**Supporting Information for:**

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

Neili Loupe[1], Khaldoon Abu-Hakmeh[2], Shuitao Gao[3], Luis Gonzalez[4], Matthew Ingargiola[1], Kayla Mathiowetz[1], Ryan Cruse[1], Jonathan Doan[1], Annie Schide[1], Isaiah Salas[5], Nicholas Dimakis[6], Seung Soon Jang[2], William A. Goddard III[7], Eugene S. Smotkin[1]*

[1]Department of Chemistry & Chemical Biology, Northeastern University, Boston, MA 02115

[2]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332

[3]School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China

[4]PSJA Thomas Jefferson T-STEM Early College HS, Pharr, TX 78577

[5]Achieve Early College High School, McAllen, TX 78501

[6]Department of Physics and Astronomy, University of Texas Rio Grande Valley, Edinburg, TX 78539

[7]Materials and Process Simulation Center, California Institute of Technology, Pasadena, CA 91125

* Corresponding Author: e.smotkin@northeastern.edu

**Comprehensive procedure for Nafion sulfur centered 10Å cube lambda analysis**

There are four major sections:

a) Creating 10 Å cubes
b) Entering molecule and sulfur information into Excel
c) Entering water molecule information into Excel
d) Creating histograms and Lambda color coordination

Organization and naming files is key, otherwise things get confusing. To begin, creating the 10 A cubes from the large Nafion block (SI Fig 1-5). Setting up organization in the beginning is ideal.

This procedure requires Maestro graphical user interface (Schrodinger Inc., New York, NY) and Excel (Microsoft, Redmond, WA).

The macro in section c is written for use in a Mac computer.

a) Creating 10 Å Nafion Blocks:

1. Create a folder for the project
2. Create a folder within the project folder that houses all the large blocks titled "Nafion (or 3M or Dow) Large Blocks"
3. Create a folder titled "Maestro files"
4. Inside "Maestro files" folder, create subsequent folders for each large block
5. Open "Maestro"
6. Click "Import"
7. Choose the first large block from the file choices
8. Click the "Ball & Stick" icon and from the drop-down menu, click "All"
9. Next, click the "Display All" button (blue eye with green plus sign) and choose "Select" from the drop-down menu
10. From the left menu, click "Atom name" so that it is highlighted in blue
11. From the right menu, scroll down until the first "S" or sulfur atom appears (i.e. "24705") *sulfur atoms are located at the end of the atom list
12. Note this number

13. Scroll to the bottom of the atom list and note the last sulfur atom (i.e. “S25024”)
14. Back where the files named for the blocks were created in the “Maestro files” fold-er, create a folder for each group of 100 atoms (i.e. “700” and “800” through the fi-nal hundred)
15. Once these folders have been created, the cubes may be created
16. Go back to Maestro, with the entire block visible in the “Ball & Stick” view
17. From the uppermost main menu bar, click “Window” and choose “Command Script Editor”
18. Paste the following into the empty box titled “Script”

    undisplayatom all
    displayatom (withinposx 5 atom.name "S24705") and (withinposy 5 atom.name "S24705") and (within-posz 5 atom.name "S24705")
19. Change the “S24705” in each parenthesis to the first atom in the block
20. Click “Run Script”
21. Click back in the main Maestro window
22. Click the “Export” button
23. Click “Home Directory“ and find the folder for the respective “hundred” of the block’s atoms (Maestro files -> Name of large block -> #00)
24. Ensure that the drop-down menu to the right of “Structure to be exported:” reads “Workspace (displayed atoms only)”
25. Save the file with the format “atomname 10 angrstroms”
26. Click “Save”
27. In the “Command Script Editor” window, edit the “Script:” text to the next num-bered atom
28. Click “Run Script”
29. Save according to the steps 20-25
30. Repeat these steps for each atom, ensuring to change folders when reaching the next hundred
31. Continue until all cubes for all blocks are created

b-1) Beginning creation of Excel sheets:

1. Create a folder within the project folder titled “List of Atoms”
2. Within that folder, create subfolders named for each of the large blocks
3. Go to Maestro
4. Click “Import” and select one of the large blocks
5. Once it is open, click “Export” and save in the folder named after the large block
6. Ensure “Structure to be exported:” says “Project Table (selected entries)”
7. Name file after the large block but add “for excel” to the end
8. Locate this file on your computer where it was saved
9. Right click on the file, and choose the “Open With” option from the drop-down menu
10. Change the settings from “Compatible Programs Only” to “All Programs”
11. From the options, choose Microsoft Excel
12. All the data will be in the “A” column
13. Highlight the entire “A” column and click the “Data” tab in Excel

