Determining Force Field Parameters Involved with Metal Organic Framework Synthesis

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Overall Goal and Problem

Metal Organic Frameworks (MOFs) are newly-developed 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 develop the theoretical framework that describes how the intermediates of a particular MOF — Cr-MIL-101 — combine during 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:

$$V(r^N) = \sum_{bonds} k_b(l - l_0)^2 + \sum_{angles} k_a(\theta - \theta_0)^2$$

$$+ \sum_{torsions} \sum_n \frac{1}{2} V_n[1 + \cos(n\omega - \gamma)]$$

$$+ \sum_{j=1}^{N-1} \sum_{i=j+1}^{N} f_{ij} \left\{ \epsilon_{ij} \left[\left(\frac{r_{0ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{r_{0ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right\}$$

- For ML_3, 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.
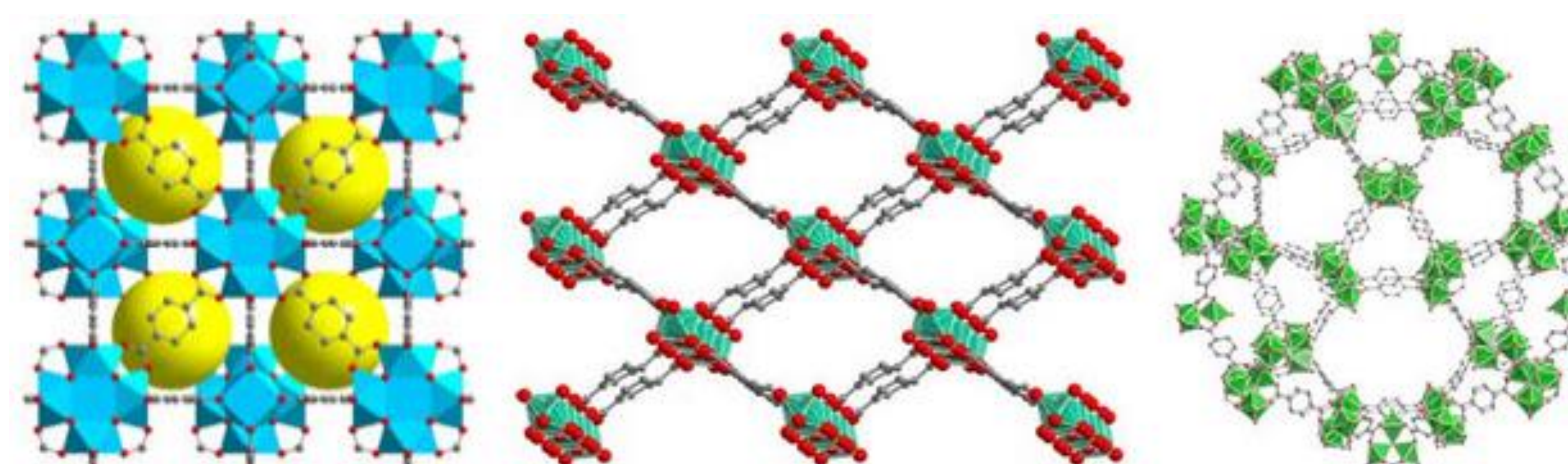
Zr-UiO-66,   Al-MIL-53   Cr-MIL-101
Three examples of Metal Organic Frameworks (MOFs)

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.


