

Using Molecular Dynamics Simulations to Detect Reaction Events: A Case Study with Iron Carbonyl Clusters

Johnson Liu*,
Marshall Hutchings†,
Lee-Ping Wang†
†University of California,
Davis
*University of the Pacific

Motivation for Developing New Analysis Tools

- A molecule can have many theoretical isomers, each existing within local minima throughout the molecule's potential energy surface.
- The computational discovery of these isomers requires the ability to overcome energy barriers that separate local minima.
- Molecular dynamics simulations are useful in traversing these barriers.
- The transition from one isomer to another is a **reaction event** in the molecular dynamics simulation.
- A new method for simulation data analysis is developed to identify the occurrences of such reactions within simulations.

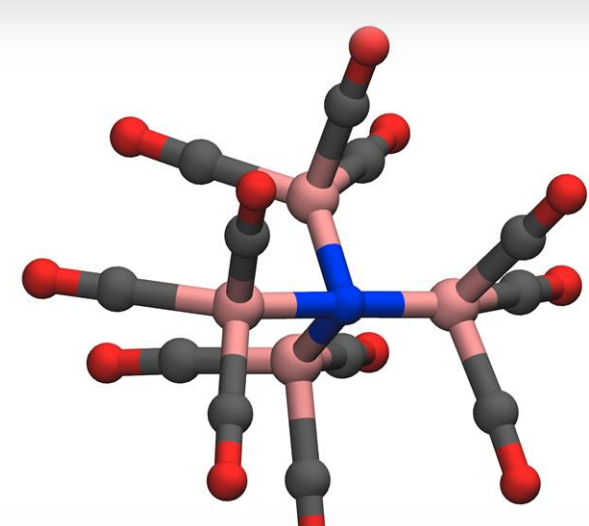


Figure 1. $\text{Fe}_4\text{N}(\text{CO})_{12}$ iron-electrocatalyst.

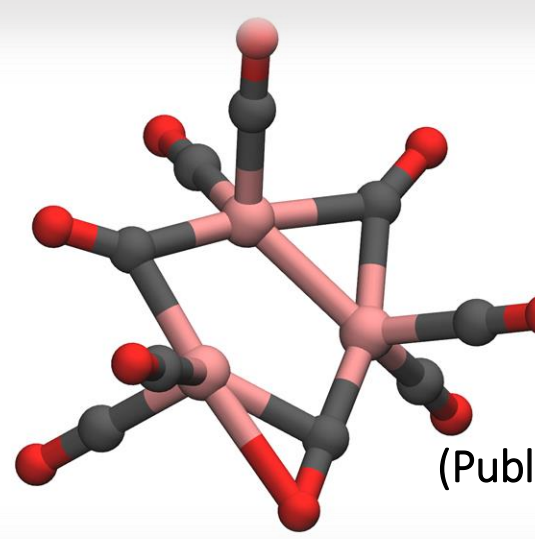


Figure 2. Sample isomer of $\text{Fe}_3(\text{CO})_9$.

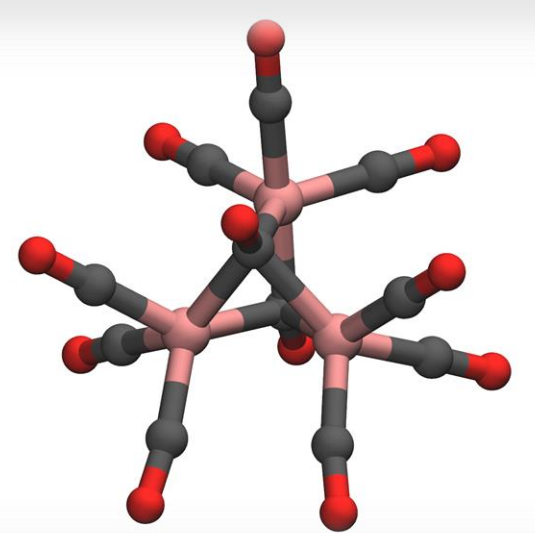


Figure 3. Sample isomer of $\text{Fe}_3(\text{CO})_{11}$.

