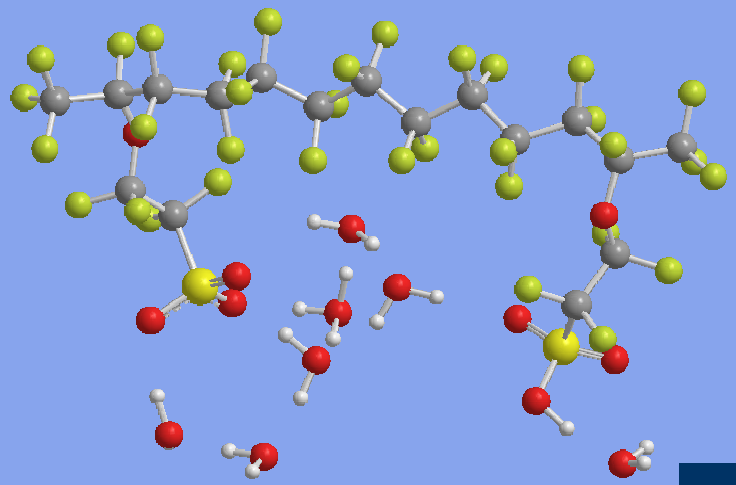
Proton Conduction in Diverse Media

12/05/2005

Mechanisms of Proton Conduction in the Dow Membrane: Complexity, Cooperativity, and Connectivity



S.J. Paddison
University of Alabama

J. A. Elliott
University of Cambridge

UAH
The University of Alabama in Huntsville

Recent Reviews

S.J. Paddison, “First principles modeling of sulfonic acid-based ionomer membranes”, in *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, edited by W. Wielstich, H. Gasteiger, A. Lamm, Volume 3: *Fuel Cell Technology and Applications*, J. Wiley and Sons, Chichester, Chapter 31 (2003).

S.J. Paddison, “Proton conduction mechanisms in Polymer Electrolyte Membranes at low degrees of hydration”, *Annual Review of Materials Research*, **33**, 289-319 (2003).

K. D. Kreuer, S.J. Paddison, E. Spohr, and M. Schuster “Transport in Proton Conductors for Fuel Cell Applications: Simulations, Elementary Reactions, and Phenomenology”, *Chemical Reviews*, **104**, 4637 (2004).

Collaboration

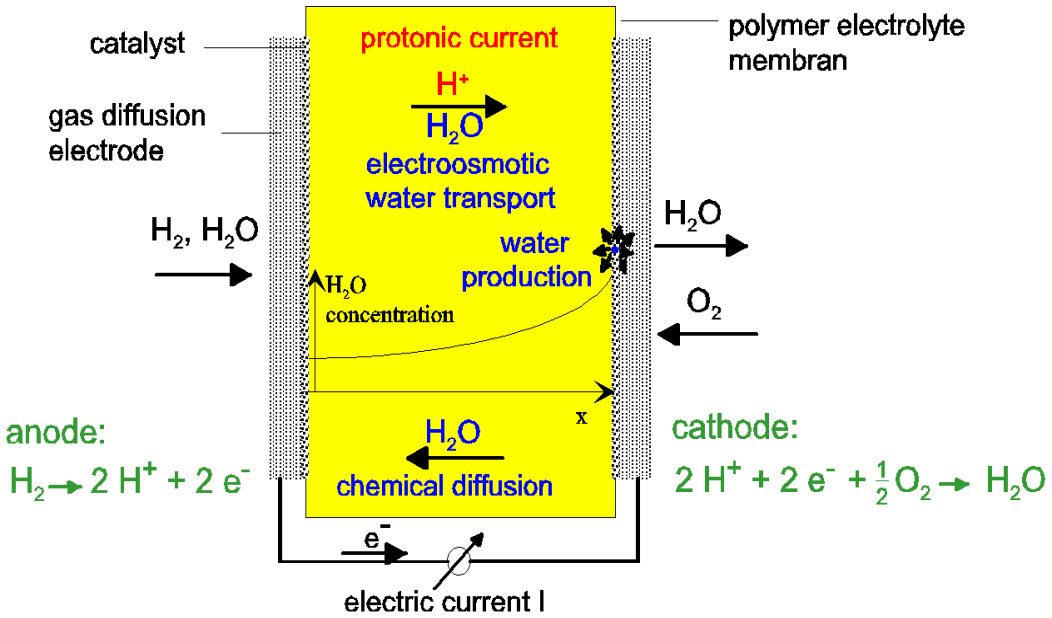
Past

- T. A. Zawodzinski Jr., MST-11, LANL – CWRU
- L. R. Pratt, T-12, LANL
- M. Eikerling, MST-11, LANL – SFU
- T. K. Mattsson, SSC, SNL

Present

- K-D. Kreuer, Max Planck Institute, Stuttgart, GERMANY
- R. Paul, The University of Calgary, CANADA
- J. A. Elliott, The University of Cambridge, UK

Polymer electrolyte membrane (PEM) fuel cell



total reaction: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

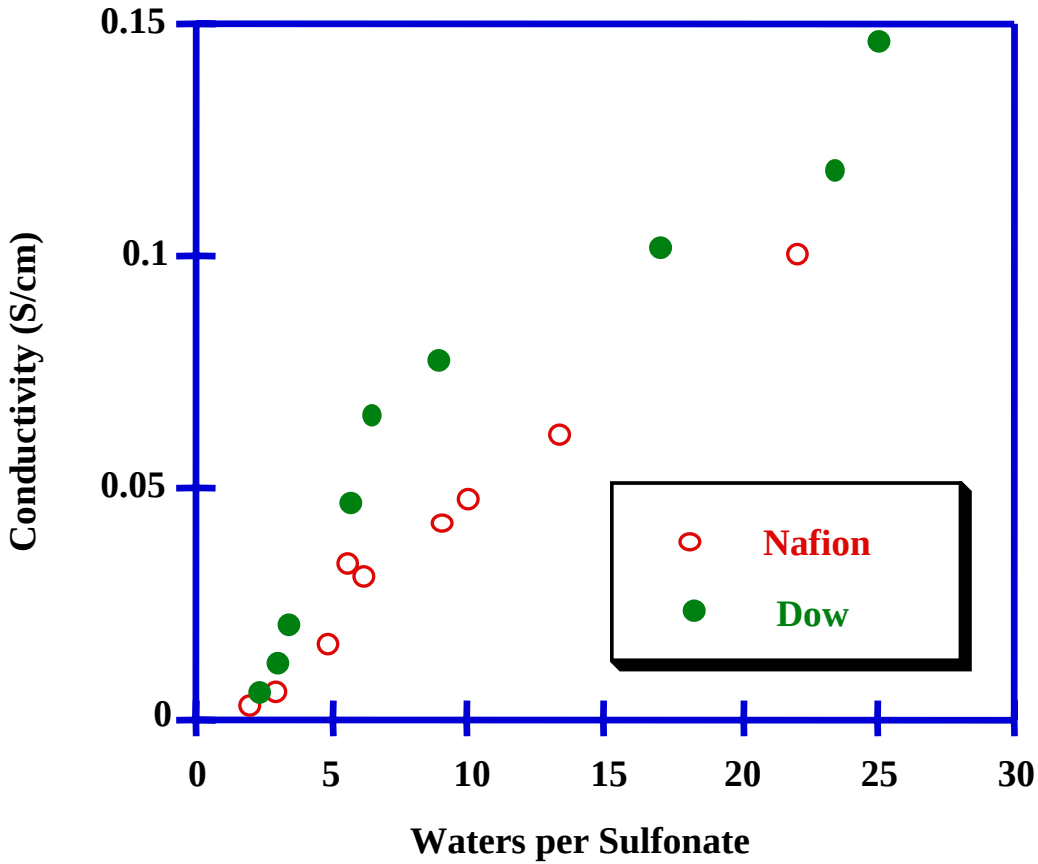
Modeling Goals

(1) To obtain a molecular-level understanding of transport mechanism(s) in polymer electrolyte membranes.

(2) To connect/correlate this information with function/properties of the materials.

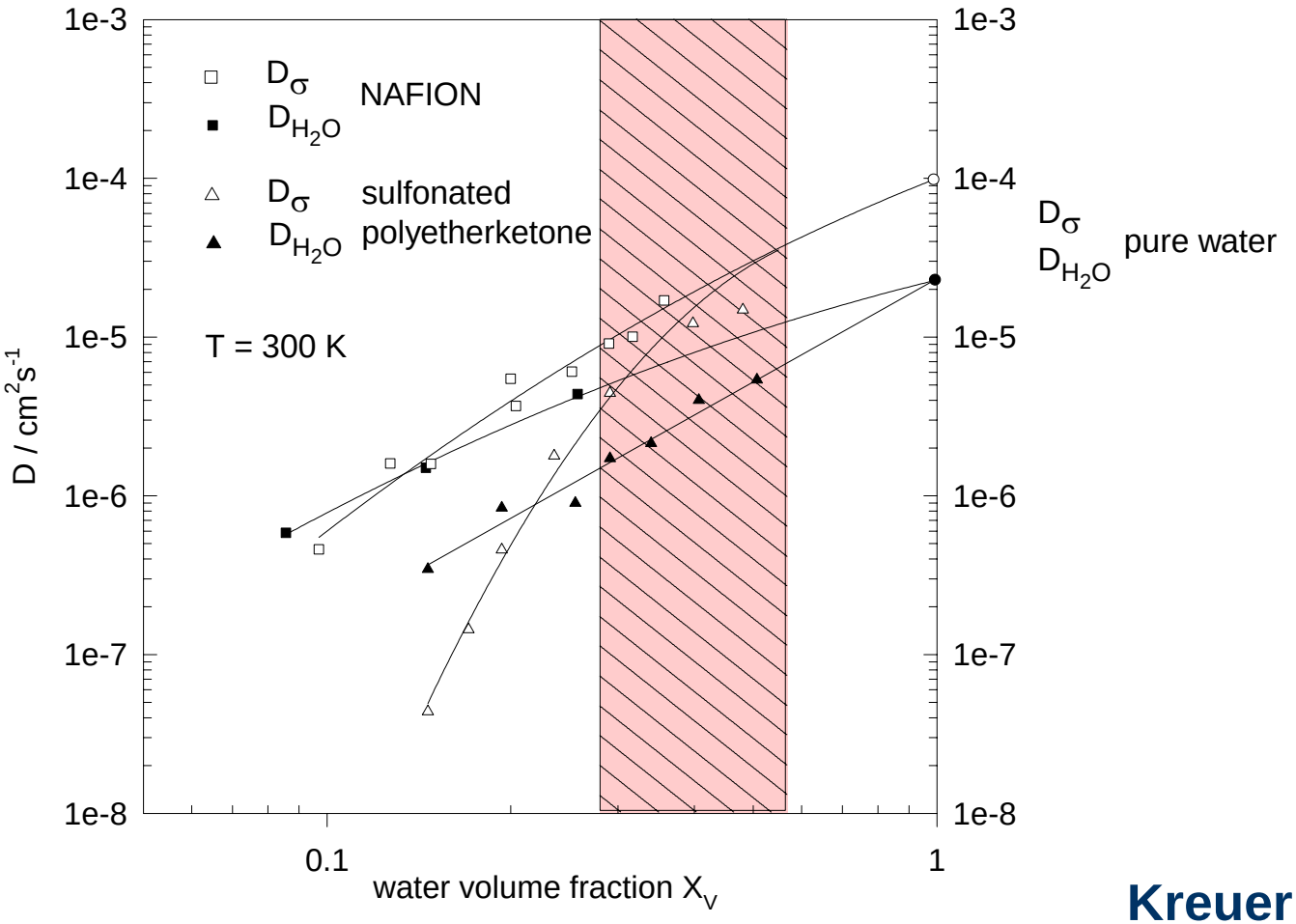
(3) To design, in collaboration with synthetic and experimental characterization efforts, improved materials.