14. Underneath that button, click the button that says “Text to Columns”
15. In the window that pops up, choose the “Delimited” option and click “Next”
16. Ensure that the box titled “Space” has a check next to it, and click “Next”
17. Click “Finish”
18. Now all the data should be split into separate columns
19. Name this sheet on the tabs at the bottom of the window “Original Export”
20. Next create new sheets for Hydrogen, Carbon, Oxygen, Fluorine, and Sulfur
21. In the “Original Export” sheet, highlight the “L” column and click the filter button
22. When the filter pops up, click the arrow to edit the filter.
23. From the drop down, choose “Begins with” and type “H” into the field
24. Use the keyboard command “cntrl+A” to highlight the entire page, then copy the data, and paste it into the “Hydrogen” sheet
25. Do this with the rest of the elements listed in the sheets
26. Create another sheet titled “Sulfur 10 A Cube”
27. Title the first 12 columns as follows:

| Atom Number | X | Y | Z | # of Atoms | # of S Atoms | # of S Neighbors Atoms | Names of Sul-furs | # of Water Atoms in waters | # of Waters | λ | λ Nearest 0.5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | |

28. Copy and paste the Atom #, X, Y, and Z data, the rest will have to be determined
29. The following columns will need their respective formulas

| # of S Neighbors | # of Waters in 10 A Cube | λ | λ Nearest 0.5 |
|---|---|---|---|
| =F2-1 | =I1/3 | =J2/F2 | =MROUND(K2,0.5) |

30. Some data will be copied and pasted, and the rest will be input, and the formulas will do the rest

b-2) Compiling Data into Sulfur 10 Å Cube Sheet:

1. Have the Excel sheet that was just created open
2. Create
3. Find the Excel file titled “Smotkin Macro” and open it.
4. Once open, if a window pops up asking if the macros should be applied, click “Enable Macros”
5. Minimize the file
6. Find the folder where the Maestro files were saved when the cubes were created
7. Start with the lowest hundred folders in the large block folder chosen to be first
8. Inside the folder, highlight all the maestro files inside, right click on them, and choose “Open With” and find the “Excel” option (you may have to change “Compati-ble Programs Only” to “All Programs”
9. Once all the files are open, the highest will be first “?99”
10. Find this cell in the compilation excel sheet
11. Now back in the Maestro file Excel sheet, click “Tools” in the uppermost menu tab, choose “Macro” from the drop-down menu, the from the next menu, choose “Mac-ros” and click the “Smotkin Macro” from the choices

12. Click “Options…” and choose a keyboard shortcut for the Macro
13. Click “OK” and the click “Cancel”
14. Now use the keyboard shortcut that was just created
15. The sulfurs will be listed with the bottom one illustrating all the sulfur listed in one cell as well as the count of sulfurs
16. The bottom sulfur will also indicate the number of total atoms
17. Note the total number of atoms, click the cell that lists all the sulfurs and copy it, and note the number of sulfurs
18. Click in the compilation sheet, input the total number of atoms and the number of sulfurs,double click in the list of names of sulfurs, and paste the names
19. Go to the atom excel file, close it. Click “Do Not Save” when the option is presented
20. Click in the next atom file window, run the macro again, note, copy and paste the vital info, paste in the compilation window in the respective cell (will be above the previous cell) close the file, do not save, and move to the next file

c-1) Listing the Waters in the Compilation Excel Sheet:

1. Once all the sulfur information is written in the compilation file, the waters info must be created
2. Make sure the compilation Excel sheet is still open
3. Open Maestro, click “Import” and select the first file
4. Click “Undisplay” then “All” then “Display” then “Waters”
5. Enter the number of water molecules in the respective cell in the compilation sheet
6. In Maestro, click “Window” in the menu bar, and choose “Command Script Editor”
7. In the editor, highlight the command that imported the file, hid the atoms, and displayed the waters
8. Click “copy selection to script”
9. Edit the file name to be the next atom in line, and click “Run Script”
10. Enter the water molecules number in the compilation sheet
11. Go back to the Script Editor and change the file name to the next number of atom in line and continue this process until the waters are all included

c-2) Determining the Full Cubes:

1. In the “Original Export” sheet of the compilation sheet, locate the highest number atom
2. Create space between the last atom and the other information that is in the sheet
3. In the B column, create 4 rows named max, min, max -5, and min +5
4. In the x coordinate column click in the “max” row and type the formula “max” and highlight the x coordinate column, and run the formula
5. Do the same with the min row with the min formula
6. Do this for the y and z coordinate columns as well

7. Do the calculations for the max minus 5 and min plus 5 rows
8. If the sulfur is located either +/- 5 of the edges of the cubes, it is not possible for the cubes to be full
9. Make filters for the coordinate columns
10. From the filter editor, make the properties “Less than or equal to” the max -5 and “Greater than or equal to” the min+5
11. When these are filtered, copy the data and paste into a new sheet called “Full Cubes Only”

d-1) Creating Histograms:

1. Go to the compilation Excel sheet. Create a new column named “Average Lambda Rounded to Nearest (0.5)” in the N column
2. In the first cell beneath the title, put the formula “=MROUND(M2, 0.5)”
3. Take the corner of the cell and drag down to final atom
4. This will round Lambda values to the nearest 0.5
5. Create a new sheet titled “Full Histogram”
6. Create 3 columns titled Data (column A), Bins (Column B), and Frequency (Column C)
7. Populate the Data column with the 0.5 Lambda values, and the bins with every 0.5 to the highest Lambda value
    a. In the Sulfur 10 A cube sheet, right click on the Lambda value column. Choose “Sort” and then “Ascending”
    b. The bottom value will be the highest
    c. In the “Full Histogram” sheet, in the Bin column, enter 0 in the first cell and 0.5 in the second.
    d. Highlight both cells. Drag the bottom right corner to populate cells in increments of 0.5 until the highest Lambda value is reached
8. Highlight the frequency column down to the same cell as the Data column is populated
9. In the formula bar enter “=frequency(A2:??, B2:??) and replace the question marks with the lowest column number and hold control and shift while hitting enter
10. This will indicate the frequency of each lambda value
11. According to the data, the hydration is determined by the separation of Lambda values as follows: Hydrated is greater than or equal to 10, moderate is between and including 4 and 9 and Dehydrated is between and including 0 and 3
12. The hydrated will be color coded red, moderate purple, and dehydrated blue
13. Highlight the “Bins” 0 through 3.5, turn them blue; “Bins” 4 through 9.5, purple, and “Bins” 10 to the highest bin value, red
14. Click the “Chart” tab and click the bar graph icon
15. Choose “clustered column” option
16. When the blank graph appears, right click on it and choose “Select Data
17. Click the “Add” button below the series window
18. Name the series “Full Histogram”
19. Click the button to the right of the “Y values” text space and drag from the top of the C column to the last populated cell

20. Click the button next to “Horizontal (category) axis labels” text space. Highlight the bins column
21. Click OK
22. Repeat this process with the Full Cubes Only Page and name the new sheet “Full Cubes Only Histogram” and name the series appropriately

d-2) Identifying Anomalous Lambda Values:

1. Most anomalous lambda values are omitted between Full Histogram and Full cubes only Histogram, however there can be outliers
2. On the histogram, low (2 or less) and high lambda values are examined
3. On the Full Cubes Only page, sort by lambda, locate these, and note atom name
4. Open Maestro and import the atom in question
5. Identify possible reasons the lambda is high, and record these observations

**Determination of waters and $\lambda_{local}$ values of sub-cubes using Excel macros**

Sulfur-centered molecular dynamics cubes were divided into sub-cubes for further analysis. For these sub-cubes, two macros (designed to count water molecules enclosed within each sub-cube and to calculate $\lambda_{local}$ values) were implemented in the Microsoft Excel Visual Basic for Applications (VBA) programming environment. These macros (Macro 1 and Macro 2) are described below.

**SI Macro 1**:

```
' SulpherID Macro
'
' Keyboard Shortcut: Option+Cmd+Shift+M
'
    Columns("A:A").Select
    Selection.TextToColumns Destination:=Range("A1"), DataType:=xlDelimited, _
        TextQualifier:=xlDoubleQuote, ConsecutiveDelimiter:=True, Tab:=False, _
        Semicolon:=False, Comma:=False, Space:=True, Other:=False, FieldInfo _
        :=Array(Array(1, 1), Array(2, 1))
    Range("N2").Select
    ActiveCell.FormulaR1C1 = _
        "=IF(LEFT(RC[-2],1) = ""S"",IF(LEFT(R[-1]C[-2],1)=""S"",R[-1]C+1,1),"""")"
    Range("M2").Select
    ActiveCell.FormulaR1C1 = ""
    Range("M2").Select
    ActiveCell.FormulaR1C1 = _
        "=IF(LEFT(RC[-1],1) =""S"",IF(LEFT(R[-1]C[-1],1)=""S"",CONCATENATE(R[-
1]C,"","",RC[-1]),RC[-1]),"""")"
    Range("M2:N2").Select
```

```
    Selection.Copy
    Range("L2").Select
    Selection.End(xlDown).Select
    Selection.End(xlDown).Select
    Range("M2:M805").Select
    ActiveSheet.Paste
    Range("M4").Select
    Columns("M:M").EntireColumn.AutoFit
    Selection.End(xlUp).Select
    Selection.End(xlToLeft).Select
    Cells.Select
    Selection.AutoFilter
    ActiveSheet.Range("$A$1:$N$1115").AutoFilter Field:=13, Criteria1:="<>"
End Sub
```