Element Legend (for figures to the left)
Iron: Pink Carbon: Grey
Oxygen: Red Nitrogen: Blue
(Bonds between atoms drawn with covalent radii thresholds.)

- The $\text{Fe}_4\text{N}(\text{CO})_{12}$ iron-electrocatalyst (Figure 1) can possibly undergo rearrangement of its carbonyl (CO) groups after the loss of a CO when the electrocatalyst is twice reduced.
- The methodological framework developed in this project will be used to study theoretical reaction events for the electrocatalyst.
- A group of simpler molecules, the $\text{Fe}_3(\text{CO})_9$ (Figure 2), $\text{Fe}_3(\text{CO})_{10}$, $\text{Fe}_3(\text{CO})_{11}$ (Figure 3), and $\text{Fe}_3(\text{CO})_{12}$ iron carbonyl clusters will be used to develop this analysis tool.

Acknowledgements

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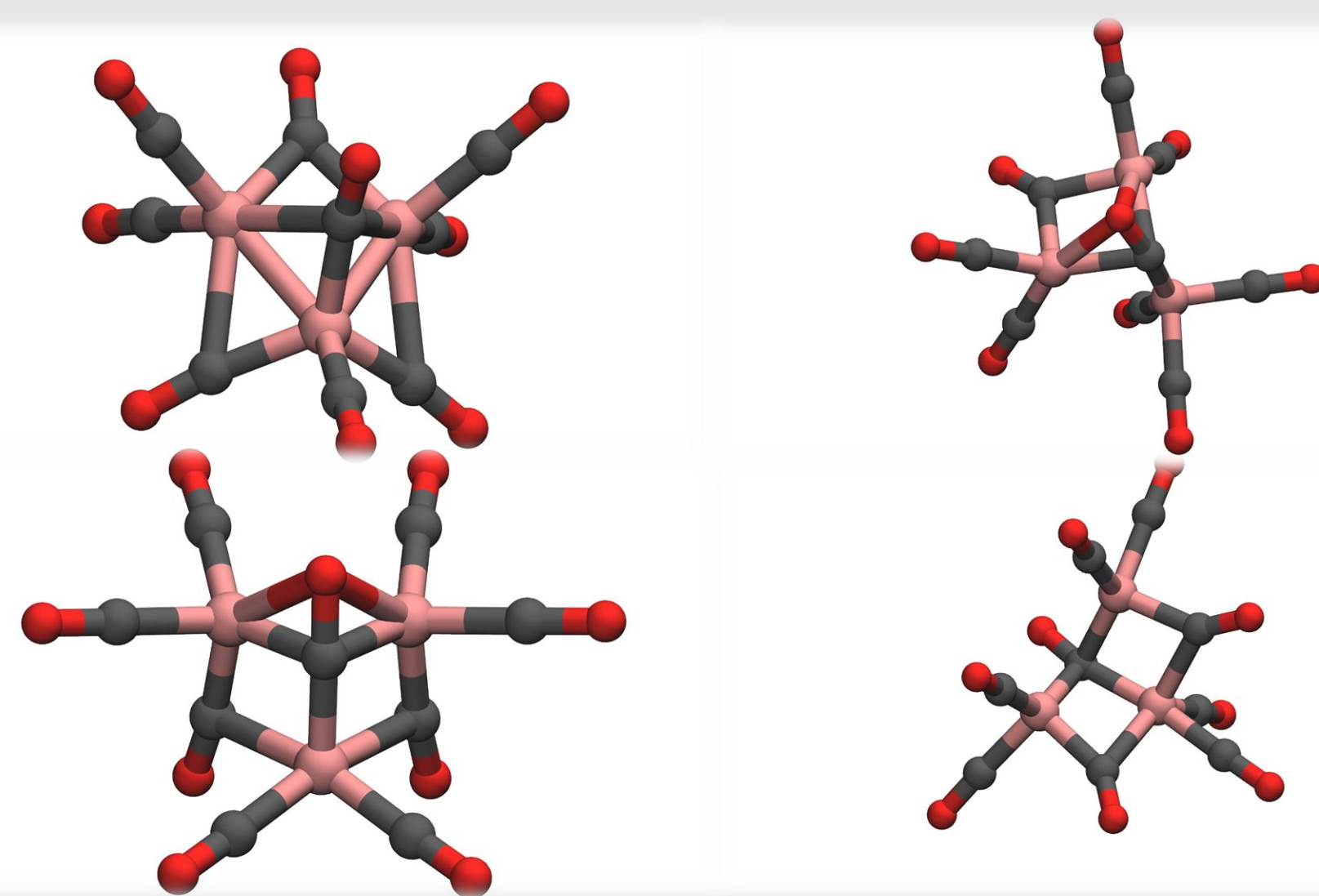
References

