain molecules as in figure 11. Wavenumbers superscripted with * are DFT calculated eigenvalues.

3.2 C_1 and $\text{C}_{3\text{V}}$ mode assignment table

Table 3 provides all the local symmetry-based IR band assignments for the dehydrated and hydrated forms of protonated Aquivion, Nafion and 3M PFSI, the side chain derivatives, and the small molecule pure modes.

1 These assignments are further supported by augmenting eigenvector animations (SI video 1-28) with
2 experimental spectra obtained by altering the exchange site environment (e.g., state of hydration, ion speciation,
3 derivatization of the ionomer, etc.).^{11, 23-28}
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Table 3: Local symmetry assignments, transmission IR bands, DFT calculated normal and group mode assignments, for dehydrated and hydrated forms of Aquivion-H, Nafion-H, 3M-H, perfluorinated (2-methoxyethane) sulfonic acid (PFMESA), perfluorinated (2-methoxyethane) sulfonate (PFMES), perfluorinated (4-methoxybutane) sulfonic acid (PFMBESA), perfluorinated (4-methoxybutane) sulfonate (PFMBES), triflate-H,

	Local symmetry	Transmission (cm ⁻¹)	DFT (cm ⁻¹)	Group mode assignment	Supporting Information
Aquivion-H					
Dehydrated	C ₁ , HF	1414	1396*	SO ₃ H v _{as} , COC v _{as}	a
		1319	1309*	SC CC v, COC v _{as}	SI 1 video
	C ₁ , MF	1001	960*	COC v _s , SO ₃ H v _{as}	SI 2 video
	C ₁ , LF	905	777*	SO ₃ H v _s , COC v _s	a
Hydrated		1319	1302*	SC CC v, COC v _{as}	SI 3 video
	C _{3v} , HF	1057	1051*	COC v _{as} , SO ₃ ⁻¹ v _s	a
	C _{3v} , LF	970	923*	SO ₃ ⁻¹ v _s , COC v _{as}	a
Nafion-H					
Dehydrated	C ₁ , HF	1414	1405*	SO ₃ H v _{as} , COC-A v _{as}	b
		1319	1313*	COC-A v _{as} , COC-B δ _s	SI 4 video
	C ₁ , MF	999s	986*	CF ₃ δ _u , COC-B δ _s , COC-A ρ _r , SO ₃ H v _{as}	SI 5 video
		983	981*	CF ₃ δ _u , COC-B v _{as}	SI 6 video
	C ₁ , LF	910	786*	SO ₃ H v _s , COC-A v _s	b
		806	820*	COC-B ω, BB	b
			731*	CF ₃ δ _u , COC-B ρ _r , COC-A ρ _r	b
	Hydrated		1322	1299*	SC CC v, COC-A v _{as} , CF ₃ δ _u
C _{3v} , HF		1058	1059*	COC-A v _{as} , SO ₃ ⁻¹ v _s	b
		983	973*	COC-B v _{as} , CF ₃ δ _u , SO ₃ ⁻¹ v _s	SI 8 video
C _{3v} , LF		969	983*	SO ₃ ⁻¹ v _s , COC-A v _{as}	b
		806	883*	BB	b
			738*	CF ₃ δ _u , COC-B δ _s , COC-A δ _s	b
3M-H					
Dehydrated	C ₁ , HF	1412	1395*	SO ₃ H v _{as}	SI 9 video
		1342	1330*	SC CC v, COC δ _s	SI 10 video
	C ₁ , MF	1031	1009*	COC v _s , SO ₃ H v _{as}	SI 11 video
		1012	984*	COC v _{as}	SI 12 video
	C ₁ , LF	926	791*	SO ₃ H v _s , COC v _s	SI 13 video
Hydrated		1342	1311*	SC CC v, COC v _{as}	SI 14 video
	C _{3v} , HF	1059	1014*	SO ₃ ⁻¹ v _s , COC v _s	SI 15 video
		1012	980*	SO ₃ ⁻¹ v _s , SC CC v, COC δ _s	SI 16 video
	C _{3v} , LF	991	975*	SO ₃ ⁻¹ v _s , COC v _{as}	SI 17 video
Side Chains					
PFMESA	C ₁ , HF		1400*	SO ₃ H v _{as} , COC v _{as}	b
			1254*	CC v, COC v _{as}	SI 18 video
	C ₁ , MF		854*	COC v _s , SO ₃ H v _{as}	SI 19 video
		C ₁ , LF		766*	SO ₃ H v _s , COC v _s
PFMES			1316*	CC v, COC v _{as}	SI 20 video
	C _{3v} , HF		1075*	COC v _{as} , SO ₃ ⁻¹ v _s	b
	C _{3v} , LF		972*	SO ₃ ⁻¹ v _s , COC v _{as}	b
PFMBSA	C ₁ , HF		1398*	SO ₃ H v _{as}	SI 21 video
			1241*	CC v, COC δ _s	SI 22 video
	C ₁ , MF		1016*	COC v _s , SO ₃ H v _{as}	SI 23 video
			892*	COC v _{as}	SI 24 video
PFMBES	C ₁ , LF		731*	SO ₃ H v _s , COC v _s	SI 25 video
			1275*	CC v, COC v _{as}	SI 26 video
	C _{3v} , HF		1013*	SO ₃ ⁻¹ v _s , COC v _s	SI 27 video
	C _{3v} , LF		982*	SO ₃ ⁻¹ v _s , COC v _{as}	SI 28 video
Pure Modes					
Triflate-H	C ₁		1398*	SO ₃ H v _{as}	b
	C ₁		795*	SO ₃ H v _s	b
Triflate	C _{3v}		981*	SO ₃ ⁻¹ v _s	b
	C _{3v}		613*	SO ₃ ⁻¹ v _s	a
PFME			1256*	COC v _s	b
			1136*	COC v _{as}	b

