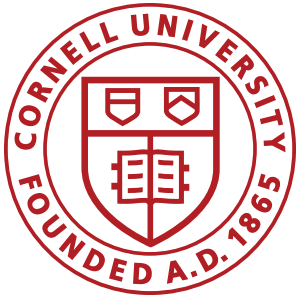


Quantum Chemistry Simulations for Dynamic Network Polymers

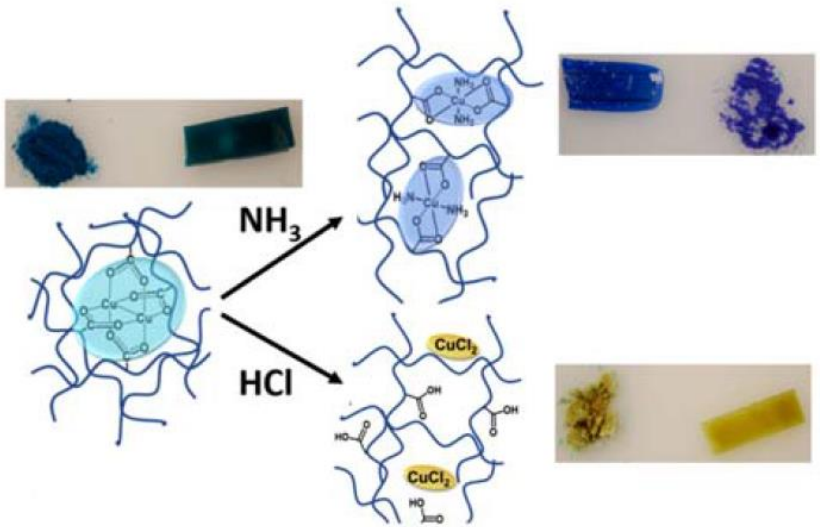
March Meeting of the American Physical Society

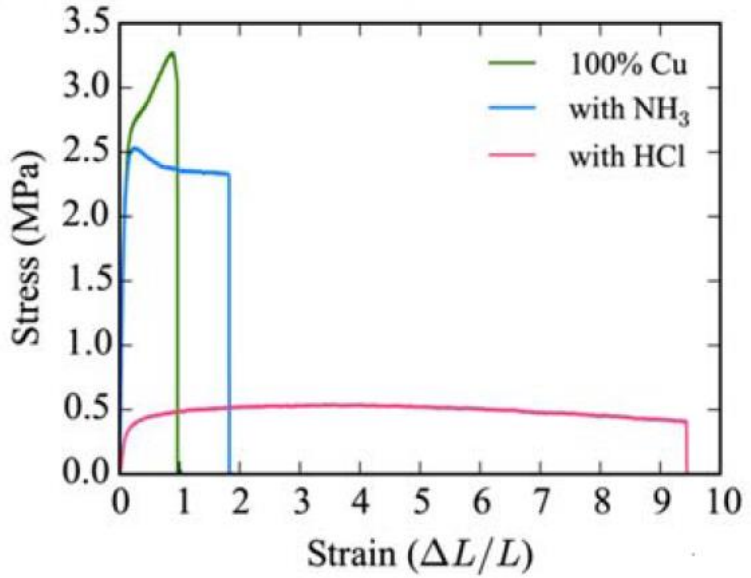
Presenter: Michael Buche

Authors: Michael Buche, Zachary Sparrow, Yuval Vidavsky, Robert DiStasio, Meredith Silberstein

3/5/2019

Dynamic Network Polymers

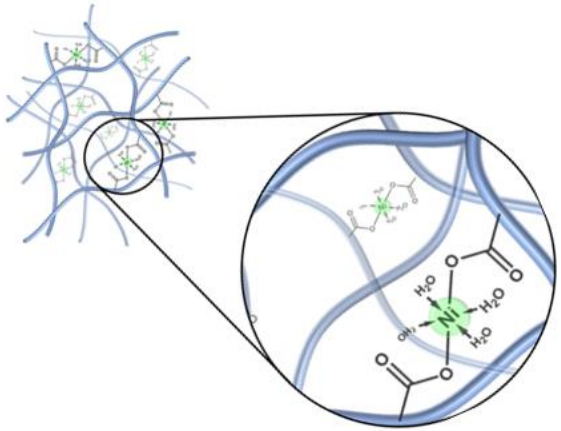




Vidavsky, Yuval, Suwon Bae, and Meredith N. Silberstein. "Modulating metallopolymer mechanical properties by controlling metal ligand crosslinking." *Journal of Polymer Science Part A: Polymer Chemistry* 56.11 (2018): 1117-1122.