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- Wang, H; Xie, Y; King, R. B.; Schaefer III, H. F. **Remarkable Aspects of Unsaturation in Trinuclear Metal Carbonyl Clusters: The Triiron Species $\text{Fe}_3(\text{CO})_n$ ($n = 12, 11, 10, 9$).** *Journal of the American Chemical Society* **2006** 128 (35): 11376–11384. DOI: 10.1021/ja055223+

Sample $\text{Fe}_3(\text{CO})_9$ Isomers

- Molecular dynamics simulations were run using the BP86 and B3LYP functionals with a modified DZP Dunning basis set.
- Theoretical isomers of several iron carbonyls published in 2006 by Wang, King, and Schaefer² were used as the initial geometries.
- A range of temperatures were used for the molecular dynamics simulations.
- The structure of molecules at selected frames within the simulations were optimized to find the lowest energy structures.
- Optimized structures examined to find new isomers.
- Optimized structures were also found automatically through RMSD comparisons.
- Many isomers were found to be lower in energy than those published in the literature.

Figure 4. Sample theoretical $\text{Fe}_3(\text{CO})_9$ isomers.



Goals for Detecting Reaction Events in Molecular Dynamics Simulations

- Produce time series of ab initio bond order indices¹ extracted from molecular dynamics simulations and geometry optimizations.
- Apply signal processing methods to the bond order time series to detect reaction events that occur within simulations.
- Use the methodology developed to find theoretical isomers of the iron carbonyls, the $\text{Fe}_4\text{N}(\text{CO})_{12}$ iron-electrocatalyst, and other systems of interest.

