Proton Dissociation and Transfer in PEM Ionomers with Multiple and Distinct Pendant Acid Groups: An *Ab Initio* Study

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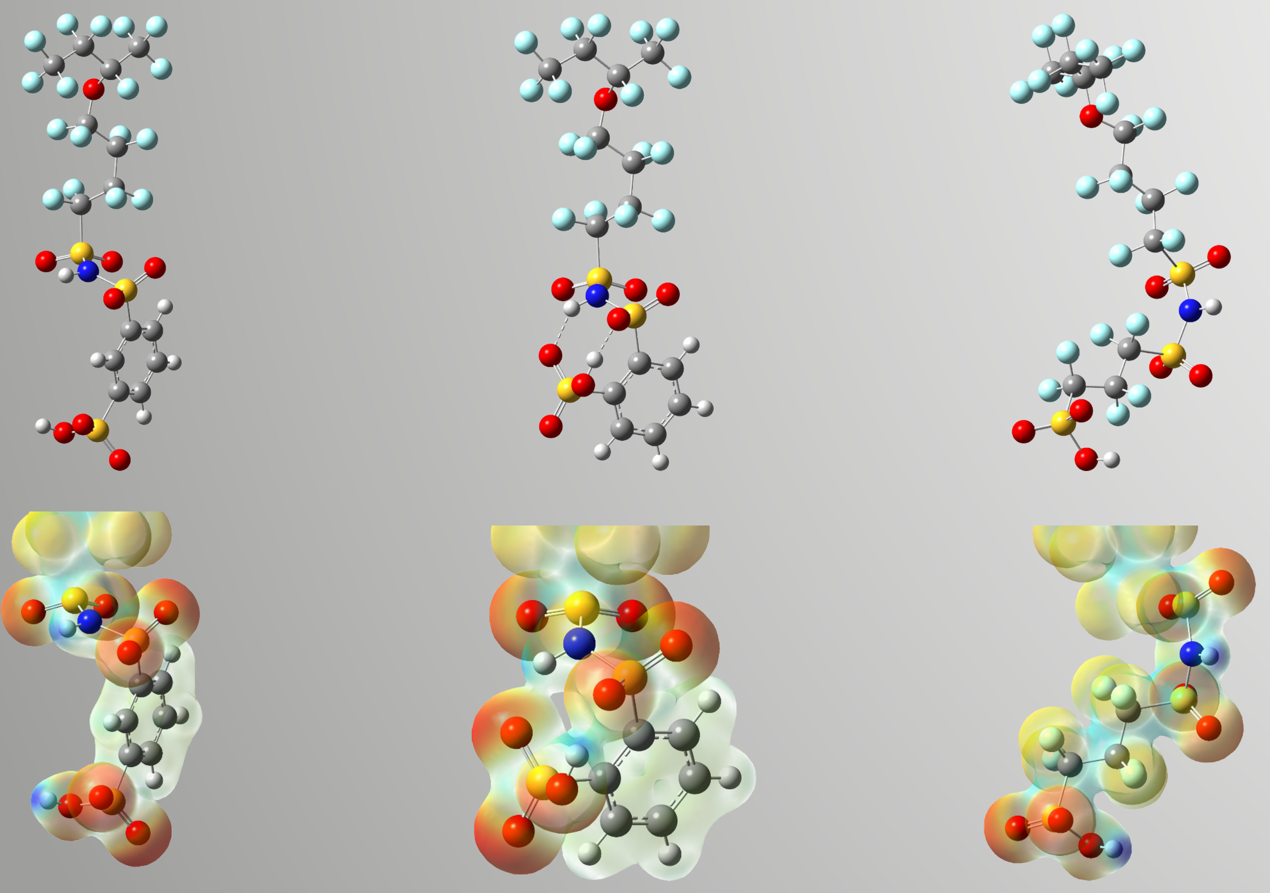
Introduction