Provocation:



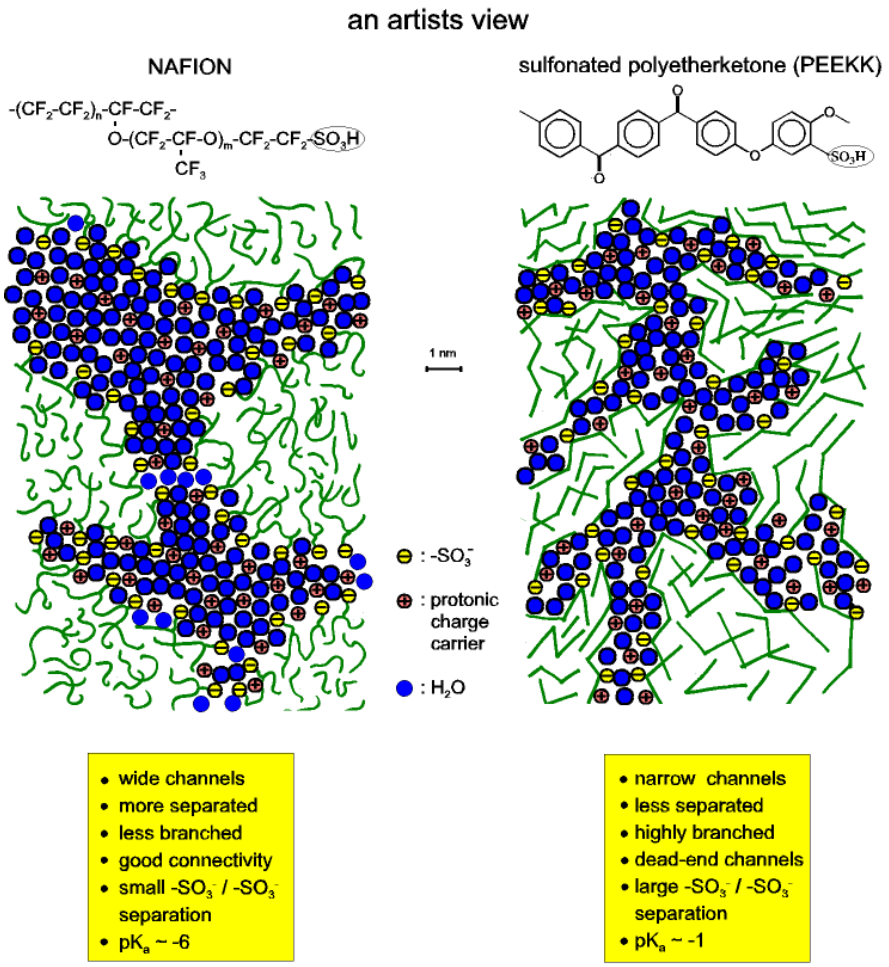
Zawodzinski, LANL

Provocation:



Kreuer, MPI

Morphology:



- model dependent
- measurement dependent

relevant scales and interactions	• 0,1 nm	reactions on molecular scale
	• 1 nm	space charge effects (electrostatics)
	• 10 nm	percolation

K. D. Kreuer, *J. Membr. Sci.* **185**, 29 (2001).

Conduction:

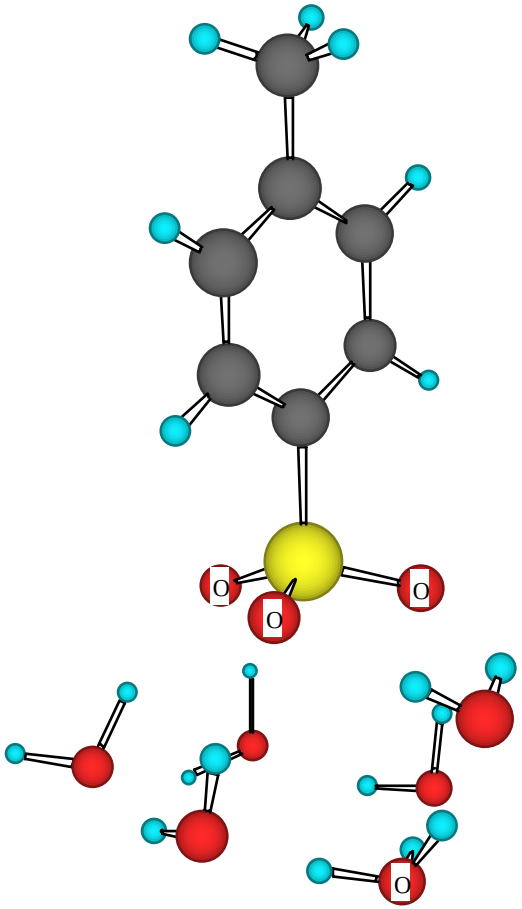
(1) Complexity: proton dissociation; transfer; transport - diffusion

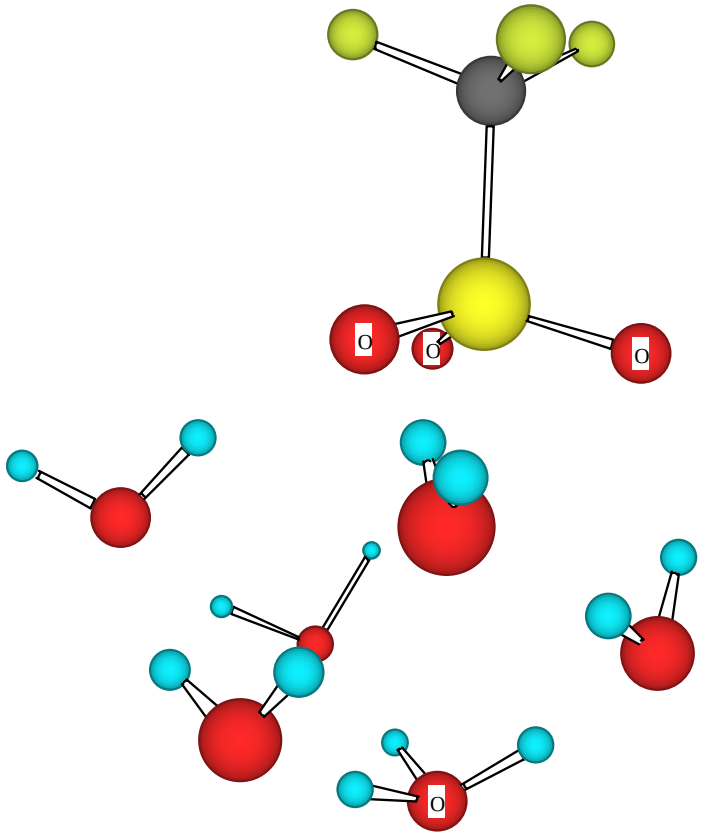
(2) Connectivity: hydrogen bonding: water to anionic sites; water to water; domain to domain

(3) Cooperativity: flexibility of polymeric groups, motion of polymeric side chains, flux of water

All depend on: polymer chemistry, degree of hydration, temperature, and presence of ‘other’ species.

Complexity: local chemistry specific separation



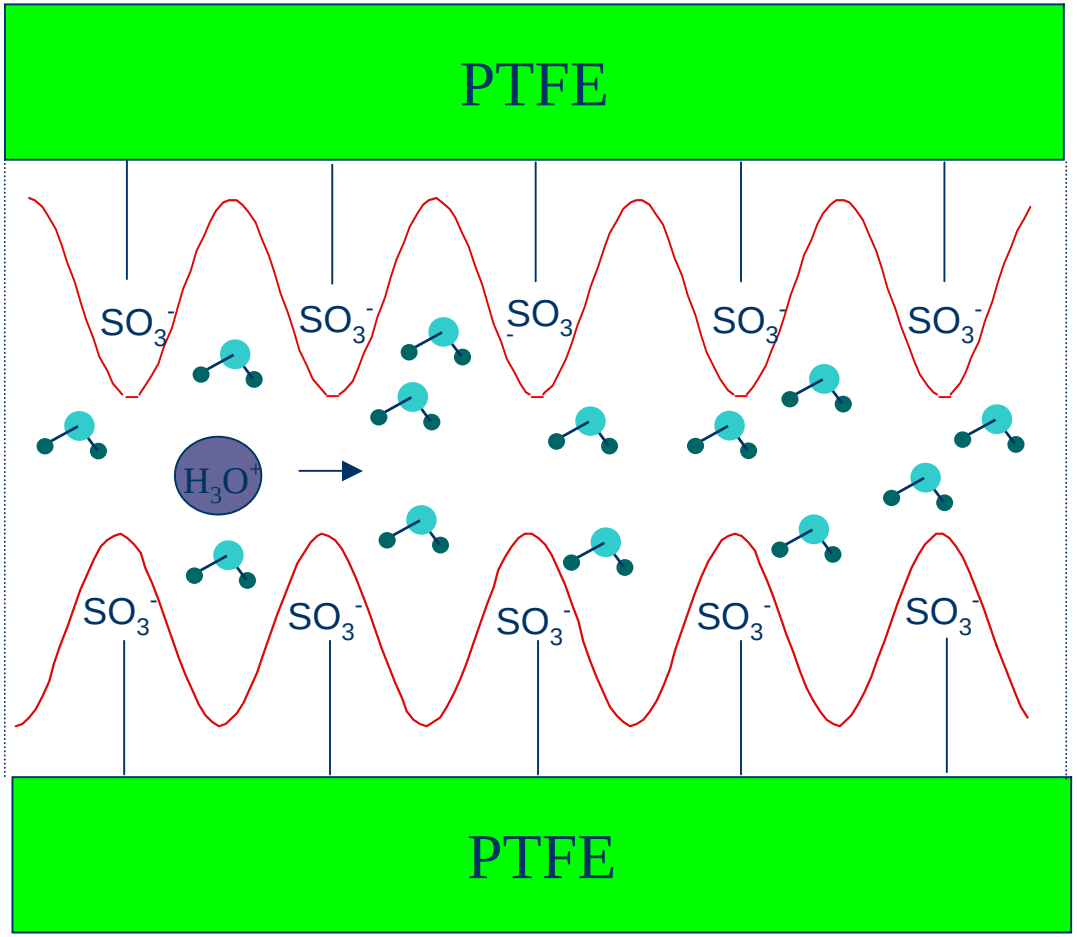


r(**O–O**)= 3.914 Å 4.235 Å

B3LYP/6-31G**

S.J. Paddison *J. New Materials for Electrochem. Sys.* **4**, 197 (2001).

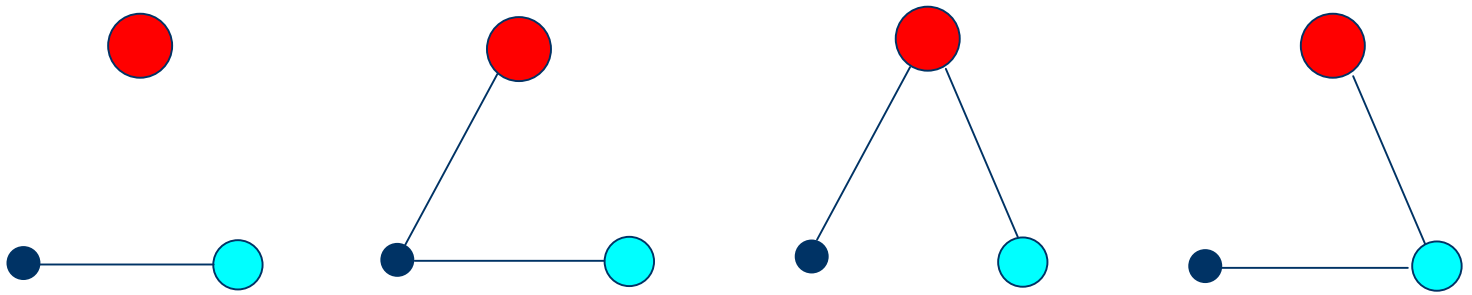
Complexity: proton diffusion



S.J. Paddison, R. Paul, and T.A. Zawodzinski, in *Proton Conducting Membrane Fuel Cells II*, S. Gottesfeld and T.F. Fuller, Editors, **PV 98-27**, 106-120, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).