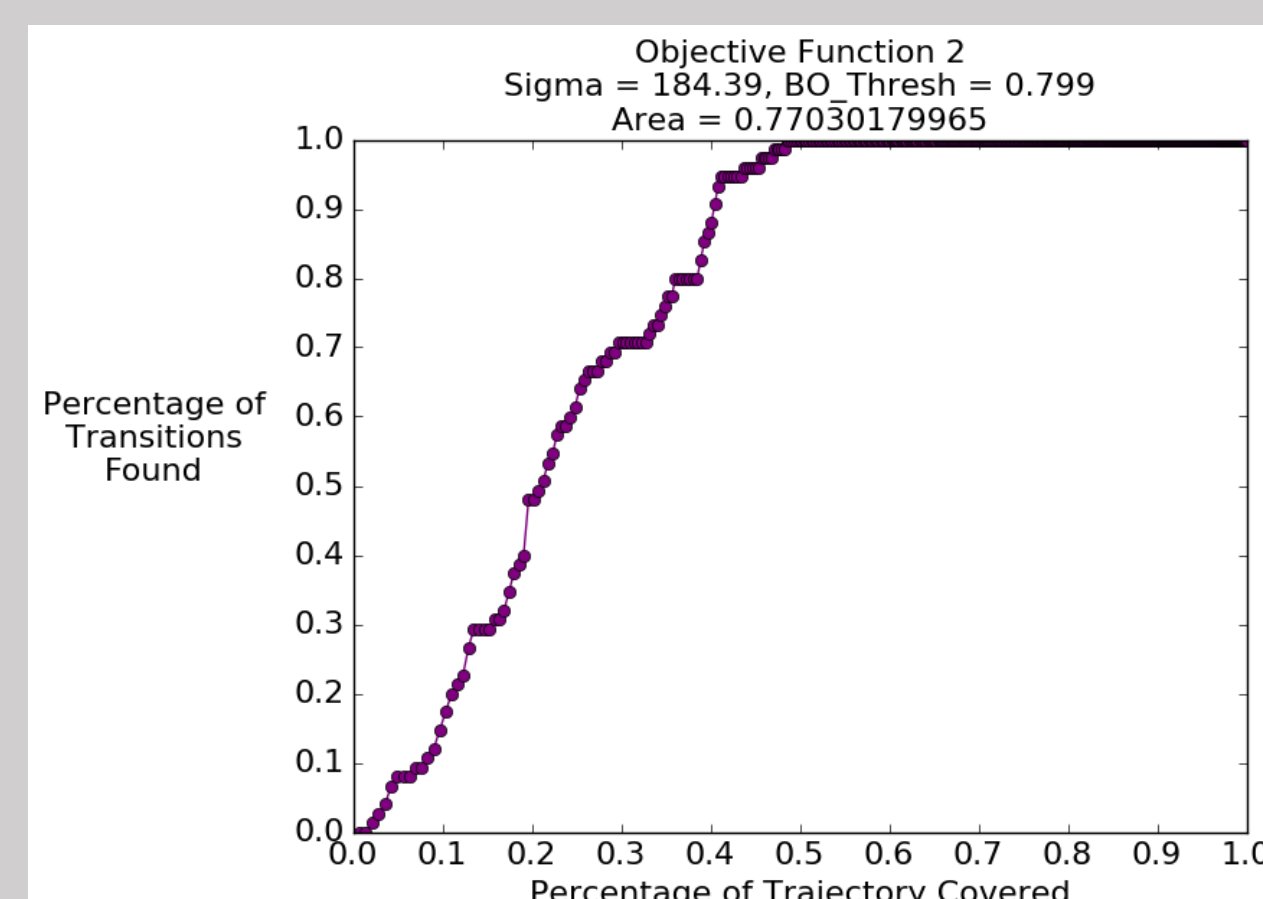
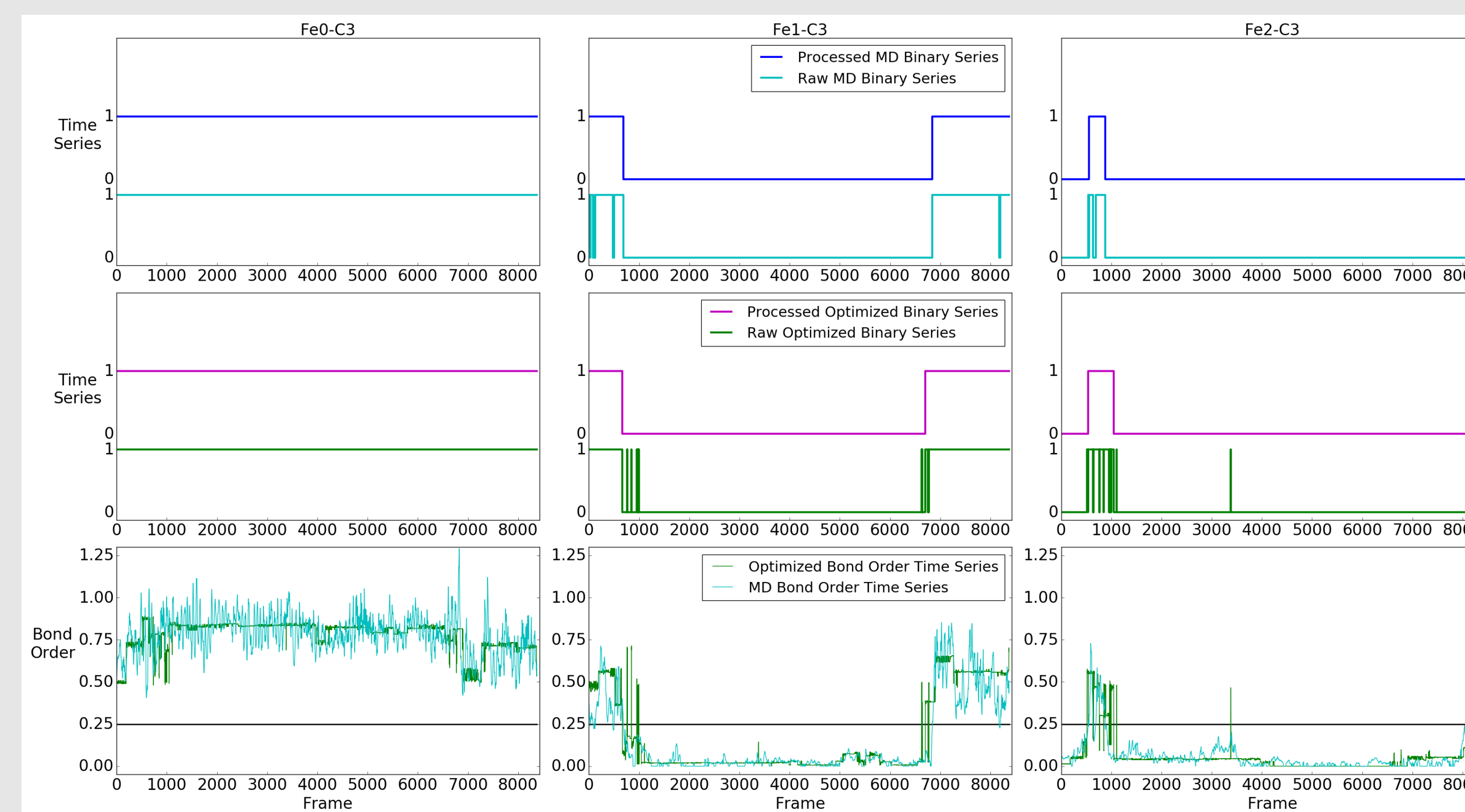