Goals of this Study

- Metal-coordination complexes as crosslinking structures in a polymer
  - Use different ligands to modify bulk material mechanical properties
- Investigate the crosslinking using quantum chemistry simulation
  - Interpret experimental results
  - Inform material design
  - Inform a constitutive model
- Specifically, the crosslinking structure's:
  - Mechanical response
  - Free energy barriers



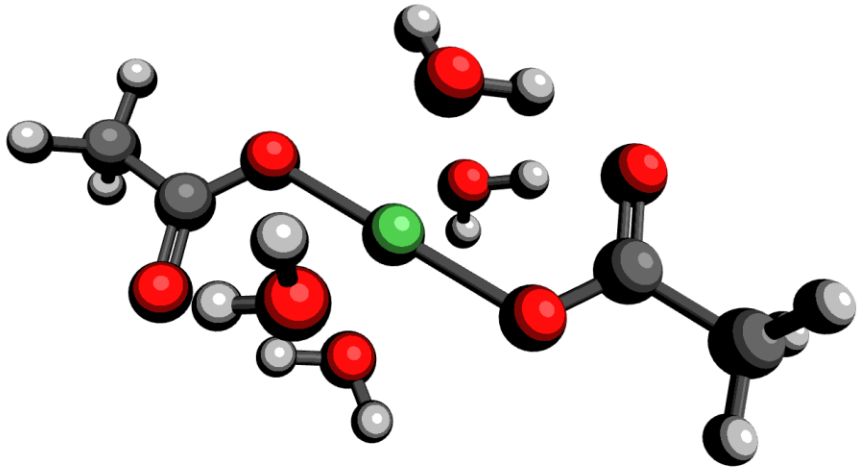
Quantum Chemistry Simulations

- Density Functional Theory (DFT)
  - Approximately solve many electron Schrödinger equation

