

Determining Force Field Parameters Involved with Metal Organic Framework Synthesis M. Tubbs, D. Cantu, V. Glezakou

Overall Goal and Problem

Metal Organic Frameworks (MOFs) are newlydeveloped porous materials that can be used to filter and capture gases of various sizes. Currently, MOF synthesis has only succeeded through a trial and error approach. Our goal is to the theoretical framework that develop describes how the intermediates of a particular Cr-MIL-101 — combine during MOF _____ synthesis. The parameters required to complete a chemical force field simulation are not yet known because the soluble intermediates were identified only recently. Finding these are the first step to completing the kinetic modeling mechanism of MIL-101 synthesis.

Force Field Parameters

• The functional form of the Assisted Model Building with Energy Refinement (AMBER) force field models bonds and angles as harmonic oscillators:

$$V(r^{N}) = \sum_{\text{bonds}} k_{b}(l-l_{0})^{2} + \sum_{\text{angles}} k_{a}(\theta-\theta_{0})^{2}$$
$$+ \sum_{\text{torsions}} \sum_{n} \frac{1}{2} V_{n} [1 + \cos(n\omega - \gamma)]$$
$$+ \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} f_{ij} \left\{ \epsilon_{ij} \left[\left(\frac{r_{0ij}}{r_{ij}}\right)^{12} - 2\left(\frac{r_{0ij}}{r_{ij}}\right)^{6} \right] - 2\left(\frac{r_{0ij}}{r_{ij}}\right)^{6} - 2\left(\frac{r_{0ij}}{r_{ij}}\right)^{6} \right] - 2\left(\frac{r_{0ij}}{r_{ij}}\right)^{6} - 2\left($$

• For ML₃, an intermediate species of MIL-101, none of the k_b , l_0 , k_a , or θ_0 parameters involving Cr were known. AMBER was used to find the equilibrium bond lengths and angles of the minimum-energy structure of ML_3 .



 $4\pi\epsilon_0 r_{ii}$



Zr-UiO-66, Cr-MIL-101 AI-MIL-53 Three examples of Metal Organic Frameworks (MOFs)

Electronic Structure Calculations

- The intermediates' geometry was optimized by varying angle and bond values with Gaussian 09.
- The PBE pseudopotential was used for core Chromium electrons, and the 6-31G** basis set for other electrons.
- The energy profile obtained served as a reference point to optimize the force field parameters.



Cr-MIL-101 intermediate: ML₃. A tri-Chromium metal center with three linkers. An example of a varied angle is shown.

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- network and initial conditions.
- coefficients.
- involved.



Electronic structure calculations for force field parameterization allows the study of MOF formation mechanisms and kinetic modeling.













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Cantera is a software suite that generates reaction path diagrams for any given reaction

Cantera requires a *mechanism*, which includes all possible reactions with their intermediate species, thermodynamic properties, and rate

The force field parameters and electronic structure calculations can be used to estimate the thermodynamic properties of the species

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