Figure 7. An objective function that gives a score by comparing the percentage of the molecular dynamics trajectory covered with the percentage of the “real” transitions found.

Binary Bond Order Time Series from Molecular Dynamics Simulations

- Molecular dynamics simulations are used to explore the potential energy surface of the iron carbonyl compounds.
- The trajectory of a high-temperature molecular dynamics simulation is able to cross energy barriers and enter the wells of multiple energy minima.
- Geometry optimizations are done on each frame in the molecular dynamics simulations to converge structures into nearby local minima.
- The optimized structures are clustered together into discrete groups of isomers using a bond order-distance metric. The clusters produce a standard set of reaction events in the molecular dynamics trajectory.
- While the method of clustering using a bond order-distance metric to distinguish between unique isomers is robust, it is computationally costly since every frame in the molecular dynamics simulation needs to be optimized.

Figure 5. Graphs of processed and unprocessed binary time series of bond order.



- For each pair of atoms, two unprocessed time series are made, one from the molecular dynamics trajectory and one from the set of optimized geometries.
- The raw time series are processed using parameters such as bond order thresholds and the persistency of bond order change.
- The specific values for the parameters are varied in order to match the processed time series made from the molecular dynamics trajectory to that made from the optimized geometries.

Objective Functions

- Multiple processing methods can be used in tandem with each other in order to process the bond order time series extracted from molecular dynamics simulations.
- Such methods include specifying bonding thresholds, recognizing only persistent changes in bond order, and smoothing the raw bond order time series by filtering out irregular fluctuations.
- The parameters used to process the raw bond order time series (the processed time series is shown by the blue lines in Figure 6a) are adjusted to maximize the detection of the reactions in the “gold standard” reaction event time series (red lines in Figure 6b).
- An objective function is defined to measure the deviation of the reaction events detected by a processed molecular dynamics bond order time series from the reference set of reaction events.
- The objective function shown in Figure 6 assigns a score to a certain combination of bond order threshold and transition gap threshold by determining how closely the processed time series matches the set of “real” reaction events.
- The objective function shown in Figure 7 is another way of assigning a score to a combination of parameters. The function measures how much of the of the “real” reactions are found as a function of the percentage of the trajectory covered.

Figure 6. a) An objective function where a score is given by determining the minimum box size required to cover all of the reaction events. b) A map of the scores made for different combination of parameter values.