Software: Q-CHEM

Functional: ωB97X-V

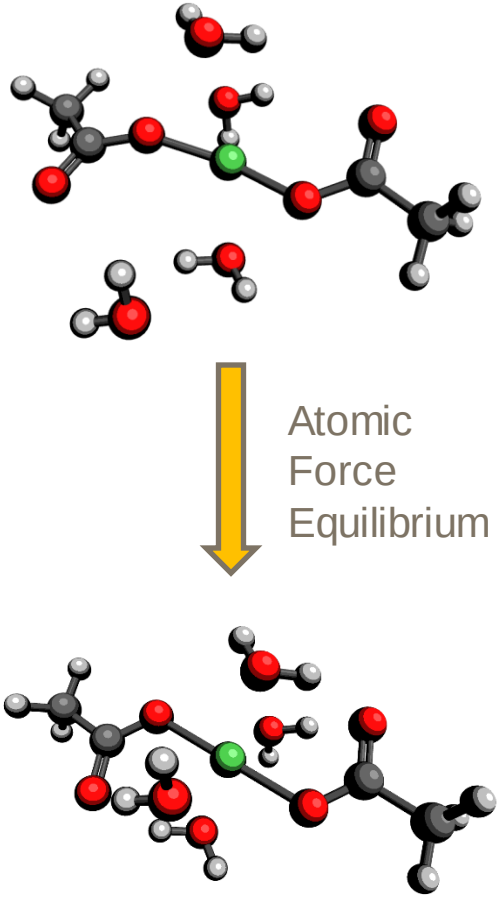
Basis set: def2-TZVPP



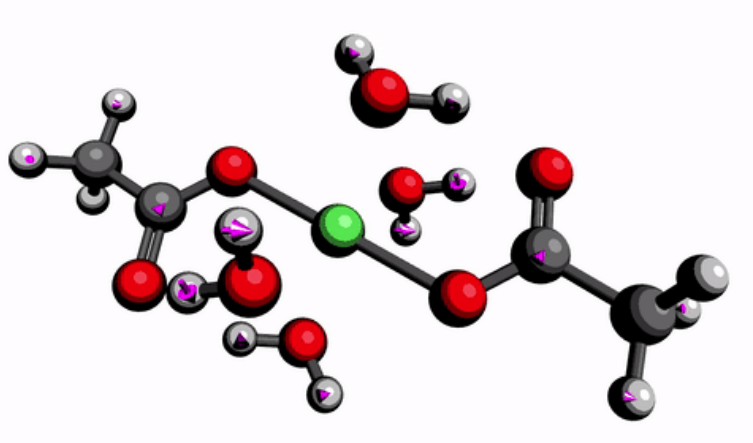
Simulation Steps

- Mechanical Response
  1. **Minima search (OPT)**
  2. Diagonalize Hessian (FREQ)
  3. Apply external forces (EFEI)

- Free Energy Barriers
  1. Approximate reaction path (FSM)
  2. Transition state search (TS)
  3. Mechanochemical activation



Simulation Steps

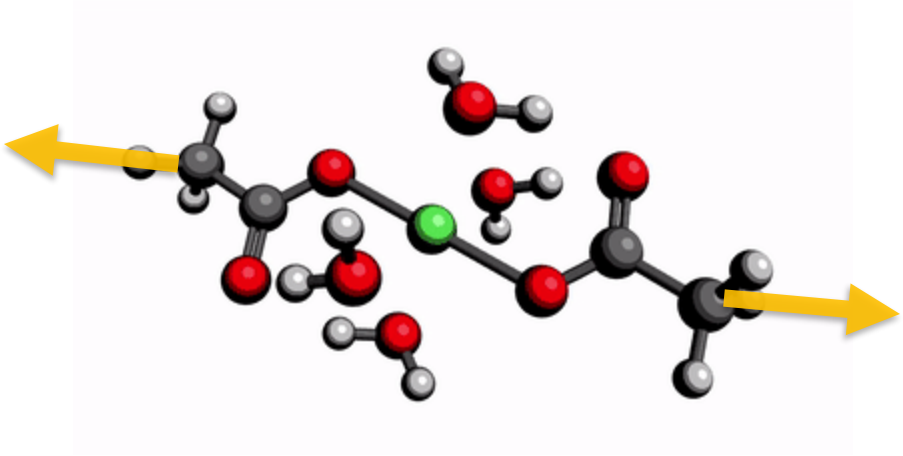


- Mechanical Response
  1. Minima search (OPT)
  2. **Diagonalize Hessian (FREQ)**
  3. Apply external forces (EFEI)

$$\mathbf{F}(\boldsymbol{\xi}_0 + \Delta\boldsymbol{\xi}) = -\mathbf{H}(\boldsymbol{\xi}_0) \cdot \Delta\boldsymbol{\xi} + O(\Delta\boldsymbol{\xi}^2)$$

- Free Energy Barriers
  1. Approximate reaction path (FSM)
  2. Transition state search (TS)
  3. Mechanochemical activation

Simulation Steps



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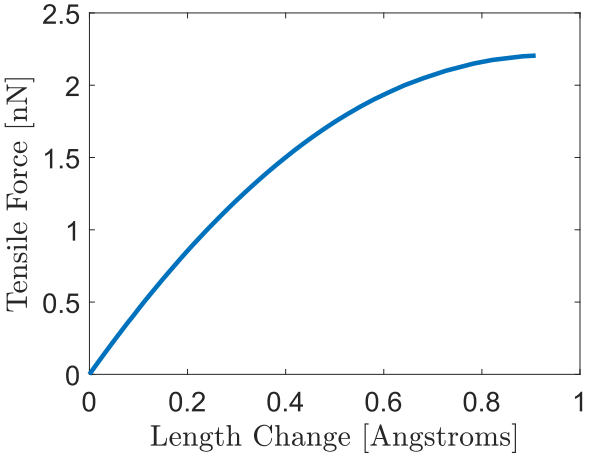