The use of hydrogen fuel cells as efficient, clean energy conversion devices is a growing area of interest as the global demand for energy continues to rise along with the pressure towards reducing emissions of carbon dioxide and other gases emitted from conventional energy systems based on fossil fuels. Central to hydrogen fuel cell operation is the proton-conducting proton exchange membrane (PEM) ionomer. Currently, high proton conductivity in PEMs is only observed under highly hydrated conditions which has negative consequences on the efficiency of the fuel cell. The pursuit of novel PEMs which exhibit high proton conductivity at lower hydration levels requires a more complete understanding of the molecular features that contribute to proton dissociation and transfer within these membranes. Presented here is a quantum chemical molecular modeling study on the roles side chain chemistry and protogenic group separation have in facilitating proton dissociation and transfer bis(sulfonyl imide)-based ionomers.

Method and Systems

Atom color in the following structures: grey – carbon, red – oxygen, yellow – sulfur, blue – nitrogen, light blue – fluorine, and white – hydrogen. Hydrogen bonds are denoted by dashed lines.

Explicit water *ab initio* electronic structure calculations were performed on three side chain fragments of 3M™ bis(sulfonyl imide)-based membranes each consisting of a poly(tetrafluoroethylene) (PTFE) backbone functionalized with pendant side chains with multiple acid groups having structural and chemical differences mediating protogenic group separation: an imide and a sulfonic acid group located in either the *meta* or *ortho* position on a phenyl ring and the PFIA with protogenic groups separated by electron withdrawing –CF_2– groups.



meta *ortho* PFIA

Optimized structures of isolated 3M™ bis(sulfonyl imide) fragments with the mapped electrostatic isosurfaces (blue regions are electron deficient and red regions are electron rich) reveal how side chain chemistry and protogenic group interactions affect the distribution of charge through delocalization.