Symmetric stretching, v_s; Asymmetric stretching, v_{as}; Wagging, ω; Bending, δ_s; Umbrella bending, δ_u; Rocking, ρ_r; Backbone, BB; Side Chain, SC; Calculated value *

triflate and perfluorinated dimethyl ether (PFME). SI marked “a” and “b” are from reference 29 and 11, respectively. Wavenumbers superscripted with * are DFT calculated eigenvalues.

3.3 DFT/MD simulated $\text{SO}_3\text{H}/\text{SO}_3^-$ solvation sphere growth correlated to IR spectroscopy.

3.3.1 DFT calculated λ_{local} from 0 – 20.

Figure 13 shows DFT modelling of the exchange site hydration process. Although the exchange site is modelled as a triflic acid small molecule, our prior work showed that the solvation sphere build-up yielded the same results when using the entire PFSI side chain.³⁰ The SO-H bond length is 0.970 Å in the absence of water and increases to 1.074 Å at $\lambda_{\text{local}} = 3$. At $\lambda_{\text{local}} = 4$ the bond length jumps to 1.522 Å: Proton dissociation yields a sulfonate group while transitioning from a local C_1 to a pseudo C_{3V} symmetry. At λ_{local} below 10, the model shows hydronium ions always within the inner sphere of the exchange site with the SO-H bond length vacillating between 1.49 – 1.53 Å. At λ_{local} 10 and higher, the SO-H bond distance widely varies between 1.5 – 3.7 Å suggesting no significant difference between the energetics of hydronium ions in the bulk phase versus complexed to the exchange site. Thus, threshold λ_{local} are at 4 and 10. At λ_{local} between 0 and 3 inclusive, the proton is covalently bound. At λ_{local} between 4 and 9 inclusive, the exchange site is dissociated, but the distance between the hydronium proton and the sulfonate oxygen never exceeds 1.528 Å. At λ_{local} 10 and above the SO-H bond length varies broadly. Figure 13 shows a gradual transition of the exchange site local symmetry from C_1 (λ_{local} : 0 – 3, blue), pseudo C_{3V} (λ_{local} : 4 – 9, dotted red) and C_{3V} (λ_{local} : 10 – 20, solid red). Molecular dynamics (MD) supports the contention that at any λ_{Avg} there is a distribution of λ_{local} where the environment of each is manifested in observed IR bands (vide infra).

Figure 13. DFT optimized structures of the triflic acid exchange site as water molecules are sequentially added: triflic acid twenty-step hydration process (λ_{local} : 0-3, blue; 4-9, dotted red; 10-20, solid red).

3.3.2 Hydration dependent IR spectra of Aquivion, Nafion, and 3M membrane.

Fully hydrated Aquivion, Nafion and 3M spectra were mounted into a controlled temperature vacuum sample compartment prior to initiating time dependent spectra until steady state spectra were attained at total dehydration (Fig. 14). C_1 (shaded blue) and C_{3V} modes (shaded red) do not coexist at extreme states of hydration (red) and dehydration (blue). The coexistence of C_1 and C_{3V} modes (shaded blue/red) at intermediate states of hydration correspond to a distribution of λ_{local} that must be considered in the interpretation of spectra and the development of rigorous proton transport models.²³ The gradual emergence of C_{3V} modes at the expense of C_1 modes has been observed in our operando Raman spectroscopy of fuel cell cathodes.¹¹ Prior to the onset of the oxygen reduction reaction (ORR), the spectra featured only C_1 modes. At the ORR onset C_1 and C_{3V} modes coexisted. At lower cathode potentials where the ORR was facile, only C_{3V} modes were observed.