Simulation Steps

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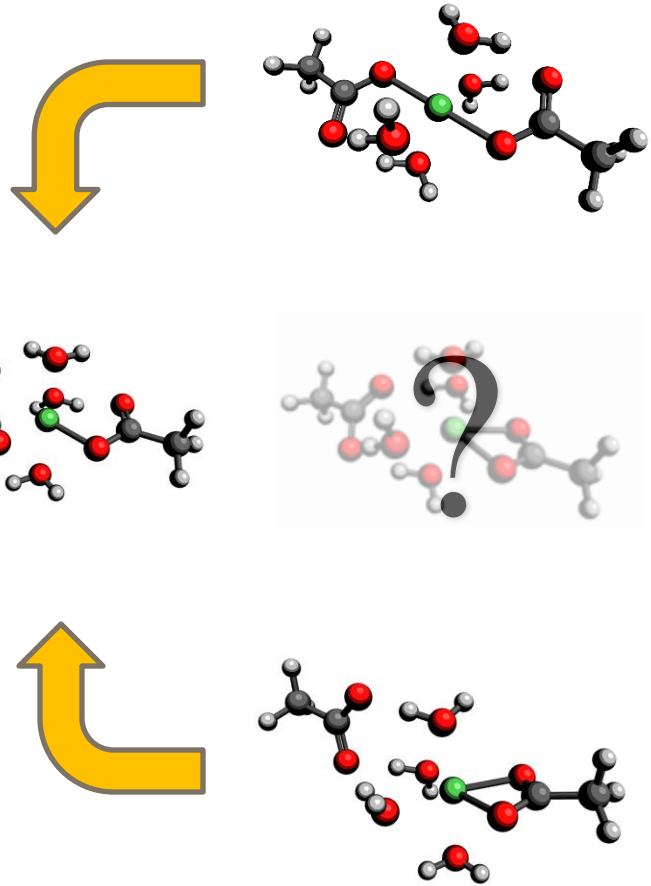


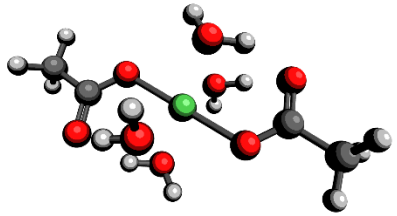
Simulation Steps

- Mechanical Response
  1. Minima search (OPT)
  2. Diagonalize Hessian (FREQ)
  3. Apply external forces (EFEI)

- Free Energy Barriers
  1. Approximate reaction path (FSM)
  2. **Transition state search (TS)**
  3. Mechanochemical activation