Acknowledgements

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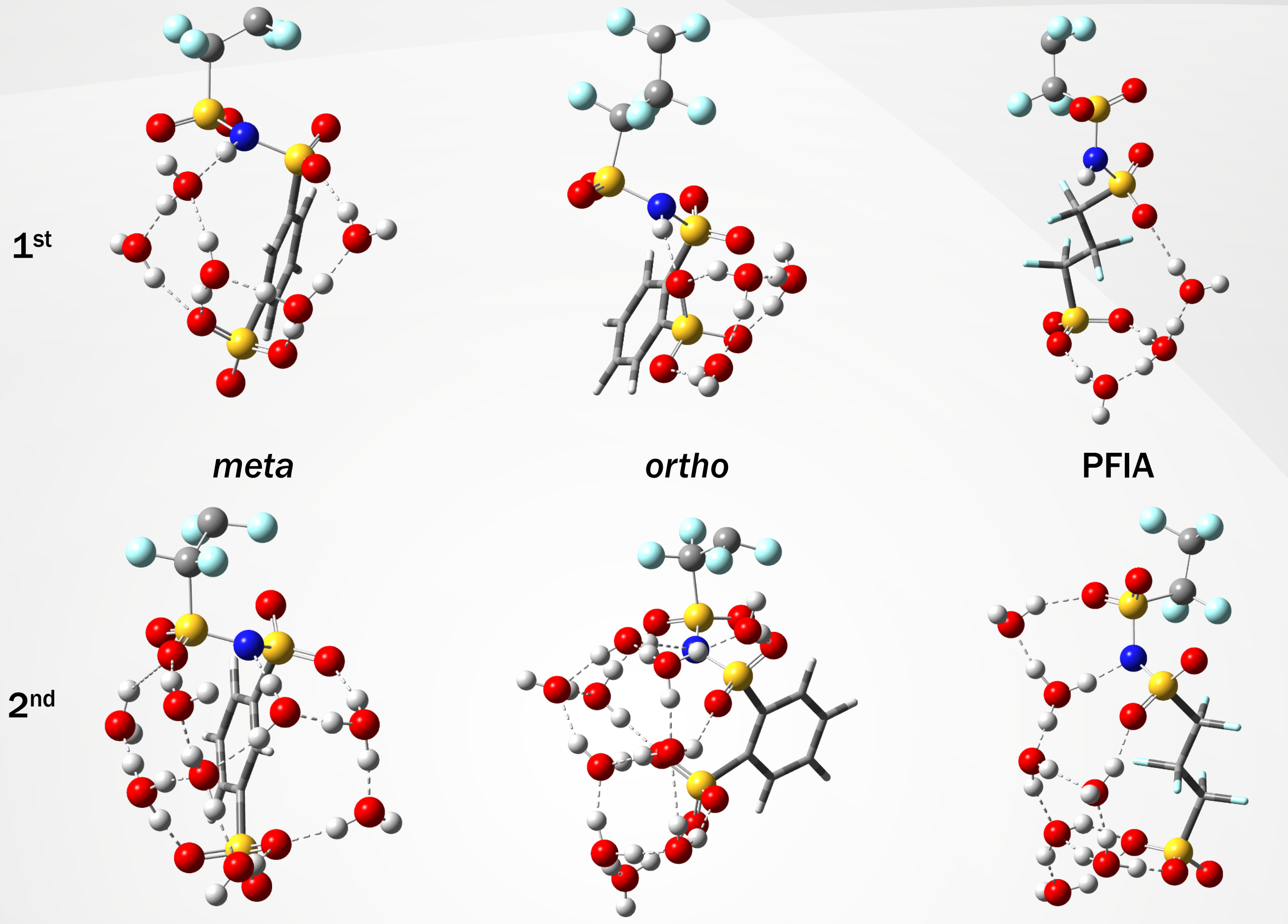
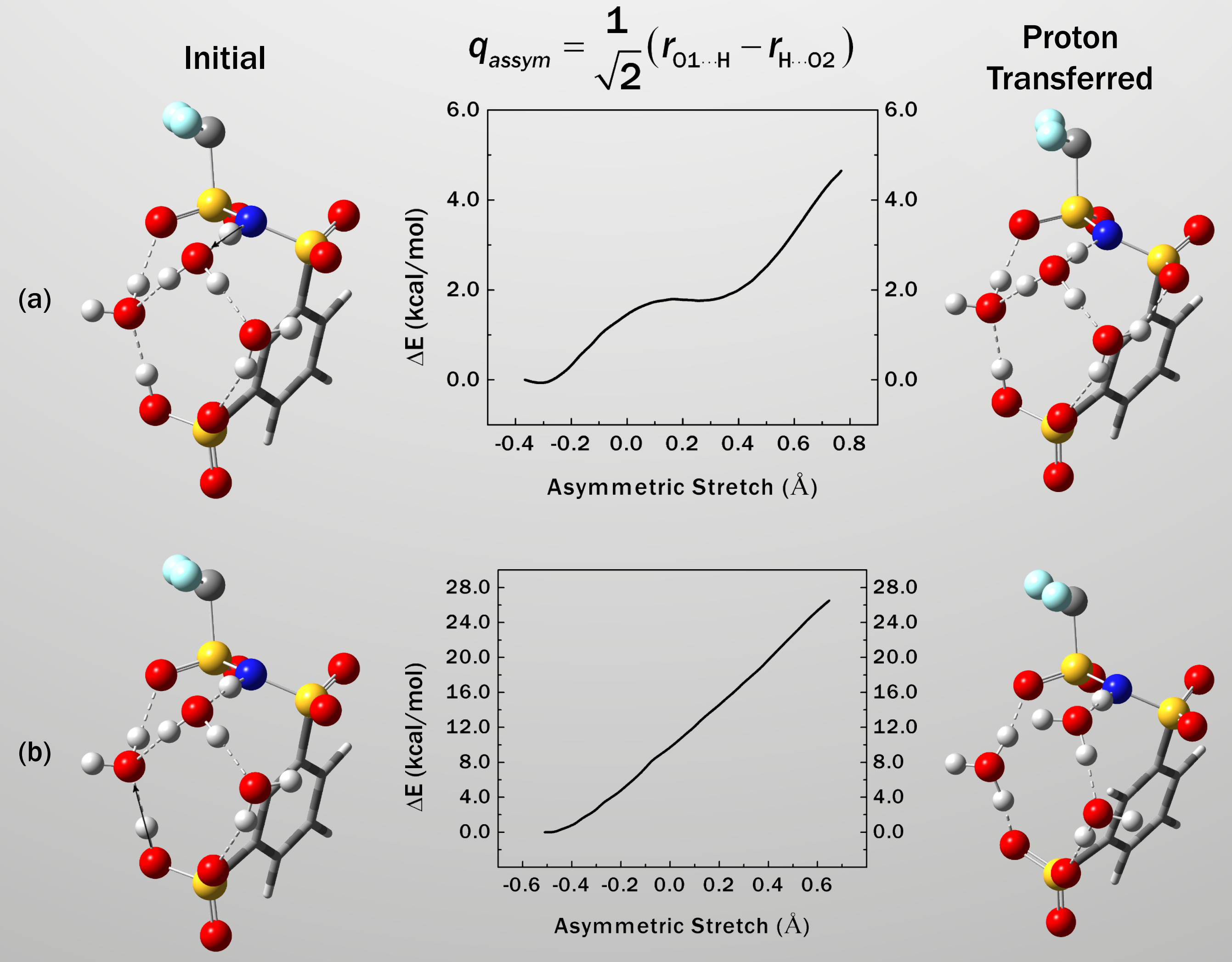
Proton Dissociation