Figure 14. Molecular structure and protonated membrane IR transmission spectra [Dehydrated (blue), partially dehydrated (purples) and hydrated (red)]: (a) Aquivion (2.00 mil), (b) Nafion (2.15 mil) and (c) 3M (1.35 mil). Spectra are plotted as normalized absorbance.

Figure 15 shows Aquivion, Nafion and 3M time-dependent C_1 (blue) and C_{3V} (red) group mode absorbances vs. time during dehydration. The left and right columns plot the high frequency (HF) and low frequency (LF) symmetry-based modes respectively. Figure 15 and the vibrational mode assignments (Table 3) clarify how changes in the local symmetry of the exchange site can be used as a basis for interpretation of IR spectra variations during hydration or dehydration. For any sulfonated ionomer, the exchange site is associated (C_1) under full dehydrations. During a hydration/dehydration cycle:

1. C_1 and C_{3V} modes are negatively correlated.
2. $C_{1, HF}$ and $C_{1, LF}$ modes are positively correlated.
3. $C_{3V, HF}$ and $C_{3V, LF}$ modes are positively correlated.
4. C_1 and C_{3V} modes do not coexist at extreme environmental conditions (e.g. states-of-hydration).

For example, Table 3 clarifies that the Nafion 1060 cm^{-1} C_{3V} band is not an SO_3^{-1} , or COC mode. It is a group mode having mechanically coupled internal coordinates of *both* functional groups, with the COC pure mode dominating. The 969 cm^{-1} is not an SO_3^{-1} or COC mode. It is a group mode with mechanically coupled internal coordinates of both the COC and sulfonate group (point 3). Therefore the 1060 cm^{-1} and 969 cm^{-1} intensity variations are positively correlated during a hydration/dehydration cycle. The heuristic rule is that positively correlated peaks have the same exchange site local symmetry. Negatively correlated peaks have different exchange site local symmetries.

Figure 15. (a) Aquivion (2.0 mil), (b) Nafion (2.15 mil) and (c) 3M (1.35 mil) absorbance vs. time plots during dehydration. Left side: High frequency modes. Right side: Low frequency modes.

3.3.3 λ_{local} distributions counted from MD state-of-hydration simulations vs. λ_{Avg}

MD simulation cube slices at λ_{Avg} 1, 3, 10, 15, and 20 are shown in Figures 16 and 17. At $\lambda_{\text{Avg}} = 1$, water molecules appear randomly throughout the cube in a near single phase morphology. As λ_{Avg} increases, phase segregation is enhanced. This trend towards phase segregated domains is consistent with simulations carried out by A-T Kuo et al.⁶⁴ at λ_{Avg} values of 3, 6, 9, 12, 15 and 20. Our simulation cubes were segmented into 320 sulfur-centered sub-cubes with 10 Å edge lengths. The sub-cube volume was selected to limit the maximum number of enclosed water molecules to 20, consistent with NMR experiments by Schaberg et al.⁶⁵ establishing a λ_{local} maximum of ~ 20. Values of λ_{local} for each sub-cube volume were determined by counting enclosed waters using output files from an excel macro for λ_{local} counting (see Supporting Information for histogram data of λ_{local} and detail of the macros used).

For an exchange site population (e.g., Avogadro's number, N_A) the sum of the waters molecules is the integral of the frequency of occurrence integrated over all λ_{local} (eq. 1). There are two reasons why sub-cubes intersecting with the MD box surface are excluded from histogram plots intended to be correlated with experimental transmission spectra (e.g., Fig. 14). First, as discussed earlier (Fig. 4), transmission spectroscopy marginalizes intensities from the membrane surface and emphasizes ionomer bulk properties. Second, the truncation of intersecting sub-cubes by the MD cube surface renders its count of waters meaningless.

$$\left(\frac{\text{mass}}{\text{EW}}\right) N_A \lambda_{\text{Avg}} = \sum_{i=1}^{\infty} f_i \lambda_{\text{local}_i} = \int_1^{\infty} f_i d\lambda_{\text{local}_i} \quad \text{Eq. 1}$$

These sub-cube topographical issues, combined with the limit of 20 waters per exchange site, are expressed in a modification of equation 1. The summation upper-bound is Schaberg's limit.

$$\left(\frac{mass}{EW}\right)N_A \lambda_{Avg} = \sum_{i=1}^{20} f_i \lambda_{local_i} + H_2O_{uncounted} \quad Eq. 2$$

Waters from sub-cubes having sulfur atom centers less than 5 Å from the MD simulation box surface are *uncounted* to avoid artifacts due to truncated sub-cubes. Fig. 16 shows a selection of 5 sub-cube components of a λ_{Avg} simulation and how they contribute to the overall distribution. This figure is also provided in the Supporting Information (SI Video 29) as a video that rotates the cubes for enhanced visualization.