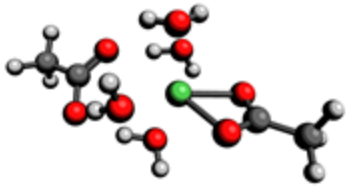
A

G = 0 kcal/mol



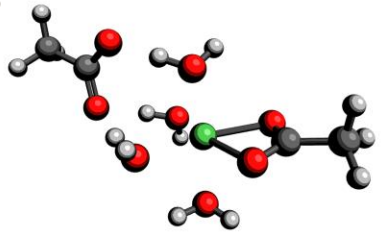
TS

G = 18.13 kcal/mol



B

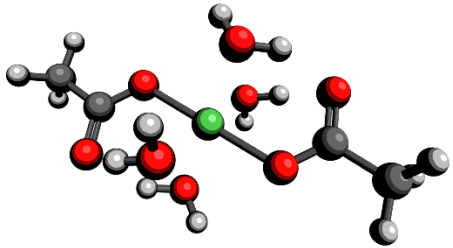
G = 5.06 kcal/mol



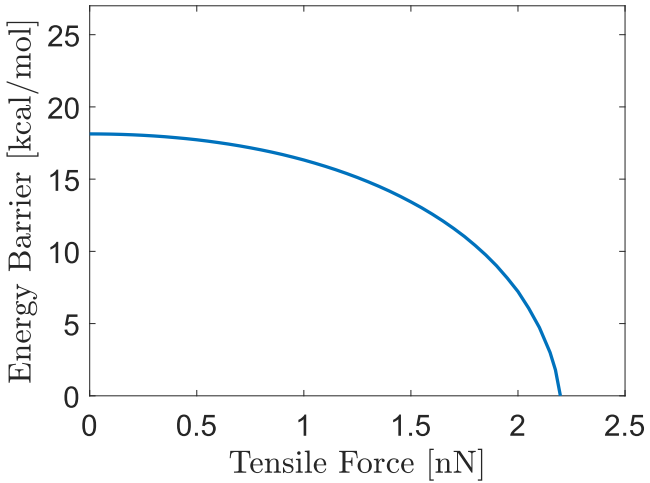
Simulation Steps

- Mechanical Response
  1. Minima search (OPT)
  2. Diagonalize Hessian (FREQ)
  3. Apply external forces (EFEI)

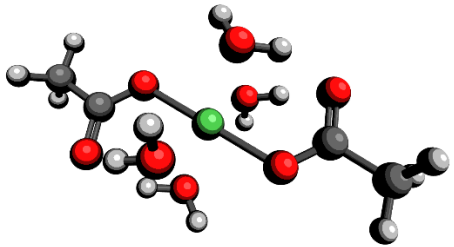
- Free Energy Barriers
  1. Approximate reaction path (FSM)
  2. Transition state search (TS)
  3. **Mechanochemical activation**