Complexity: proton diffusion

$$\text{"}Friction\ Coefficient\text{"} = \beta\int_0^\infty dt\left\langle \vec{F}_{\alpha s} e^{-iL_0 t}\vec{F}_{\alpha s}\right\rangle_0 + \beta\int_0^\infty dt\left\langle \vec{F}_{\alpha s} e^{-iL_0 t}\vec{F}_{ps}\right\rangle_0 + \beta\int_0^\infty dt\left\langle \vec{F}_{\alpha p} e^{-iL_0 t}\vec{F}_{ps}\right\rangle_0 + \beta\int_0^\infty dt\left\langle \vec{F}_{\alpha p} e^{-iL_0 t}\vec{F}_{\alpha s}\right\rangle_0$$

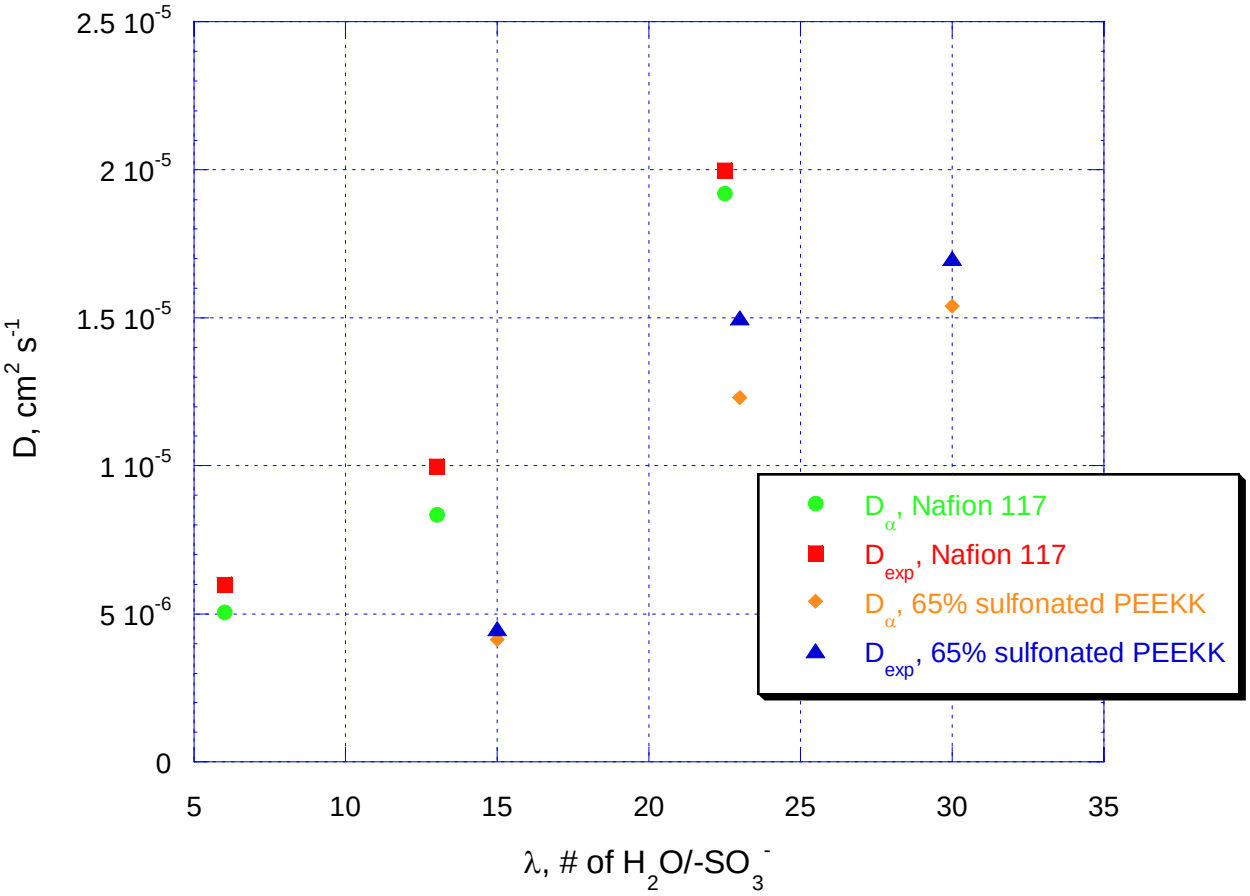


$$\underline{\underline{\zeta}} = \boxed{\zeta^{(0)}} + \zeta^{(c)}$$

Einstein Relation $\Rightarrow D_\alpha = \dfrac{kT}{\zeta_\alpha}$

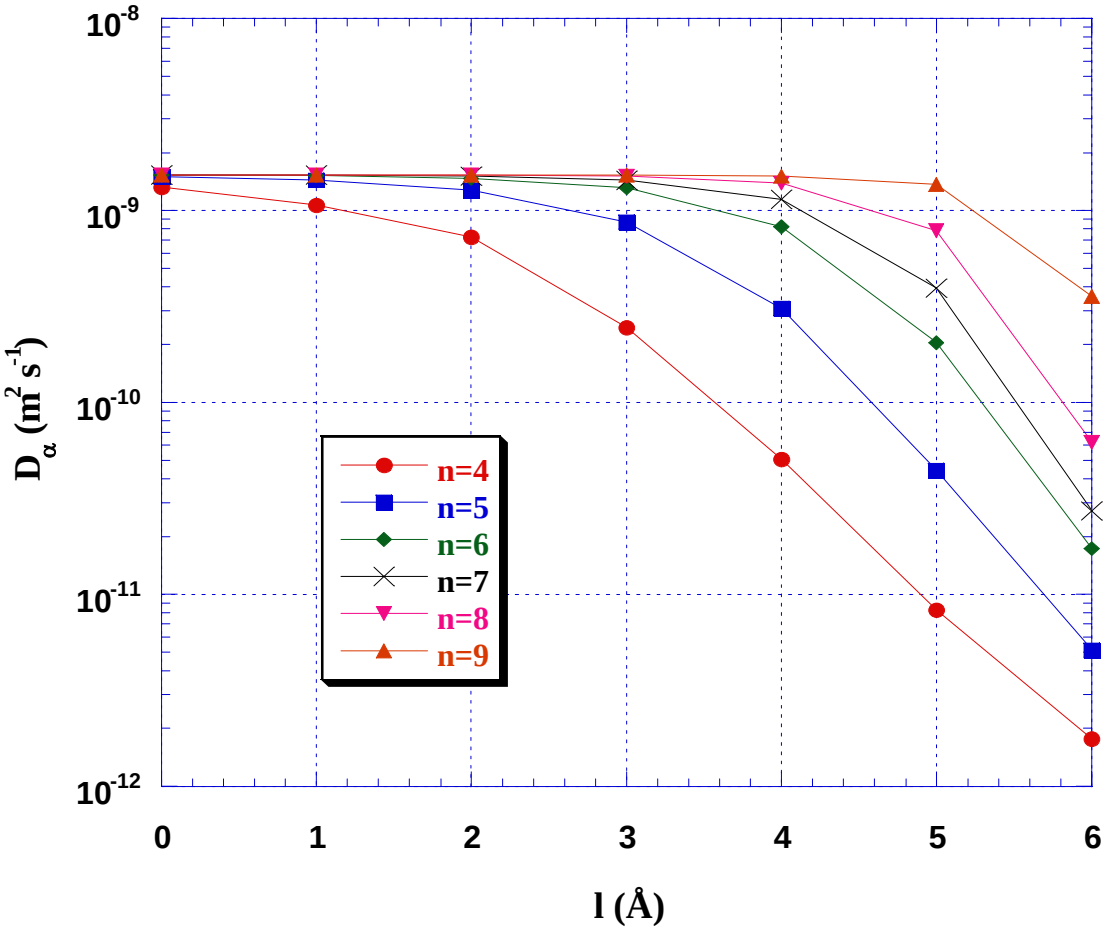
S.J. Paddison, R. Paul, and T.A. Zawodzinski Jr., *J. Electrochem. Soc.*, **147**, 617 (2000).

Complexity: proton diffusion



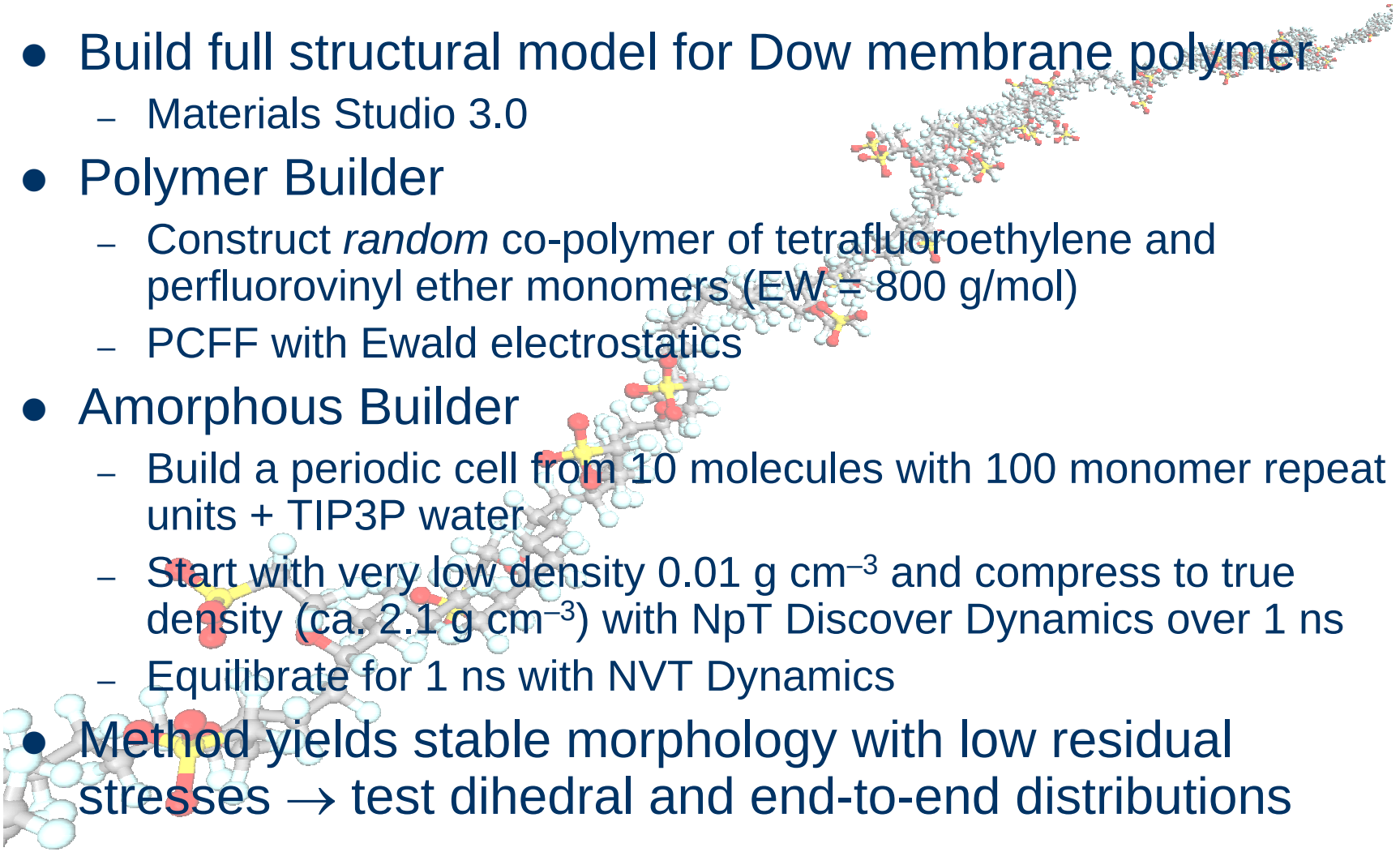
S. J. Paddison, *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, W. Vielstich, A. Lamm, and H. Gasteiger, Editors-in-Chief, Chapter 31, pp. 396-411, J. Wiley and Sons Ltd, Chichester (2003).