o-CR-o Angle
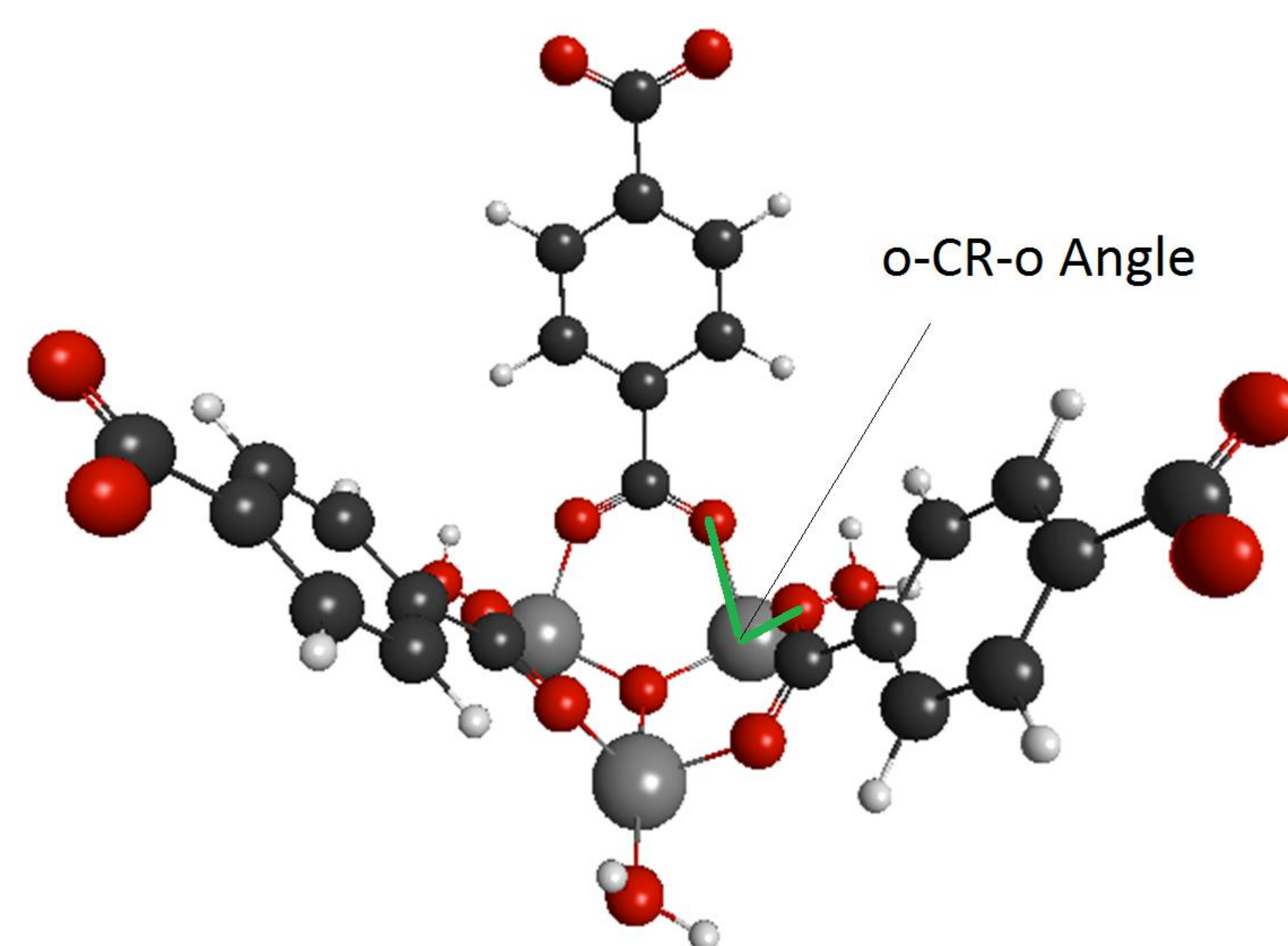
Cr-MIL-101 intermediate: ML_3. A tri-Chromium metal center with three linkers. An example of a varied angle is shown.