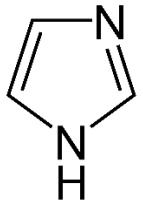


$$\Delta G_f = \Delta G_f^0 - \int \mathbf{F} \cdot d\mathbf{r}$$

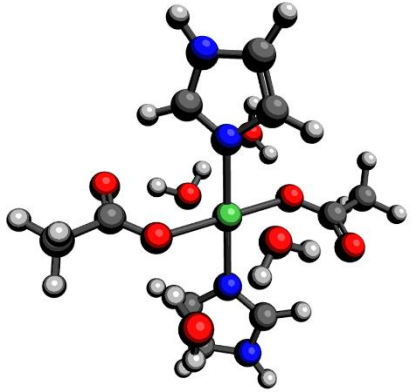


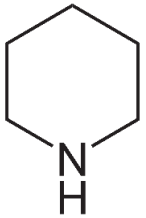
Adding Different Ligands



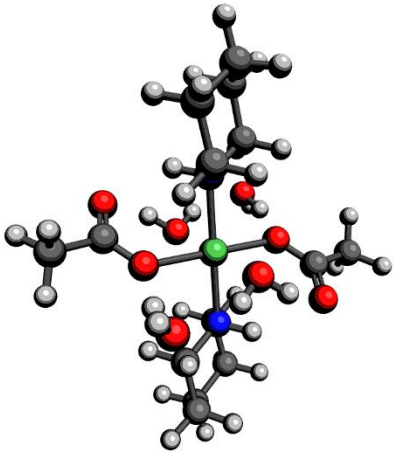


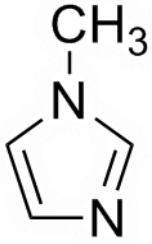
Imidazole



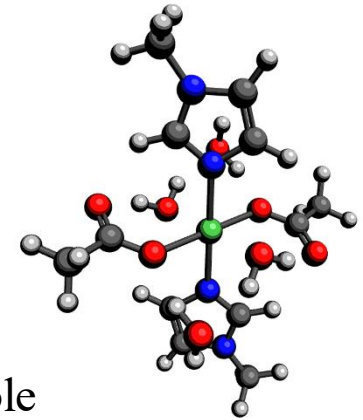


Piperidine

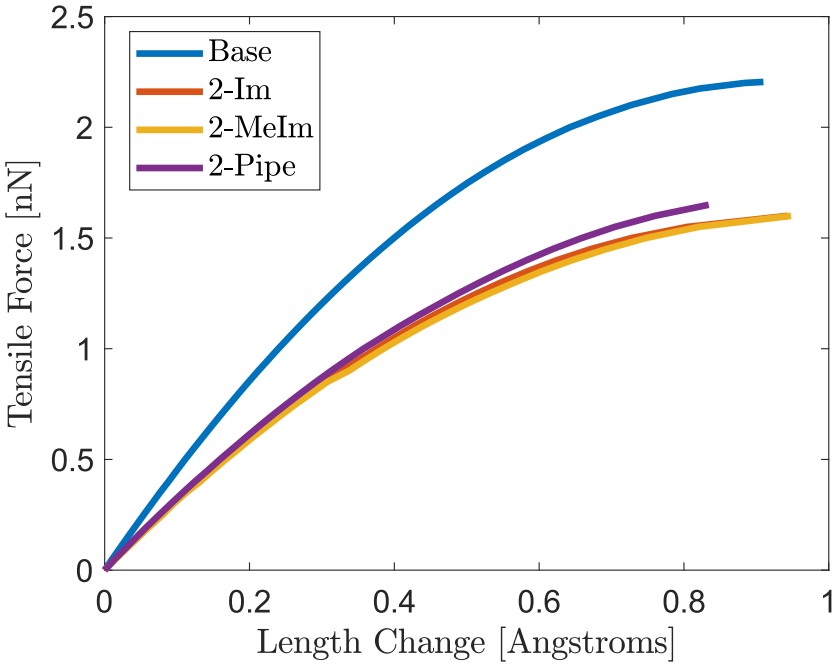


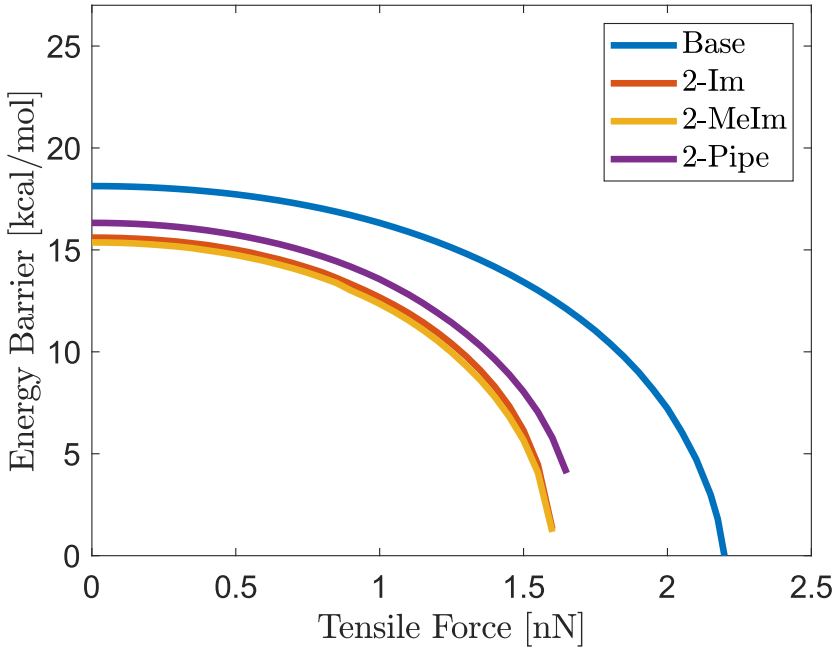


Methylimidazole



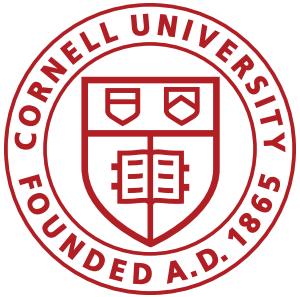
Simulation Results





Conclusions and Future Work

- Simulation illustrates differences in crosslinking structures when adding different ligands
  - Adding ligands reduces bond stiffness and strength
  - Force-modified free energy barriers vary with ligands
- Qualitative predictions can be made about the bulk material from these quantitative simulation results
- These and other simulation results will be used to inform a physics-based constitutive model



XSEDE
Extreme Science and Engineering Discovery Environment

Thank you

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MMD Lab[1]: Meredith Silberstein, Yuval Vidavsky, Suwon Bae, Steven Yang, Joy Zhang, Prathamesh Raiter, Alison Rzepka

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