Complexity: proton diffusion



S. J. Paddison and R. Paul, *J. Chem. Phys.*, **115**, 7753 (2001).

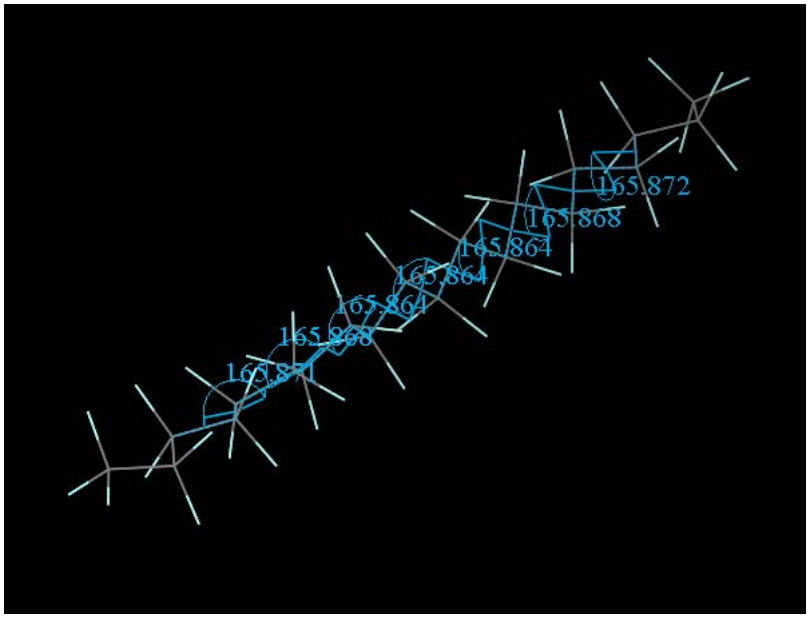
Molecular mechanics modelling of Dow polymer

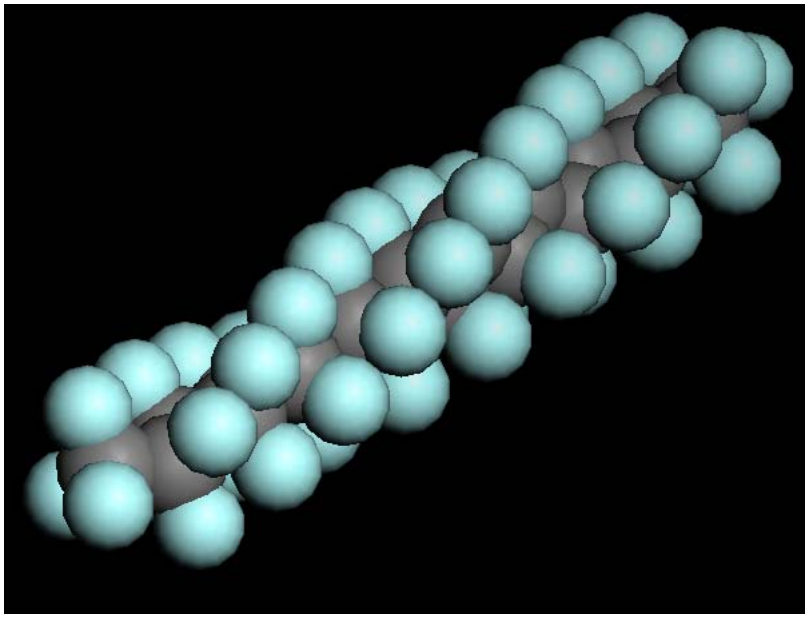


- Build full structural model for Dow membrane polymer
  - Materials Studio 3.0
- Polymer Builder
  - Construct *random* co-polymer of tetrafluoroethylene and perfluorovinyl ether monomers (EW = 800 g/mol)
  - PCFF with Ewald electrostatics
- Amorphous Builder
  - Build a periodic cell from 10 molecules with 100 monomer repeat units + TIP3P water
  - Start with very low density 0.01 g cm^{-3} and compress to true density (ca. 2.1 g cm^{-3}) with NpT Discover Dynamics over 1 ns
  - Equilibrate for 1 ns with NVT Dynamics
- Method yields stable morphology with low residual stresses $\rightarrow$ test dihedral and end-to-end distributions

Perfluoroalkane dihedral distribution

- Fluorines induce a helical pitch in backbone (ϕ = 165º) for an unsubstituted, isolated oligomeric chain

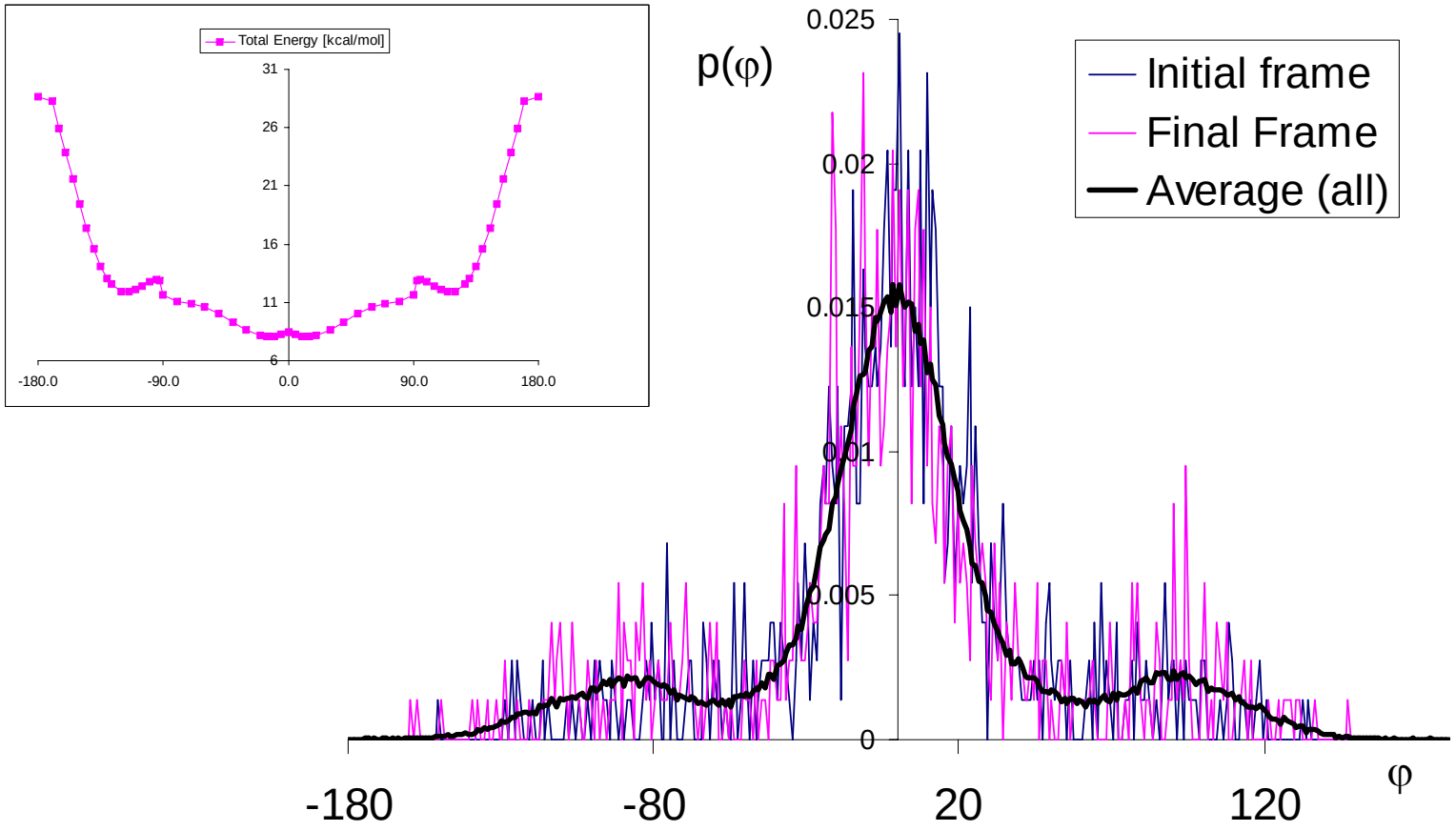




- In PTFE, *trans* and *gauche* states are known to ‘split’

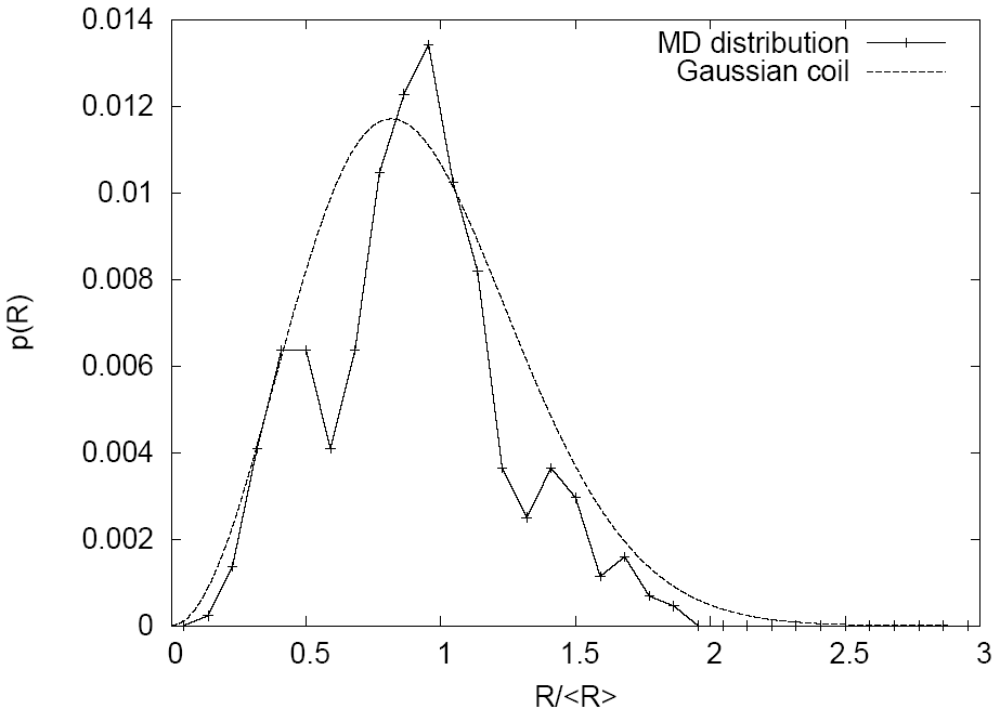
Perfluoroalkane dihedral distribution

- Dihedral angle distribution from MD simulations



Perfluoroalkane end-to-end distributions

- For Gaussian coils,



$$p(r_{ij}) = \left(\frac{3}{2\pi \left\langle r_{ij}^2 \right\rangle} \right)^{3/2} \exp\left(-\frac{3r_{ij}^2}{2\left\langle r_{ij}^2 \right\rangle} \right)$$

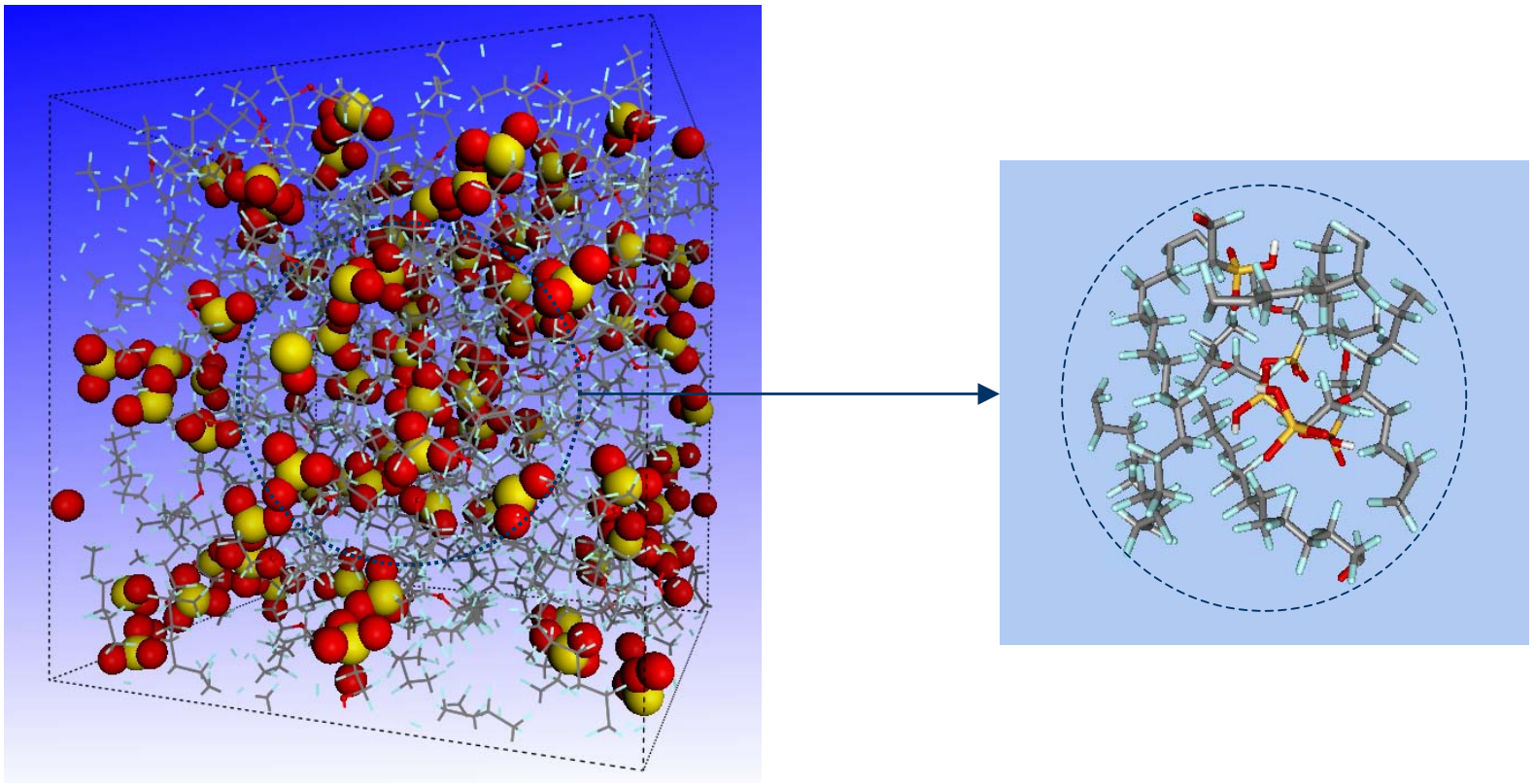
$$C_\infty[\text{PTFE}\,@\,300\ \text{K}] \simeq 11$$

$$\therefore \sqrt{\left\langle R^2 \right\rangle} \simeq 8.5\ \text{nm for N = 100}$$

$$\text{c.f. } \sqrt{\left\langle R^2 \right\rangle} = 9.8\ \text{nm from MD}$$

- Chain trajectories are reasonably well relaxed

Dow membrane – multi-scale modeling



- predict morphology to understand proton transport

Dow membrane – molecular modeling

(1) How does side-chain separation affect connectivity of neighboring sulfonic acid groups?