Protogenic group interactions in *ortho* and electron withdrawing -CF_2- groups in PFIA delocalize charge promoting 1st dissociation after addition of only 3 H_2O molecules while the *meta* lacks the charge delocalizing effects requiring 5 H_2O. However, close proximity of protogenic groups in *ortho* hinders 2nd proton dissociation due to localized excess positive charge and congested hydrogen bonding in the surrounding water cluster requiring 10 H_2O, the others have a more widely spread charge distribution needing only 7 H_2O (PFIA) and 8 H_2O (*meta*).



Energetics of Proton Transfer

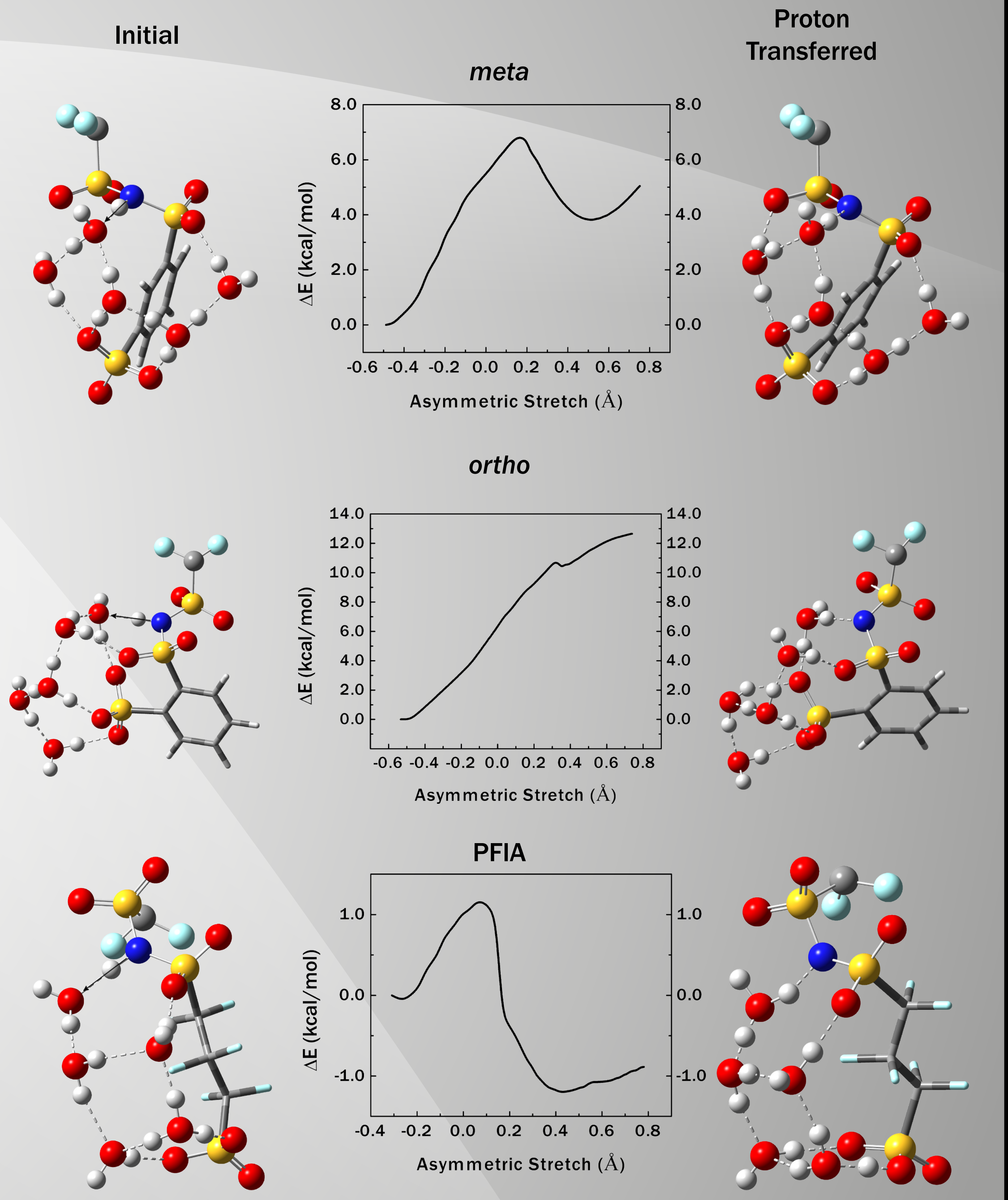
Relative energy profiles for proton transfer from (a) the imide and (b) the sulfonic acid to a neighboring water molecule in the *meta* bis acid at a hydration of 3 H_2O molecules reveal that the proton preferentially transfers via the past of least resistance. The breaking of hydrogen bonds results in a much higher energetic barrier to proton transfer.



$$q_{assym} = \frac{1}{\sqrt{2}}\left(r_{O1\cdots H} - r_{H\cdots O2}\right)$$

Energetics of Proton Transfer

Relative energy profiles for proton transfer from the imide group to a neighboring water molecule in the bis acids at a hydration of 5 H_2O molecules are shown below. The close proximity of protogenic groups in *ortho* results in a clustered hydrogen bond network that more greatly resists acceptance of additional positive charge leading to breaking of hydrogen bonds while the spread out hydrogen bonding in *meta* and PFIA more readily reorients to accommodate charge transfer.



Conclusions

- 1st proton dissociation at low hydration is heavily influenced by delocalization of charge brought about by side chain chemistry and protogenic group interaction
- 2nd proton dissociation is more influenced by the nature of hydrogen bonding with the ionomer and the surrounding water cluster and the associated distribution of charge
- The energetic penalty for proton transfer depends on the extent of the disruption of hydrogen bonds: bond breaking is resisted, bond forming has a stabilizing effect
- These calculations provide fundamental insight into how ionomer chemistry affects transport properties in PEMs of this type under minimally hydrated conditions