Looking ahead:
Kinetic Modeling with Cantera
Chemical Kinetics • Thermodynamics • Transport Processes

- Cantera is a software suite that generates reaction path diagrams for any given reaction network and initial conditions.
- Cantera requires a *mechanism*, which includes all possible reactions with their intermediate species, thermodynamic properties, and rate coefficients.
- The force field parameters and electronic structure calculations can be used to estimate the thermodynamic properties of the species involved.

o-CR-o Angle vs. Energy
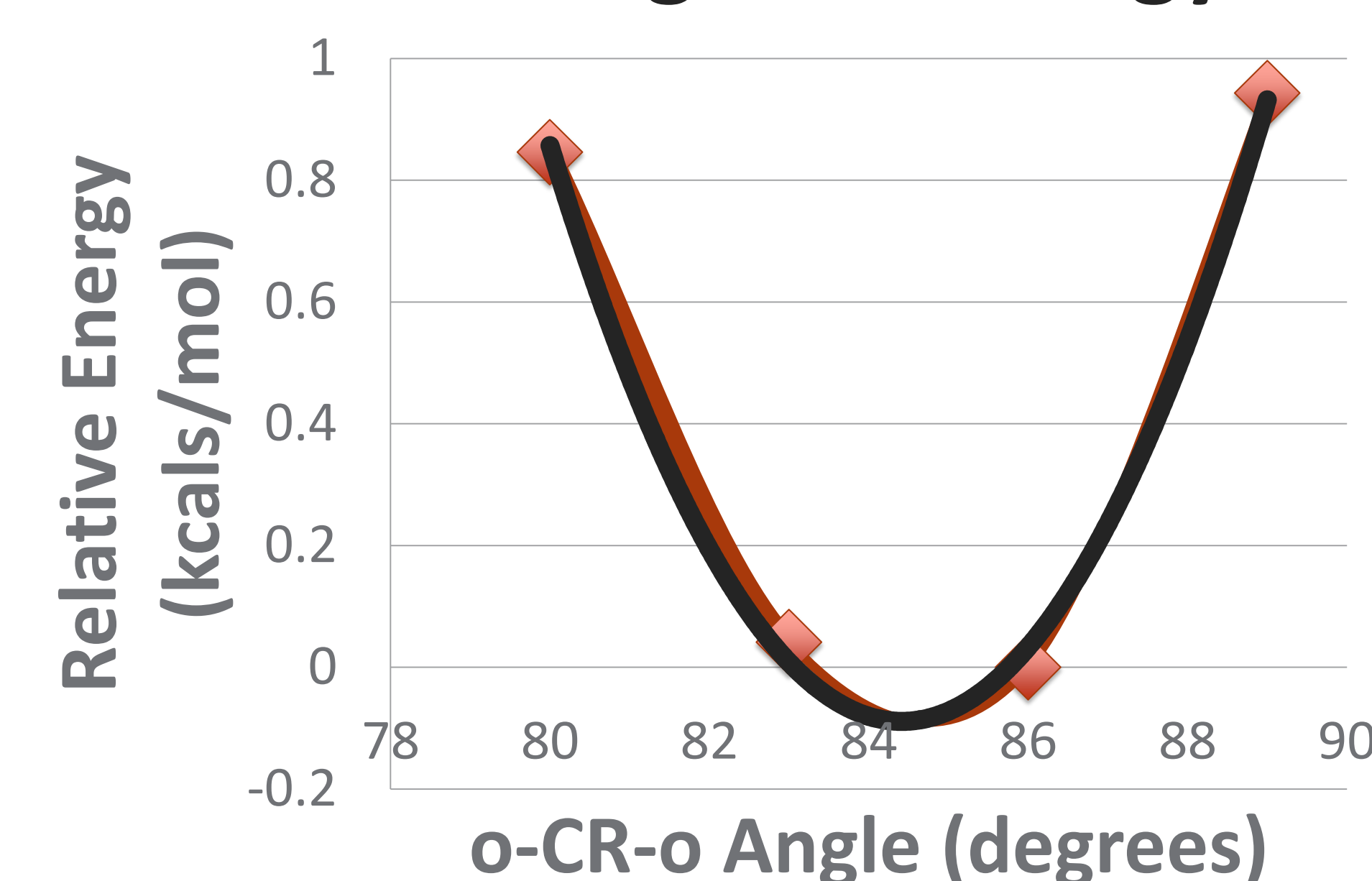
Electronic structure calculations for force field parameterization allows the study of MOF formation mechanisms and kinetic modeling.

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