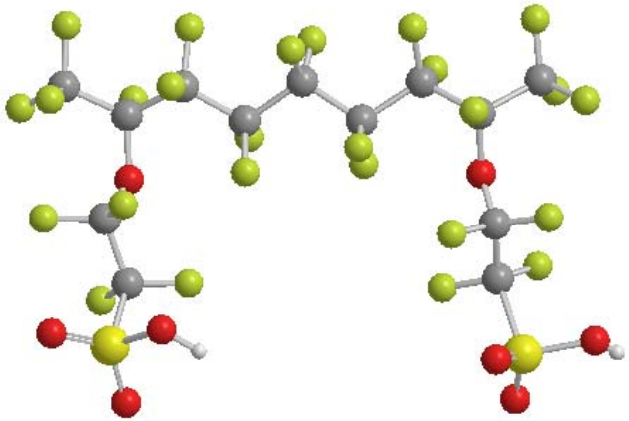
(2) How does side-chain separation affect amount of water required to affect proton transfer and separation (i.e. complexity)?

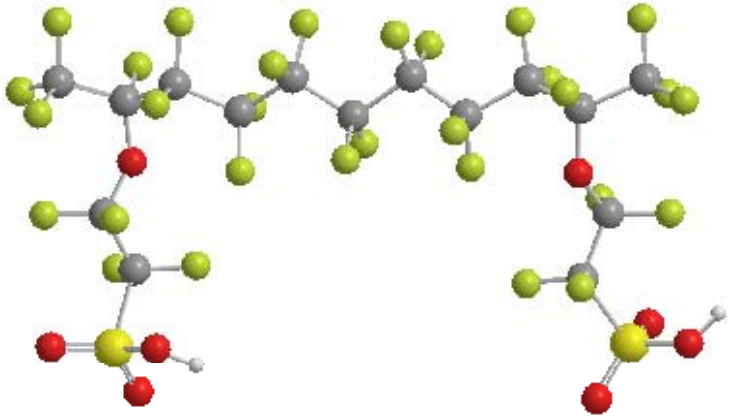
(3) Does side chain separation influence side chain and/or backbone conformation (i.e. cooperativity)?

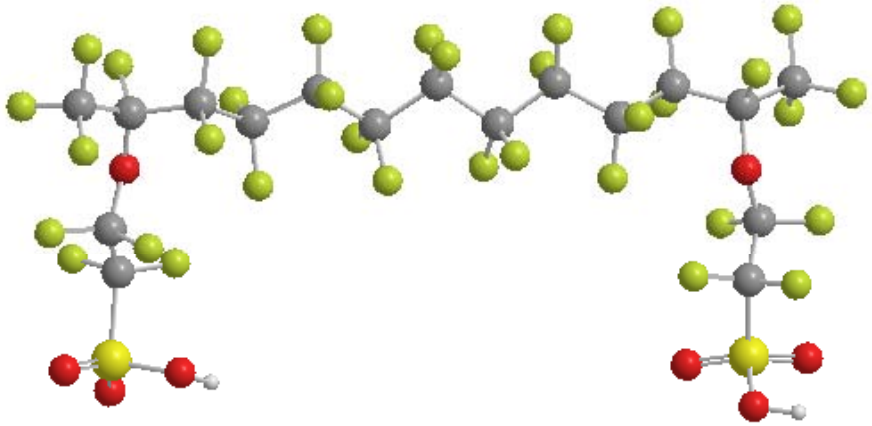
Connectivity: ?

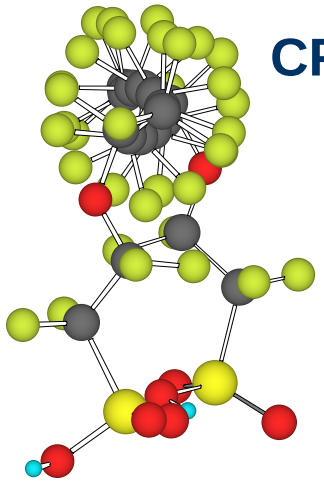
Dow $CF_3CF(-O(CF_2)_2SO_3H)-(CF_2)_n-CF(-O(CF_2)_2SO_3H)CF_3$

n = 5, 7 and 9









CF – CF: 7.9, 10.5, 13.1 Å

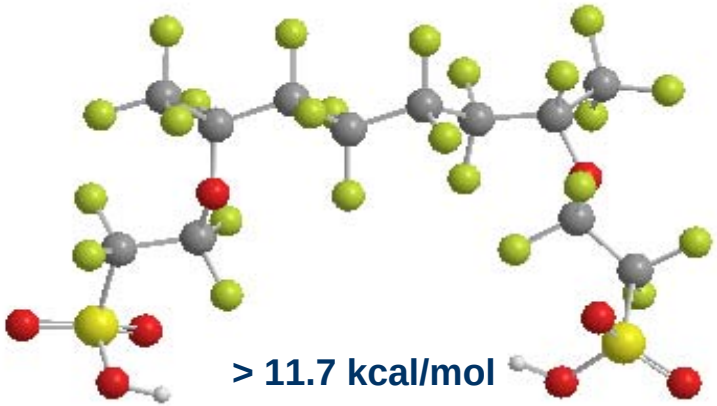
S – S: 9.0, 11.4, 13.5 Å

B3LYP/6-311G**

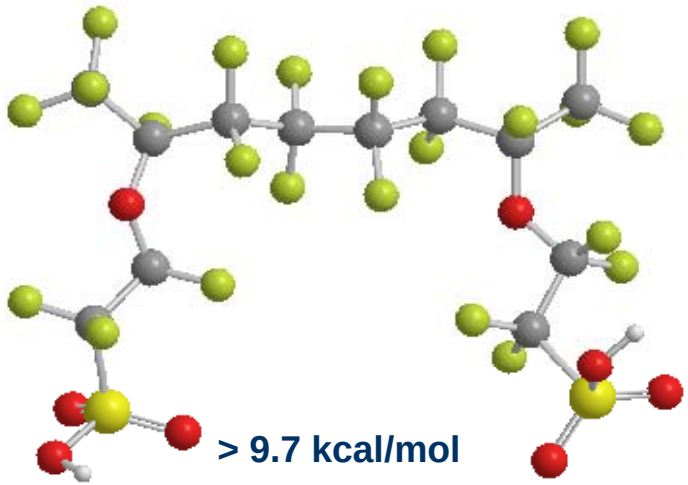
S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

Connectivity: ?

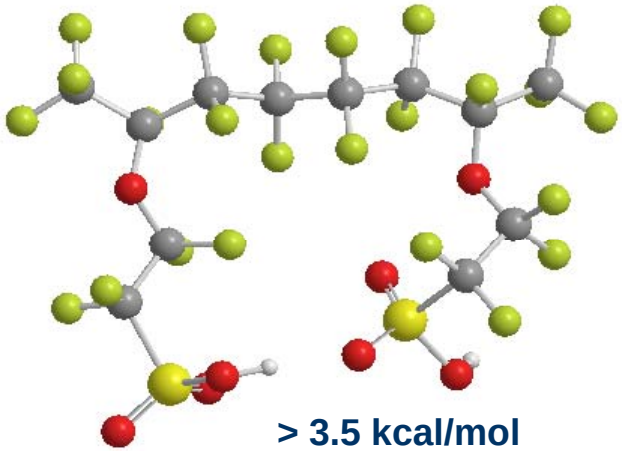
$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_4–CF(–O(CF_2)_2SO_3H)CF_3$



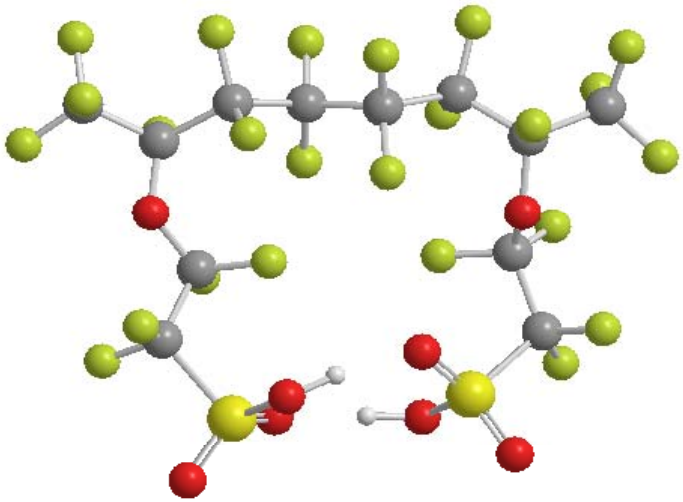
> 11.7 kcal/mol



> 9.7 kcal/mol



> 3.5 kcal/mol



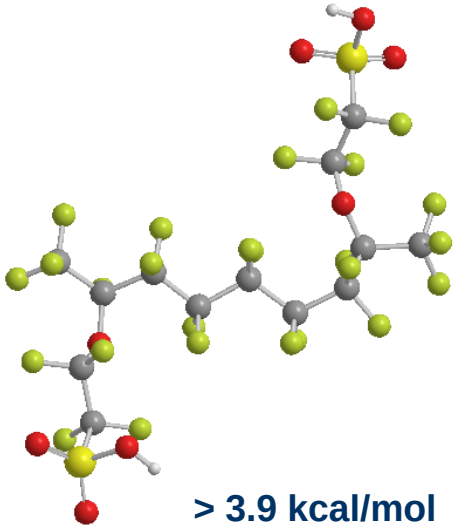
S.J. Paddison and J.A. Elliott, *Solid State Ionics* in preparation (2005).

B3LYP/6-311G**

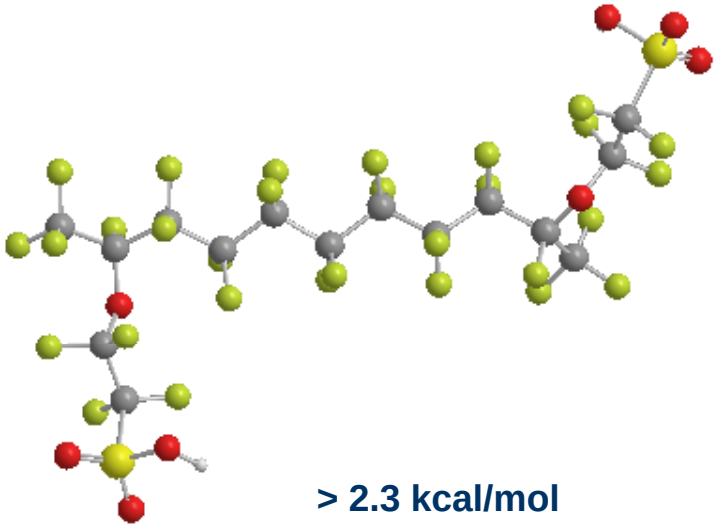
Cooperativity: ?