**SI Macro 2**:

```
Sub SulpherID()
'
' SulpherID Macro
'
' Keyboard Shortcut: Option+Cmd+Shift+M
'
    Columns("A:A").Select
    Selection.TextToColumns Destination:=Range("A1"), DataType:=xlDelimited, _
        TextQualifier:=xlDoubleQuote, ConsecutiveDelimiter:=True, Tab:=False, _
        Semicolon:=False, Comma:=False, Space:=True, Other:=False, FieldInfo _
        :=Array(Array(1, 1), Array(2, 1))
    Range("N2").Select
    ActiveCell.FormulaR1C1 = _
        "=IF(LEFT(RC[-2],1) = ""S"",IF(LEFT(R[-1]C[-2],1)=""S"",R[-1]C+1,1),""""""
    Range("M2").Select
    ActiveCell.FormulaR1C1 = ""
    Range("M2").Select
    ActiveCell.FormulaR1C1 = _
        "=IF(LEFT(RC[-1],1) = ""S"",IF(LEFT(R[-1]C[-1],1)=""S"",CONCATENATE(R[-
1]C,"","",RC[-1]),RC[-1]),"""")"
    Range("M2:N2").Select
    Selection.Copy
    Range("L2").Select
    Selection.End(xlDown).Select
    Selection.End(xlDown).Select
    Range("M2:M805").Select
    ActiveSheet.Paste
```

```
    Range("M4").Select
    Columns("M:M").EntireColumn.AutoFit
    Selection.End(xlUp).Select
    Selection.End(xlToLeft).Select
    Cells.Select
    Selection.AutoFilter
    ActiveSheet.Range("$A$1:$N$1115").AutoFilter Field:=13, Criteria1:="<>"
End Sub
```

**Table S1 – $\lambda_{local}$ values calculated from a molecular dynamics simulation for Nafion, using a $\lambda_{Avg}$ value equal to 1, along with the frequency of each $\lambda_{local}$ event.**

| $\lambda_{local}$ | Frequency | $\lambda_{local}$ | Frequency |
|---|---|---|---|
| 0 | 0 | 10 | 0 |
| 0.5 | 21 | 10.5 | 0 |
| 1 | 176 | 11 | 0 |
| 1.5 | 19 | 11.5 | 0 |
| 2 | 1 | 12 | 0 |
| 2.5 | 0 | 12.5 | 0 |
| 3 | 0 | 13 | 0 |
| 3.5 | 0 | 13.5 | 0 |
| 4 | 0 | 14 | 0 |
| 4.5 | 0 | 14.5 | 0 |
| 5 | 0 | 15 | 0 |
| 5.5 | 0 | 15.5 | 0 |
| 6 | 0 | 16 | 0 |
| 6.5 | 0 | 16.5 | 0 |
| 7 | 0 | 17 | 0 |
| 7.5 | 0 | 17.5 | 0 |
| 8 | 0 | 18 | 0 |
| 8.5 | 0 | 18.5 | 0 |
| 9 | 0 | 19 | 0 |
| 9.5 | 0 | 19.5 | 0 |
| | | 20 | 0 |

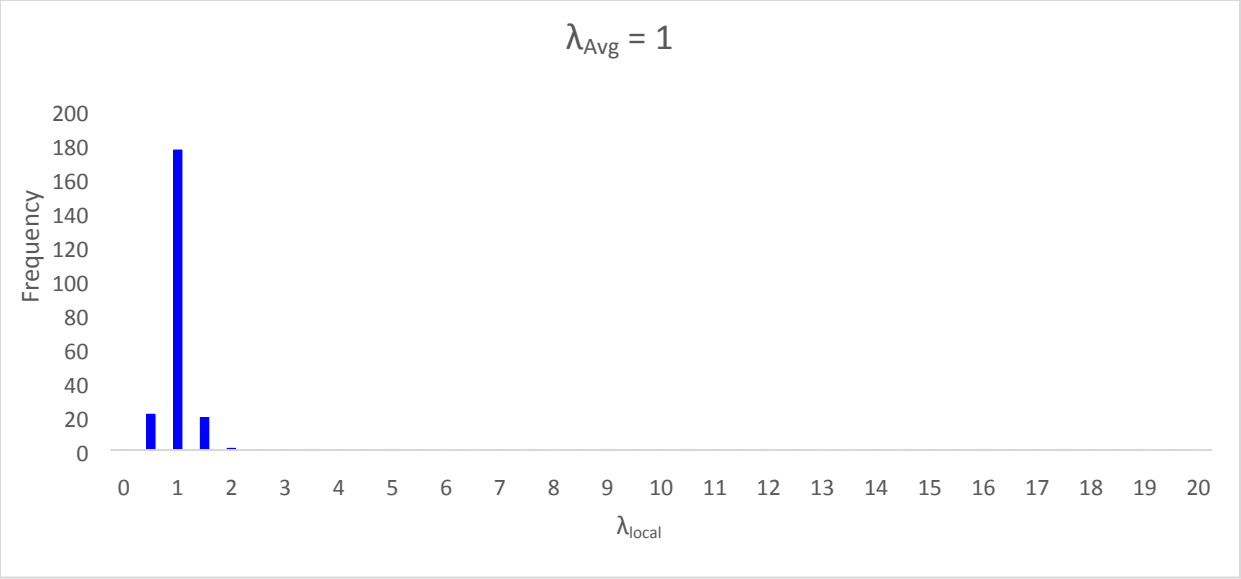


**Figure S1. Graphical distribution of $\lambda_{local}$ values determined through MD analysis of a sulfur-centered cube with $\lambda_{Avg} = 1$ and which consisted of Nafion and water molecules. Blue lines represent $\lambda_{local}$ 0 – 3, dotted red lines represent $\lambda_{local}$ 4 – 9, and solid red lines represent $\lambda_{local}$ 10 – 20.**