The histogram bars of Fig. 17 are color-coded consistently with the border colors of the DFT λ_{local} simulations summarized in Fig. 13. Each λ_{Avg} histogram is a λ_{local} distribution over the range of 0 to 20 waters. At $\lambda_{Avg} = 1$, the uniformly blue λ_{local} bars correspond to the dehydrated spectra with only C_1 modes detectable (Fig. 14, far left). At $\lambda_{Avg} 3$, the λ_{local} distribution corresponds to the intermediate spectra primarily featuring contributions from C_1 (i.e., blue lines) and some pseudo C_{3V} (i.e., dotted red lines) modes. As λ_{Avg} increases from 3 to 20, the shift in the λ_{local} distribution corresponds to spectra (Fig. 14, far right) predominantly exhibiting C_{3V} (i.e., solid red lines) modes. Hydration dependent spectra (Fig. 14) are a consequence of a distribution local exchange site hydration environments.

Figure 16. Nafion MD simulated for $\lambda_{Avg} = 15$ showing 5 different λ_{local} members of the distribution of λ_{local} that make up λ_{Avg} . The counted distribution at left indicate that the FTIR will show both C_1 (blue) and C_{3v} (red) group modes.

Figure 17. Nafion MD simulated λ_{local} distribution for λ_{Avg} values 1, 3, 10, 15 and 20 with images of each Nafion MD simulation above. Blue lines represent λ_{local} 0 - 3, dotted red lines represent λ_{local} 4 - 9, and solid red lines represent λ_{local} 10 - 20.

4. Conclusion

Transmission IR spectroscopy, a powerful yet underutilized tool for understanding hydration-induced structural changes in polymer electrolytes, have been correlated to density functional theory and molecular dynamic simulations to show that IR bands are a consequence of distributions of local exchange site environments responsive to hydration equilibria. A set of IR bands at full hydration are negatively correlated to a set of IR bands at total dehydration, and both sets are observed at partial degrees of membrane hydration. Totally dehydrated membranes host an ensemble of sulfonic acid form of the exchange site with no local symmetry (C_1). These bands are exemplified by Nafion bands at $\sim 1414\text{ cm}^{-1}$, $\sim 1000\text{ cm}^{-1}$, and $\sim 910\text{ cm}^{-1}$. During hydration, sulfonic acids transition to dissociated sulfonate groups with C_{3v} local symmetry having bands at $\sim 1060\text{ cm}^{-1}$ and $\sim 970\text{ cm}^{-1}$. The C_1 and C_{3v} set of modes arise from a pair of mechanically coupled internal coordinates of an exchange site and a nearest neighbor ether link.

The incremental build-up of the hydration sphere of sulfonic acid exchange sites was modeled by DFT to yield structures corresponding to λ_{local} values of 0-20 water molecules per site. Each λ_{local} contributes to a distribution that integrates to a λ_{Avg} . At $0 \leq \lambda_{\text{local}} \leq 3$, the exchange site is associated, whereas at $4 \leq \lambda_{\text{local}} \leq 9$ the dissociated proton is always in the exchange site inner solvation sphere. Finally, at $10 \leq \lambda_{\text{local}} \leq 20$, the hydronium ion is randomly distributed inside and outside the first solvation sphere of the exchange site. Distributions of λ_{local} with upper limits below 4 would yield spectra featuring only C_1 modes. As the degree of hydration increases, C_{3v} modes emerge at the expense of C_1 modes.

The reassignment of these highly cited bands as group modes rather than single functional group modes, and their categorization in terms of exchange site local symmetry, yields a symmetry-based methodology of vibrational group mode classification that can be applied to any class of ionomer having exchange sites with hydration-dependent local symmetries.

This methodology provides a broadly applicable tool for characterizing ionomer membrane structure as a function of the degree of hydration. Beyond aqueous membrane systems, our method is also relevant to emerging applications, such as metal ion batteries in which ion exchange and solvent plasticization drive changes in local symmetry.

5. Associated Content

5.1 Supporting Information

The Supporting Information is available free of charge via the internet at <https://pubs.acs.org>.

Instructions for running MD simulations on Nafion sulfur-centered 10 Å cubes and creating histograms for data, macros used in the Microsoft Excel Visual Basic for Applications (VBA) programming language, histogram data for five different values of λ_{Avg} , examples of calculation of effective depth of penetration for the evanescent wave in ATR-IR, MD simulation trajectory coordinates, and videos of vibrational modes in Aquivion, Nafion, and 3M polymer membranes.

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6.3 Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

6.4 Notes

The authors declare no competing financial interest.

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