Dow $CF_3CF(-O(CF_2)_2SO_3H)-(CF_2)_n-CF(-O(CF_2)_2SO_3H)CF_3$

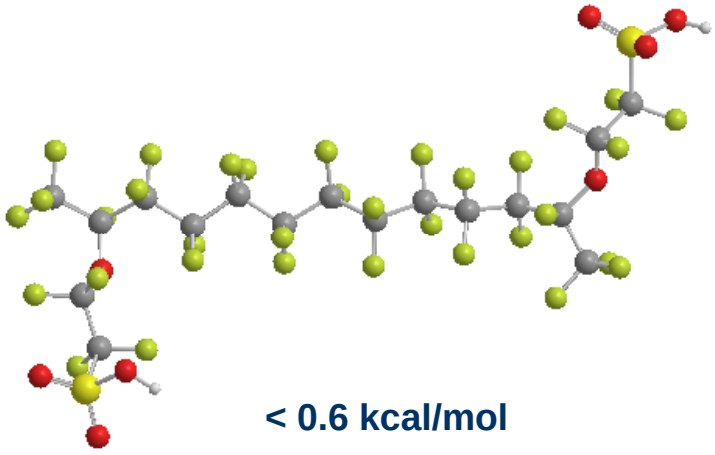
n = 5, 7 and 9



> 3.9 kcal/mol



> 2.3 kcal/mol



< 0.6 kcal/mol

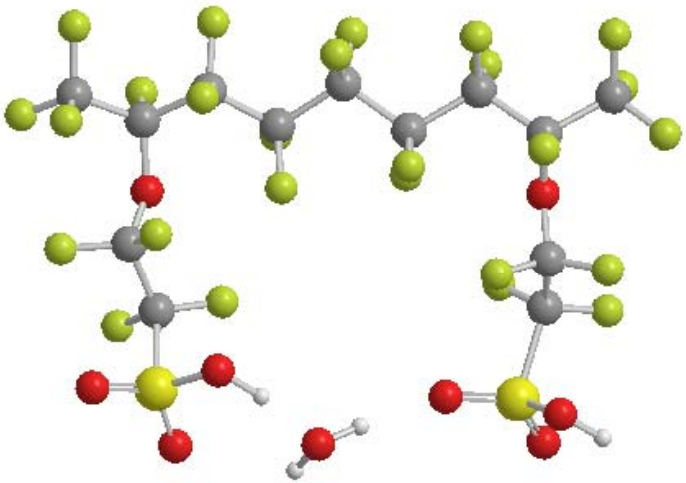
CF – CF: 7.2, 10.5, 13.1 Å

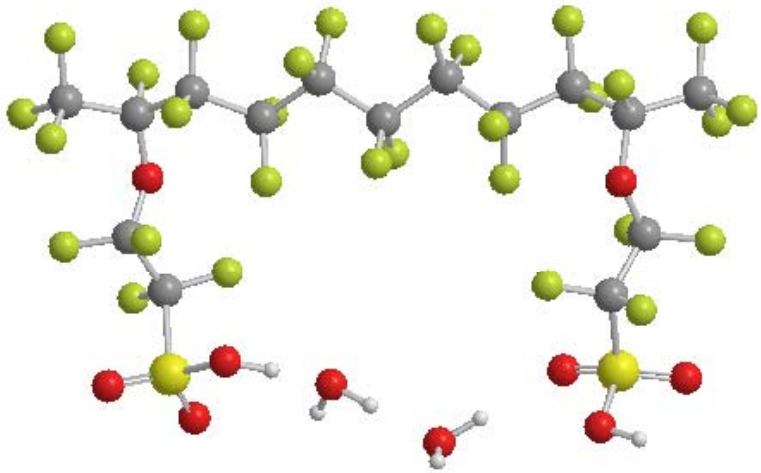
S – S: 13.8, 16.6, 18.2 Å

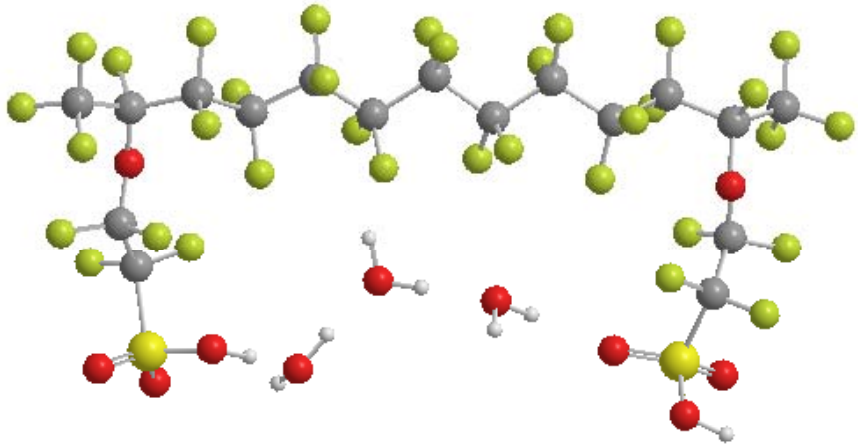
B3LYP/6-311G**

S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

Connectivity: water hydrogen bonding







CF – CF: 7.9, 10.5, 13.1 Å

S – S: 7.2, 9.4, 11.5 Å

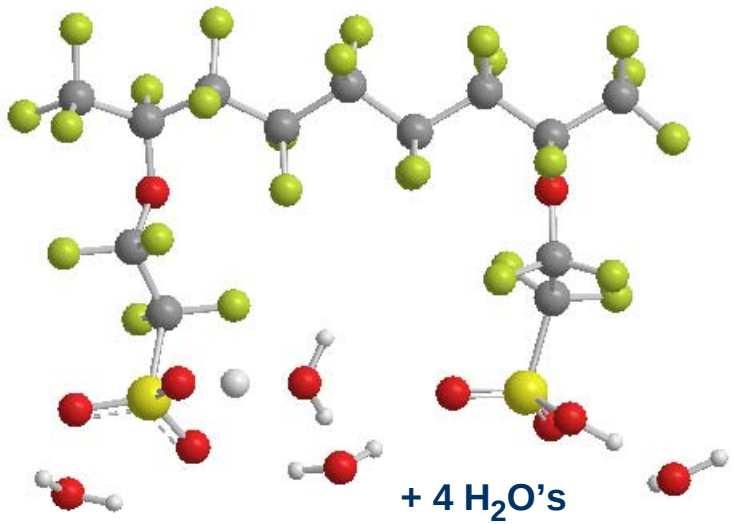
B3LYP/6-311G**

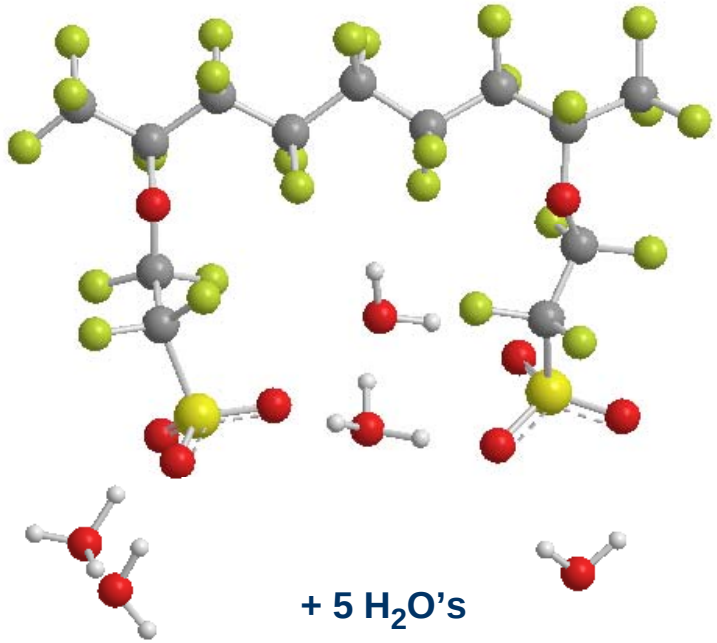
S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

Complexity: proton dissociation

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_5–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$





CF – CF: **7.9, 7.6 Å**

S – S: **7.5, 7.0 Å**

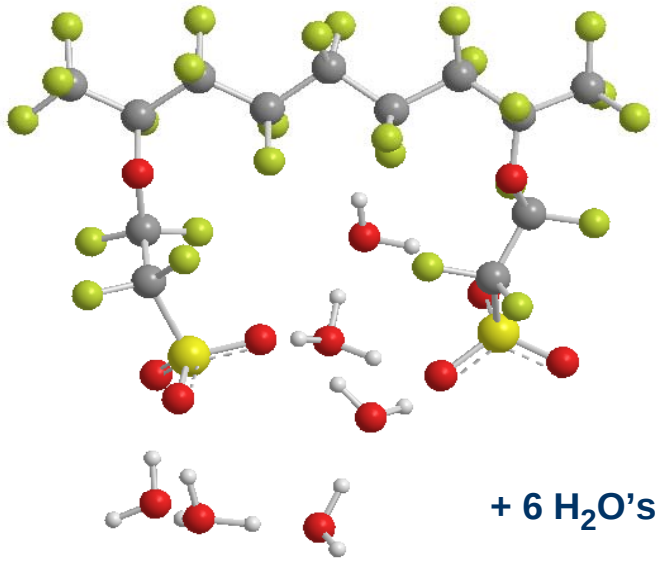
B3LYP/6-311G**

S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

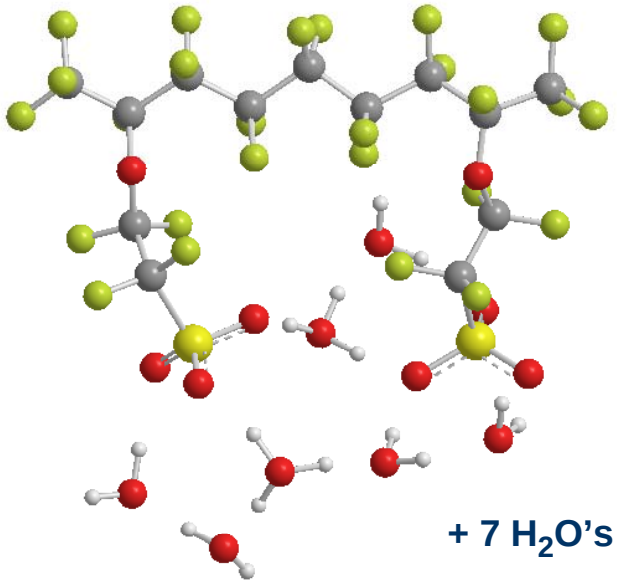
Complexity: proton separation

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_5–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$



+ 6 H_2O's



+ 7 H_2O's

CF – CF: 7.8, 7.8 Å

S – S: 6.5, 6.3 Å

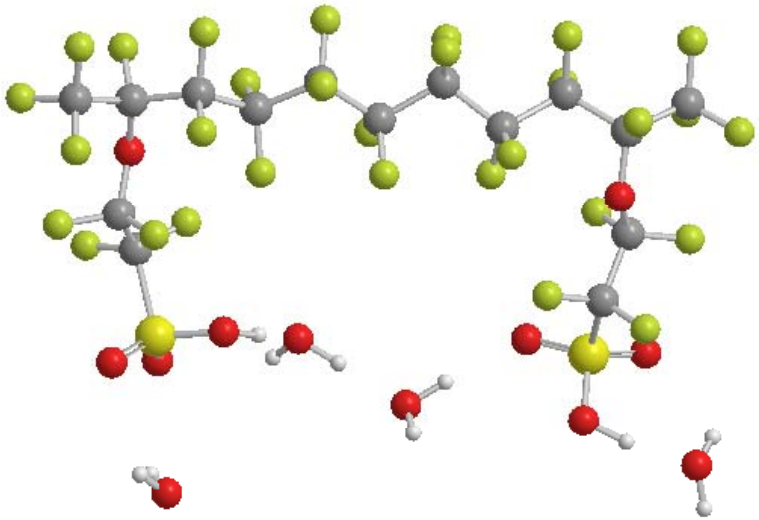
B3LYP/6-311G**

S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

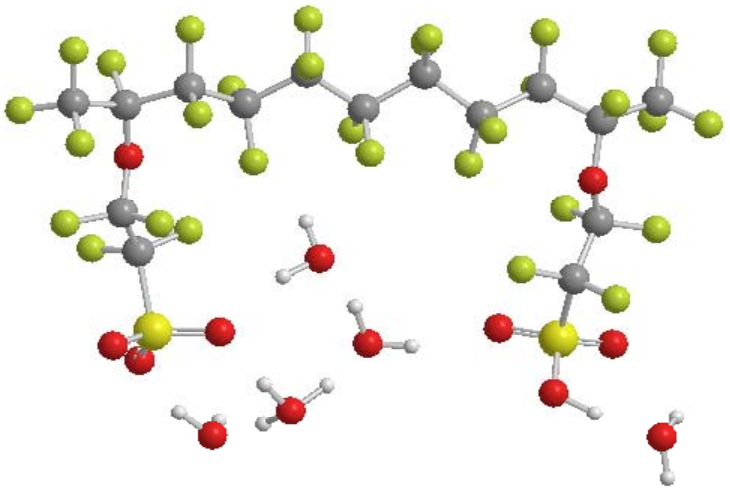
Complexity: proton dissociation

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_7–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$