**Table S2 – $\lambda_{local}$ values calculated from a molecular dynamics simulation for Nafion, using a $\lambda_{Avg}$ value equal to 3, along with the frequency of each $\lambda_{local}$ event.**

| $\lambda_{local}$ | Frequency | $\lambda_{local}$ | Frequency |
|---|---|---|---|
| 0 | 0 | 10 | 0 |
| 0.5 | 0 | 10.5 | 0 |
| 1 | 16 | 11 | 1 |
| 1.5 | 43 | 11.5 | 0 |
| 2 | 42 | 12 | 0 |
| 2.5 | 36 | 12.5 | 0 |
| 3 | 30 | 13 | 0 |
| 3.5 | 24 | 13.5 | 0 |
| 4 | 16 | 14 | 0 |
| 4.5 | 8 | 14.5 | 0 |
| 5 | 6 | 15 | 0 |
| 5.5 | 3 | 15.5 | 0 |
| 6 | 9 | 16 | 0 |
| 6.5 | 0 | 16.5 | 0 |
| 7 | 7 | 17 | 0 |
| 7.5 | 0 | 17.5 | 0 |
| 8 | 4 | 18 | 0 |
| 8.5 | 0 | 18.5 | 0 |
| 9 | 5 | 19 | 0 |
| 9.5 | 0 | 19.5 | 0 |
| | | 20 | 0 |

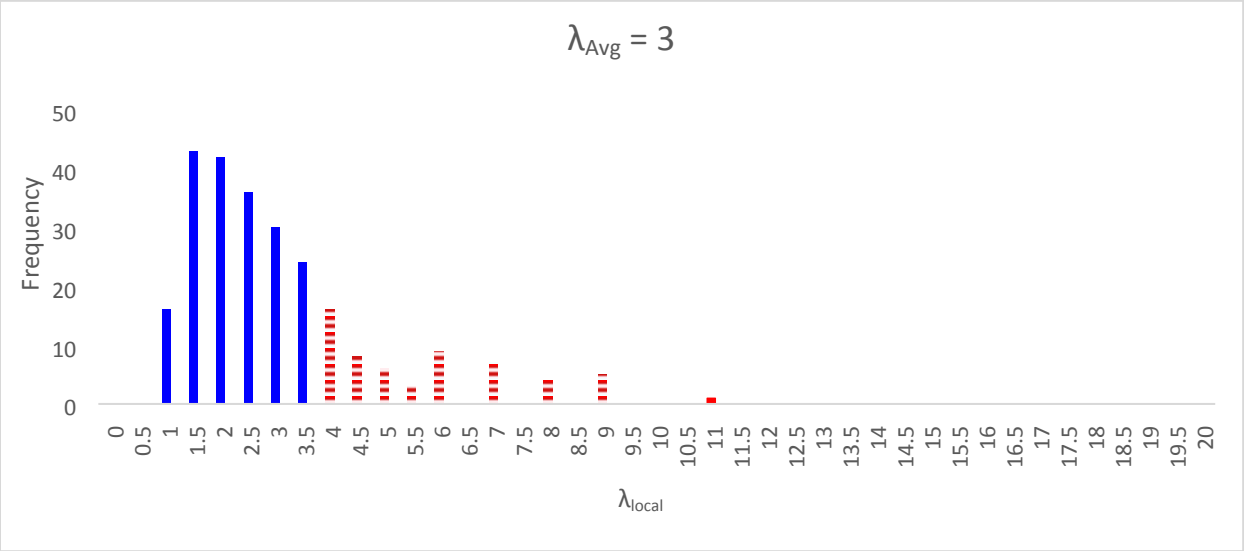


**Figure S2. Graphical distribution of $\lambda_{local}$ values determined through MD analysis of a sulfur-centered cube with $\lambda_{Avg}$ = 3 and which consisted of Nafion and water molecules. Blue lines represent $\lambda_{local}$ 0 – 3, dotted red lines represent $\lambda_{local}$ 4 – 9, and solid red lines represent $\lambda_{local}$ 10 – 20.**

**Table S3 – $\lambda_{local}$ values calculated from a molecular dynamics simulation for Nafion, using a $\lambda_{Avg}$ value equal to 10, along with the frequency of each $\lambda_{local}$ event.**

| $\lambda_{local}$ | Frequency | $\lambda_{local}$ | Frequency |
|---|---|---|---|
| 0 | 0 | 10 | 15 |
| 0.5 | 0 | 10.5 | 0 |
| 1 | 1 | 11 | 19 |
| 1.5 | 2 | 11.5 | 0 |
| 2 | 4 | 12 | 12 |
| 2.5 | 8 | 12.5 | 1 |
| 3 | 11 | 13 | 10 |
| 3.5 | 12 | 13.5 | 0 |
| 4 | 15 | 14 | 4 |
| 4.5 | 10 | 14.5 | 0 |
| 5 | 10 | 15 | 4 |
| 5.5 | 11 | 15.5 | 0 |
| 6 | 12 | 16 | 2 |
| 6.5 | 9 | 16.5 | 0 |
| 7 | 13 | 17 | 3 |
| 7.5 | 1 | 17.5 | 0 |
| 8 | 8 | 18 | 5 |
| 8.5 | 1 | 18.5 | 0 |
| 9 | 14 | 19 | 0 |
| 9.5 | 0 | 19.5 | 0 |

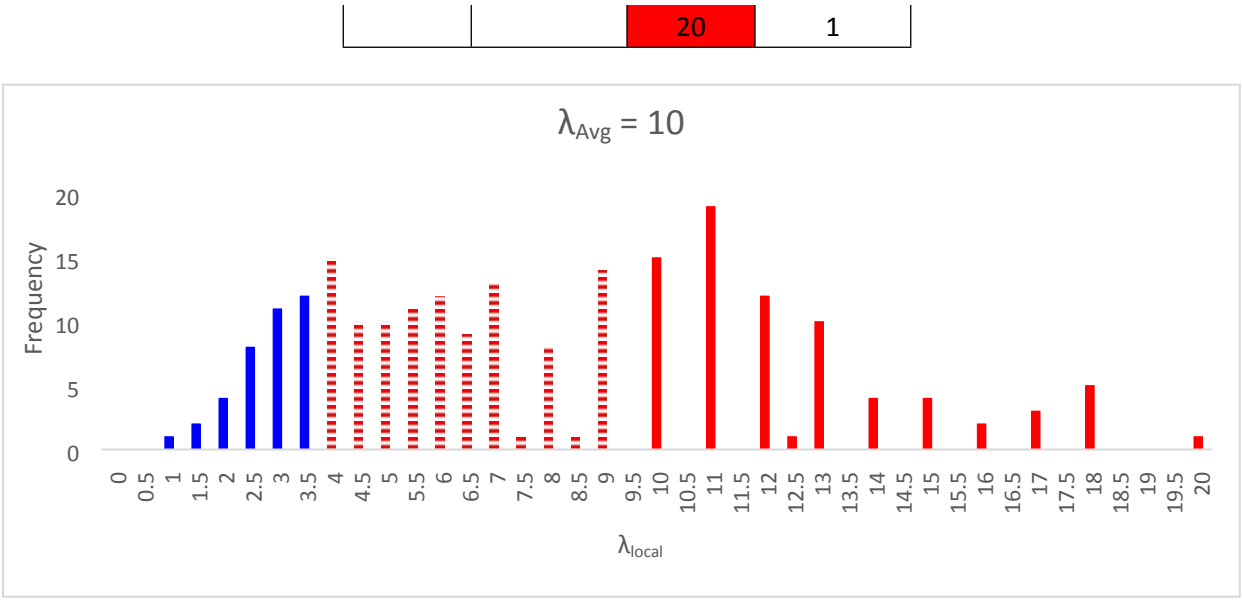


**Figure S3. Graphical distribution of $\lambda_{local}$ values determined through MD analysis of a sulfur-centered cube with $\lambda_{Avg}$ = 10 and which consisted of Nafion and water molecules. Blue lines represent $\lambda_{local}$ 0 – 3, dotted red lines represent $\lambda_{local}$ 4 – 9, and solid red lines represent $\lambda_{local}$ 10 – 20.**

**Table S4 – $\lambda_{local}$ values calculated from a molecular dynamics simulation for Nafion, using a $\lambda_{Avg}$ value equal to 15, along with the frequency of each $\lambda_{local}$ event.**

| $\lambda_{local}$ | Frequency | $\lambda_{local}$ | Frequency |
|---|---|---|---|
| 0 | 0 | 10 | 14 |
| 0.5 | 0 | 10.5 | 0 |
| 1 | 0 | 11 | 18 |
| 1.5 | 0 | 11.5 | 0 |
| 2 | 5 | 12 | 18 |
| 2.5 | 5 | 12.5 | 0 |
| 3 | 9 | 13 | 11 |
| 3.5 | 7 | 13.5 | 0 |
| 4 | 8 | 14 | 15 |
| 4.5 | 4 | 14.5 | 0 |
| 5 | 6 | 15 | 9 |
| 5.5 | 10 | 15.5 | 0 |
| 6 | 5 | 16 | 6 |
| 6.5 | 8 | 16.5 | 0 |
| 7 | 8 | 17 | 6 |
| 7.5 | 6 | 17.5 | 0 |
| 8 | 11 | 18 | 2 |
| 8.5 | 2 | 18.5 | 0 |
| 9 | 7 | 19 | 1 |
| 9.5 | 1 | 19.5 | 0 |