+ 4 H_2O's



+ 5 H_2O's

CF – CF: **10.5, 10.5 Å**

S – S: **9.2, 9.0 Å**

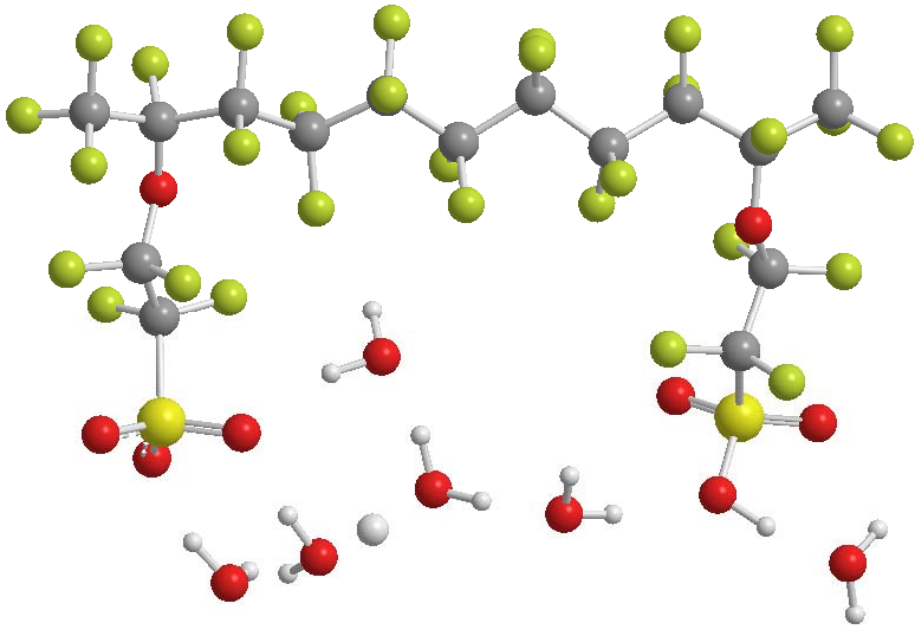
B3LYP/6-311G**

S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

Complexity: proton dissociation

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_7–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$



+ 6 H_2O's

CF – CF: **10.5 Å**

S – S: **10.2 Å**

B3LYP/6-311G**

S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

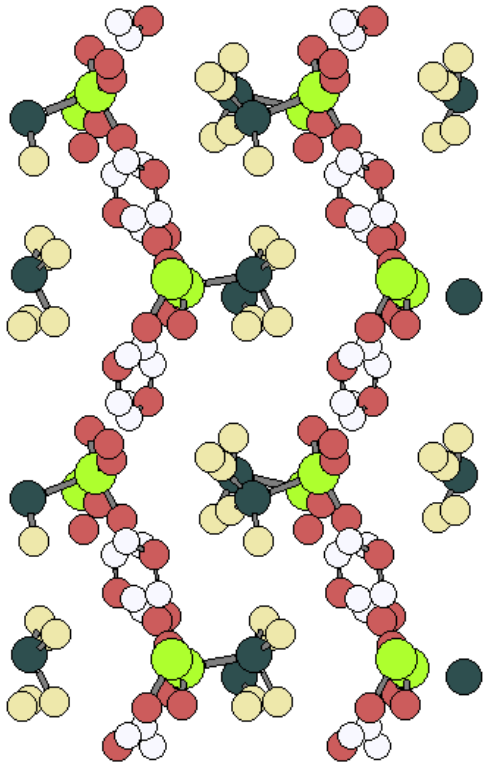
Complexity: conduction under minimal hydration

Triflic Acid Monohydrate Solid

J.B. Spencer and J.-O. Lundgren, *Acta Cryst.*, **B29**, 1923 (1973).

$4 \times (CF_3SO_3H \bullet H_2O)$: a=5.9634, b= 9.975, c=9.708 Å, β=98.661°

with κ = 0.96281 Sm^{-1} @ 309.15 K, diffusion of a proton $\Rightarrow$

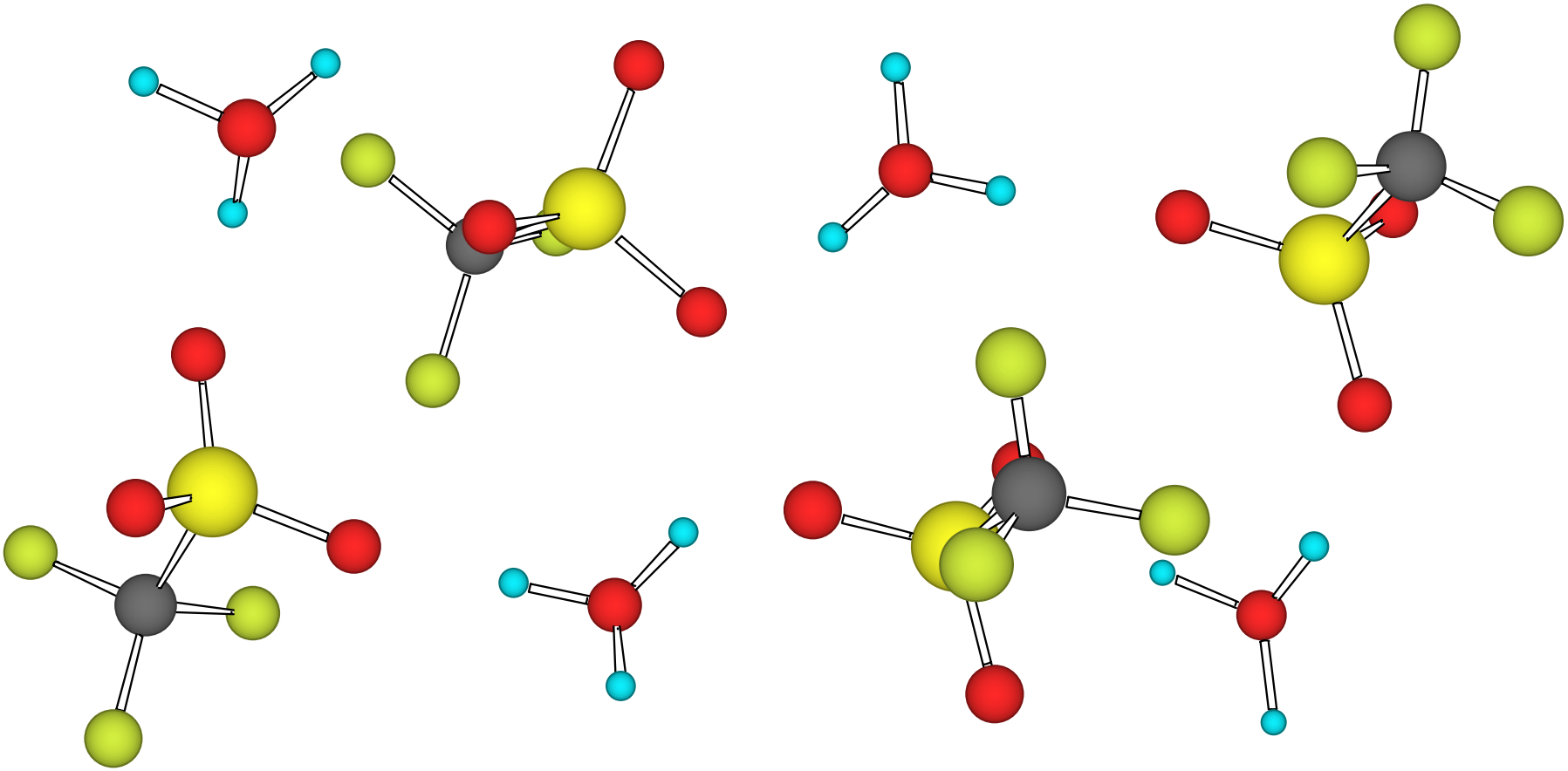


AIMD

M. Eikerling, S.J. Paddison, L. R. Pratt, and T.A. Zawodzinski Jr., *Chem. Phys. Lett.* **368**, 108 (2003).

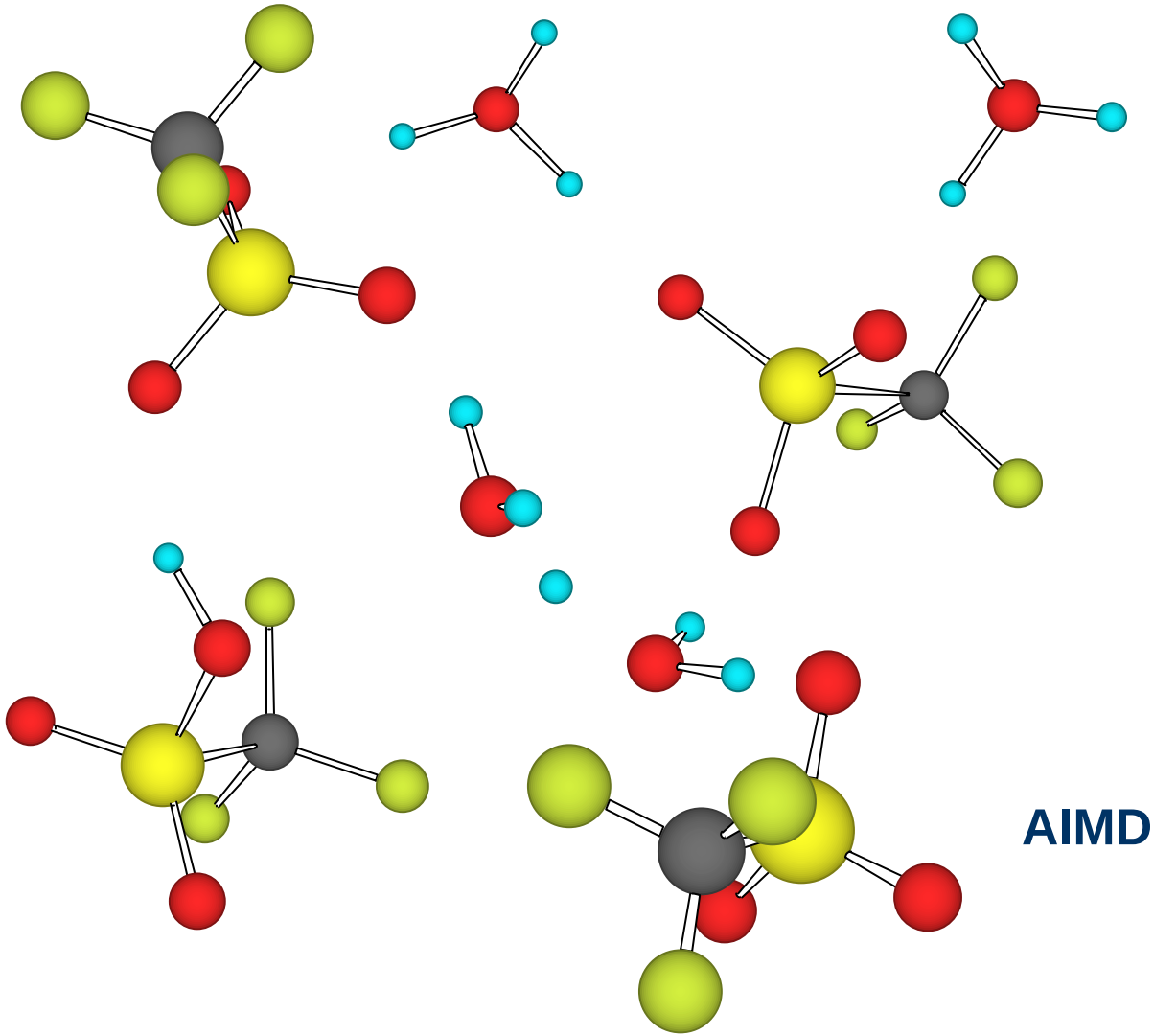
Trifluoromethanesulfonic acid monohydrate