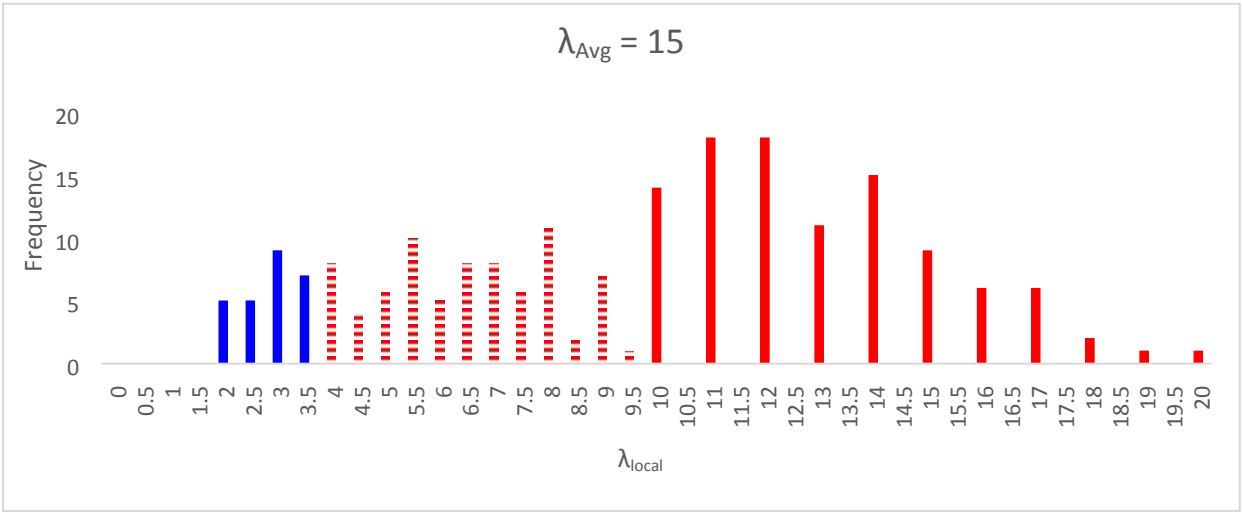


**Figure S4. Graphical distribution of $\lambda_{local}$ values determined through MD analysis of a sulfur-centered cube with $\lambda_{Avg}$ = 15 and which consisted of Nafion and water molecules. Blue lines represent $\lambda_{local}$ 0 – 3, dotted red lines represent $\lambda_{local}$ 4 – 9, and solid red lines represent $\lambda_{local}$ 10 – 20.**

**Table S5 – $\lambda_{local}$ values calculated from a molecular dynamics simulation for Nafion, using a $\lambda_{Avg}$ value equal to 20, along with the frequency of each $\lambda_{local}$ event.**

| $\lambda_{local}$ | Frequency | $\lambda_{local}$ | Frequency |
|---|---|---|---|
| 0 | 0 | 10 | 9 |
| 0.5 | 0 | 10.5 | 2 |
| 1 | 0 | 11 | 19 |
| 1.5 | 1 | 11.5 | 2 |
| 2 | 0 | 12 | 18 |
| 2.5 | 12 | 12.5 | 0 |
| 3 | 7 | 13 | 10 |
| 3.5 | 12 | 13.5 | 0 |
| 4 | 11 | 14 | 11 |
| 4.5 | 13 | 14.5 | 1 |
| 5 | 5 | 15 | 11 |
| 5.5 | 4 | 15.5 | 1 |
| 6 | 7 | 16 | 6 |
| 6.5 | 7 | 16.5 | 0 |
| 7 | 4 | 17 | 14 |
| 7.5 | 5 | 17.5 | 0 |
| 8 | 3 | 18 | 5 |
| 8.5 | 2 | 18.5 | 0 |
| 9 | 6 | 19 | 2 |
| 9.5 | 0 | 19.5 | 1 |
| | | 20 | 1 |

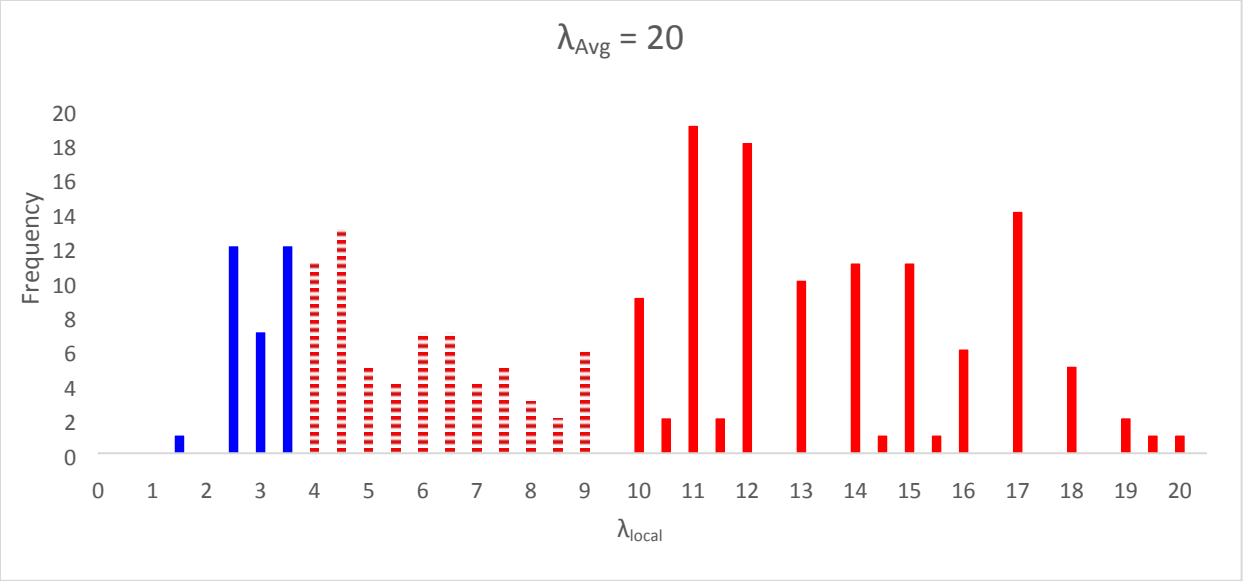


**Figure S5. Graphical distribution of $\lambda_{local}$ values determined through MD analysis of a sulfur-centered cube with $\lambda_{Avg}$ = 20 and which consisted of Nafion and water molecules. Blue lines represent $\lambda_{local}$ 0 – 3, dotted red lines represent $\lambda_{local}$ 4 – 9, and solid red lines represent $\lambda_{local}$ 10 – 20.**

**SI Calculations.**

The effective depth of penetration of the evanescent wave: $d_e = \frac{(d_{e\perp} + d_{e\parallel})}{2}$

Is unique for perpendicular polarization: $d_{e\perp} = \frac{n_1^2 n_2 \cos\theta}{(n_1^2 - n_2^2)} \times \frac{\lambda_1}{\pi\sqrt{n_1^2 \sin^2\theta - n_2^2}}$

And parallel polarization: $d_{e\parallel} = \frac{n_1^2 n_2 \cos\theta}{(n_1^2 - n_2^2)} \times \frac{2n_1^2 \sin^2\theta - n_2^2}{(n_1^2 - n_2^2)\sin^2\theta - n_2^2} \times \frac{\lambda_1}{\pi\sqrt{n_1^2 \sin^2\theta - n_2^2}}$

Where $\lambda_1 = \frac{\lambda}{n_1}$

$\lambda \rightarrow$ Wavelength of light

$n_1 \rightarrow$ Refractive index of ATR crystal

$n_2 \rightarrow$ Refractive index of sample

$n_{ZnSe} = n_1 = 2.4$

$n_{Nafion} = n_2 =$

| State of Nafion Film | Refractive Index $n_2$ | |
|---|---|---|
| | In-plane polarization (Transverse Electric) | Perpendicular polarization (Transverse Magnetic) |
| Dry | $1.3539^a$ | $1.3472^a$ |
| Wet | $1.3433^a$ | $1.3366^a$ |

$\lambda_{MIR} \approx 3 - 8\ \mu m$; at $1300\ cm^{-1}$ $\lambda = 7.692\ \mu m$

$\theta = 45°$

$\lambda_1 = \frac{7.692\ \mu m}{2.4} = 3.205\ \mu m$

$$d_{e\ \perp} = \frac{2.4^2 n_2 \cos 45°}{(2.4^2 - {n_2}^2)} \times \frac{3.205}{\pi\sqrt{2.4^2 \sin^2 45° - {n_2}^2}} = \frac{2.4^2 n_2 \cos 45°}{(2.4^2 - {n_2}^2)} \times \frac{3.205\ \mu m}{\pi\sqrt{2.4^2 \sin^2 45° - {n_2}^2}}$$

$$d_{e\ \parallel} = \frac{2.4^2 n_2 \cos 45°}{(2.4^2 - {n_2}^2)} \times \frac{2 \cdot 2.4^2 \sin^2 45° - {n_2}^2}{(2.4^2 - {n_2}^2)\sin^2 45° - {n_2}^2} \times \frac{3.205\ \mu m}{\pi\sqrt{2.4^2 \sin^2 45° - {n_2}^2}}$$

| State of Nafion Film | $d_{e\ \parallel}$ | $d_{e\ \perp}$ |
|---|---|---|
| Dry | $3.977116\ \mu m$ | $0.660127\ \mu m$ |
| Wet | $3.750029\ \mu m$ | $0.646747\ \mu m$ |

$$d_{e,\ dry} = \frac{(0.660127\ \mu m + 3.977116\ \mu m)}{2} = 2.318621\ \mu m$$

$$d_{e,\ wet} = \frac{(0.646747\ \mu m + 3.750029\ \mu m)}{2} = 2.198388\ \mu m$$