- expanded unit cell



Trifluoromethanesulfonic acid monohydrate

- defect state

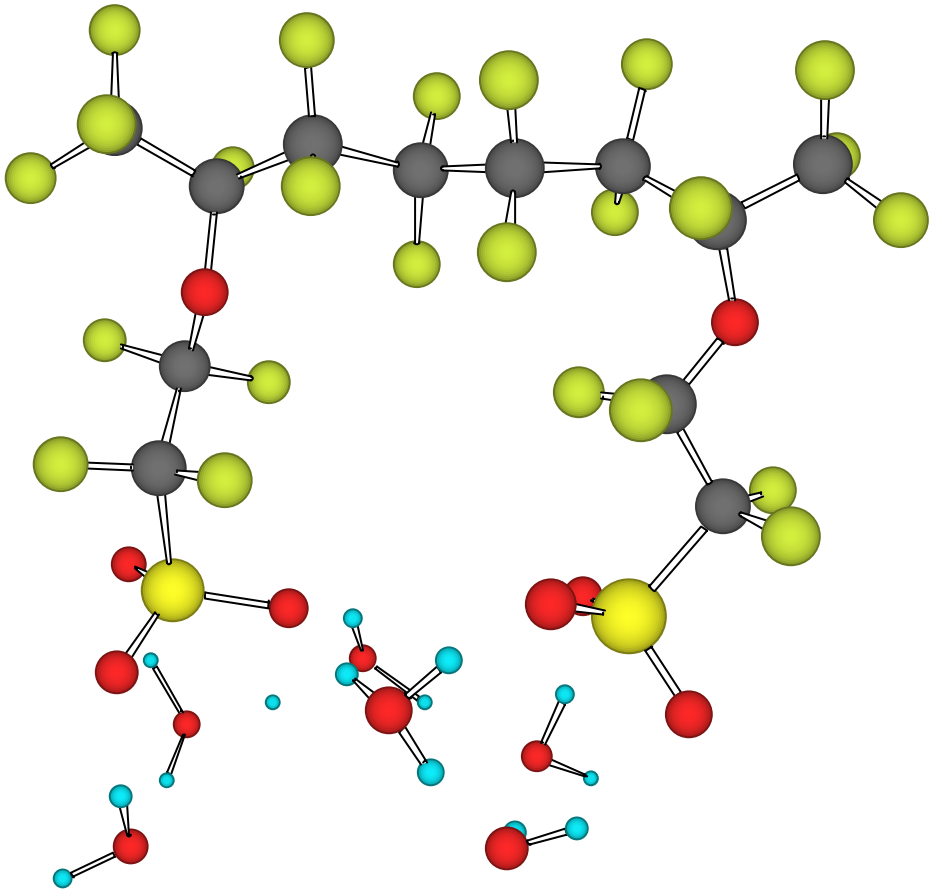


AIMD

$\Delta G_f = 0.2$ eV

M. Eikerling, S.J. Paddison, L. R. Pratt, and T.A. Zawodzinski Jr., *Chem. Phys. Letters* **368**, 108 (2003).

Dow Membrane with two side chains + 6 H_2O



B3LYP/6-31G**

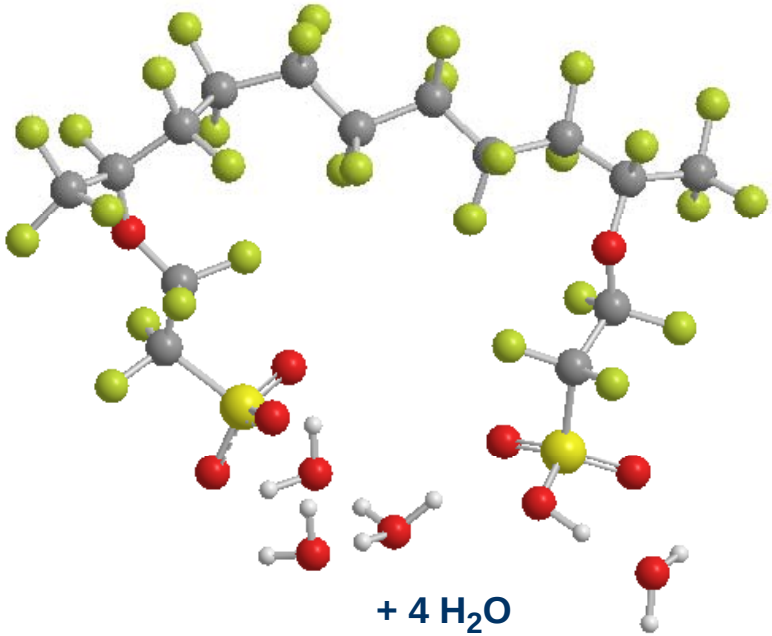
Acidic protons: H_3O^+ & $H_5O_2^+$

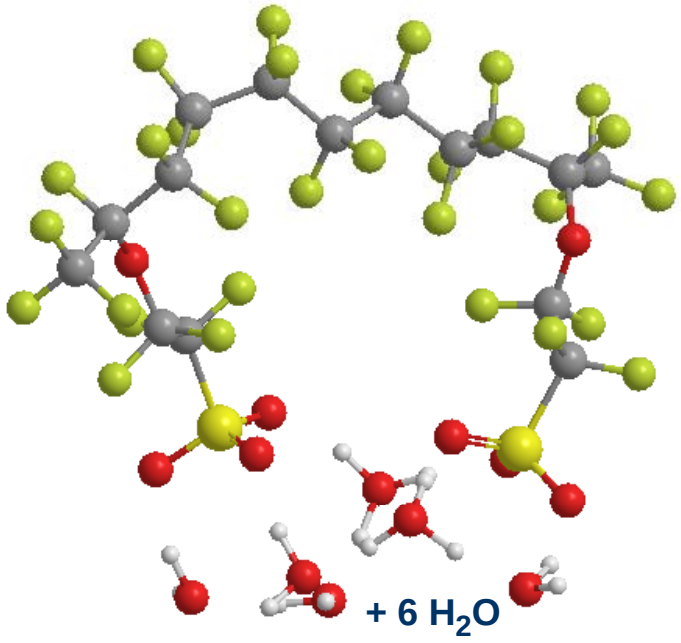
S.J. Paddison, “Proton conduction mechanisms in Polymer Electrolyte Membranes at low degrees of hydration”, Volume 33, *Annual Review of Materials Research*, 289-319 (2003).

Complexity & cooperativity: proton dissociation

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_7–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$





CF – CF: 9.7, 9.4 Å

S – S: 6.1, 5.8 Å

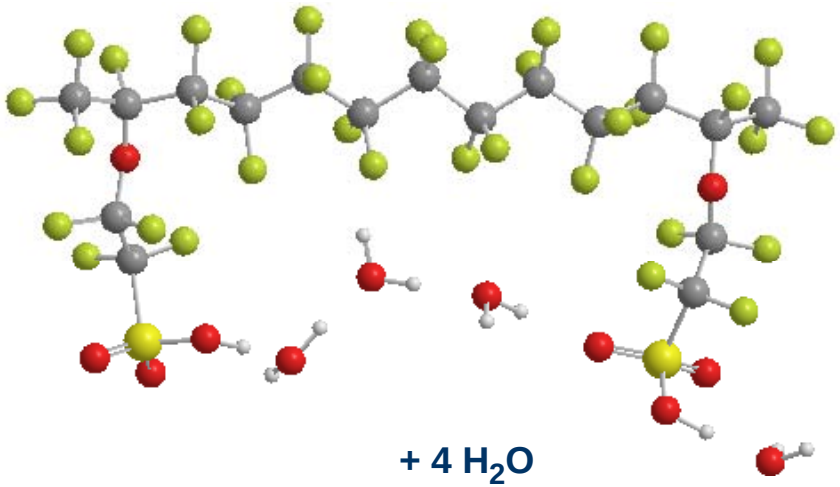
B3LYP/6-311G**

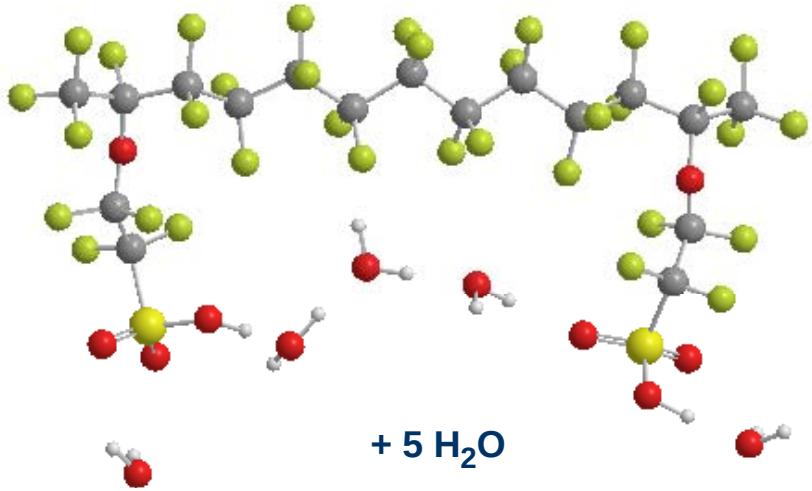
S.J. Paddison and J.A. Elliott, *Solid State Ionics* in preparation (2005).

Complexity: proton dissociation

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_9–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$





CF – CF: **13.1, 13.1 Å**

S – S: **11.5, 11.4 Å**

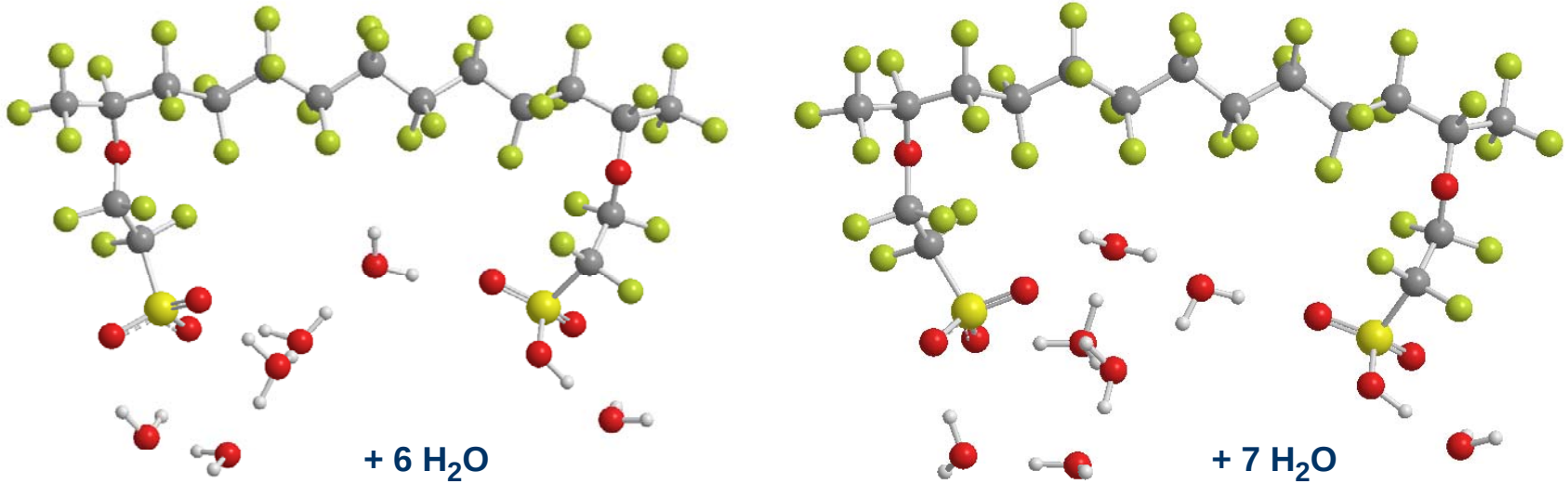
B3LYP/6-311G**

S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

Complexity: proton dissociation

$CF_3CF(–O(CF_2)_2SO_3H)–(CF_2)_9–CF(–O(CF_2)_2SO_3H)CF_3$

$+ ? H_2O$



CF – CF: **13.0, 13.0 Å**

S – S: **9.7, 9.6 Å**

B3LYP/6-311G**

S.J. Paddison and J.A. Elliott, *J. Phys. Chem. A* submitted (2005).

Summary

• The extent of separation of the side chains affects the **connectivity** of the sulfonic acid groups via a hydrogen bond network with the first hydration shell water.

• Proton dissociation (i.e. **complexity**) is affected by the separation of the sulfonic acid groups.

- influenced by conformational change in the backbone and/or side chains (**cooperativity**)

• The molecular results provide a ‘base-line’ set of results for which the effects of distinct: acidic groups, side chain length and polymer chemistry may be examined.