

Zachary Giovanini, Amelia Paus, Kimberley M. Christopher<sup>1</sup>, Bruce Locke<sup>2</sup>, and \*Igor V. Alabugin<sup>1</sup>

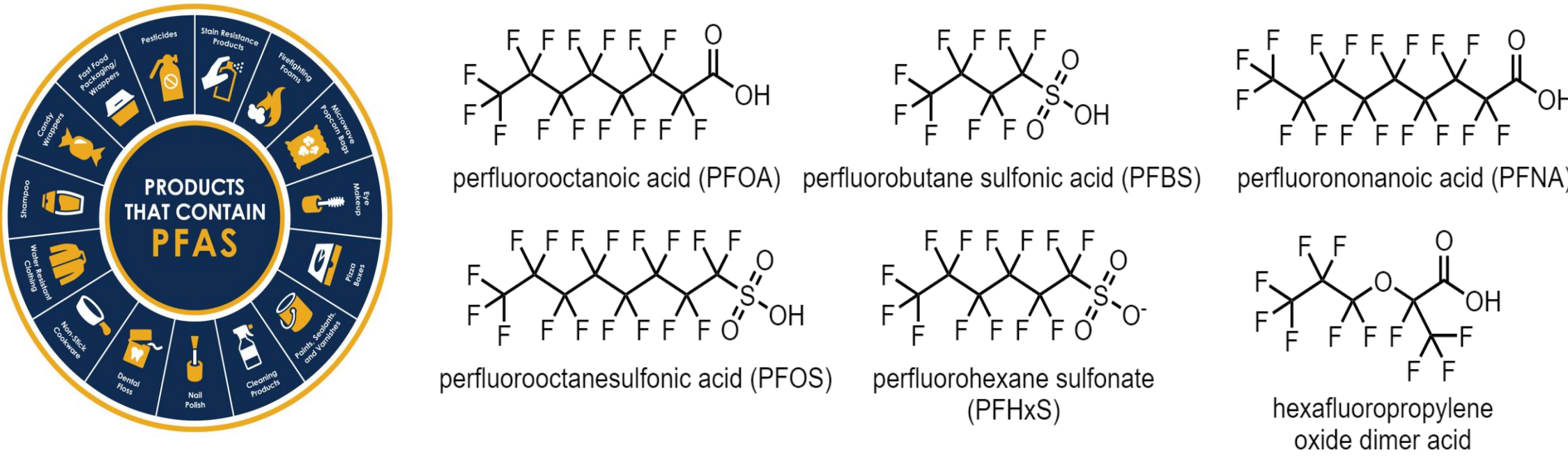
<sup>1</sup>Department of Chemistry and Biochemistry and <sup>2</sup>Department of Chemical and Biomedical Engineering

## Abstract

Perfluoroalkyl substances (PFAS), also known as “forever molecules,” are compounds that contain multiple carbon-fluorine bonds. They get the moniker “forever molecules” because the carbon-fluorine bond is the strongest single bond in organic chemistry, making PFAS very difficult to degrade; because of this, PFAS bioaccumulate and pose an extremely hazardous issue to humans and the environment. Our collaborators in chemical engineering found that their nonthermal plasma reactor effectively degrades PFAS, but the mechanism remains unknown.<sup>1</sup> Additionally many reactive intermediates like electrons, hydroxide radicals, and hydrogen radicals are formed which makes studying the degradation mechanism experimentally challenging. With computations, we hope to establish a benchmark to determine the appropriate level of theory to study these compounds and investigate their degradation mechanisms. Using the Conformer-Rotamer Ensemble Sampling Tool (CREST) conformer search program, Gaussian 16, ORCA 5.0.4, and the supercomputer at FSU, we were able to evaluate multiple different levels of theory specifically for perfluorosulfonic acids (PFSAs) reactive intermediates, and our benchmark is in agreement with literature findings that the M06-2X functional is the best model for PFAS.<sup>2</sup> Additionally, we explored how the concept of electron upconversion and electron catalysis that we recently showed can yield quantum yields greater than unity can be applied to efficiently degrade PFAS.<sup>3</sup> PFAS can be degraded in nonthermal plasma via electron catalysis, this would greatly increase efficiency and cost-effectiveness to practically address PFAS remediation.

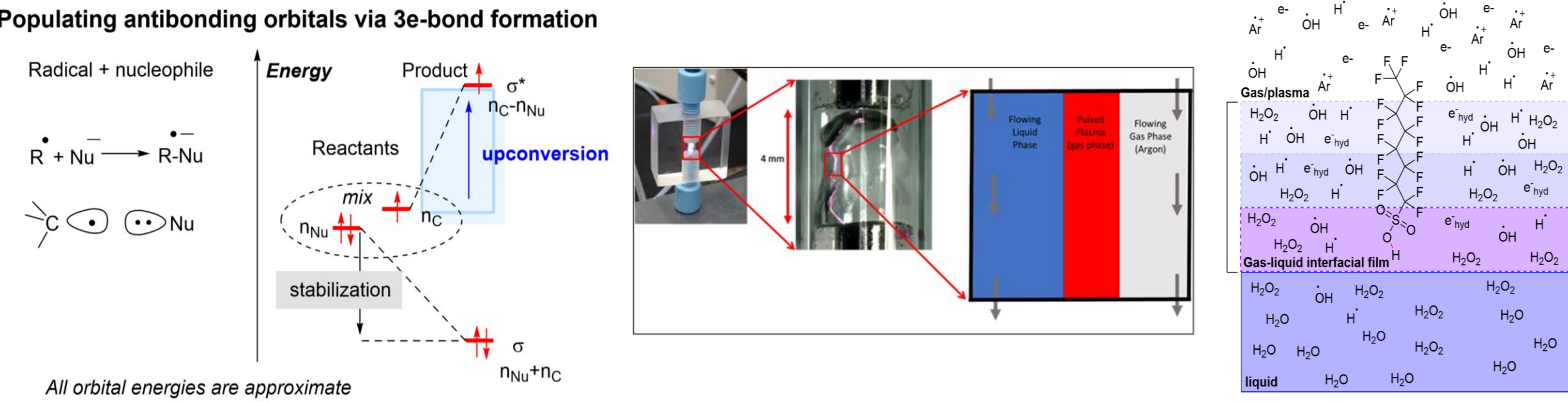
## Introduction

- PFAS can be found in many different parts of our lives and environments: nonstick cookware in our kitchens, cleaning products in our bathrooms, water-resistant fabrics in our closets, and even inside of our own bodies.<sup>4,5</sup>
- Accumulation of these strong compounds over time can become very harmful to ourselves and our world.<sup>6</sup>
- In order to change the destructive directionality of these compounds, degradation in an **efficient and cost-effective** way is necessary.



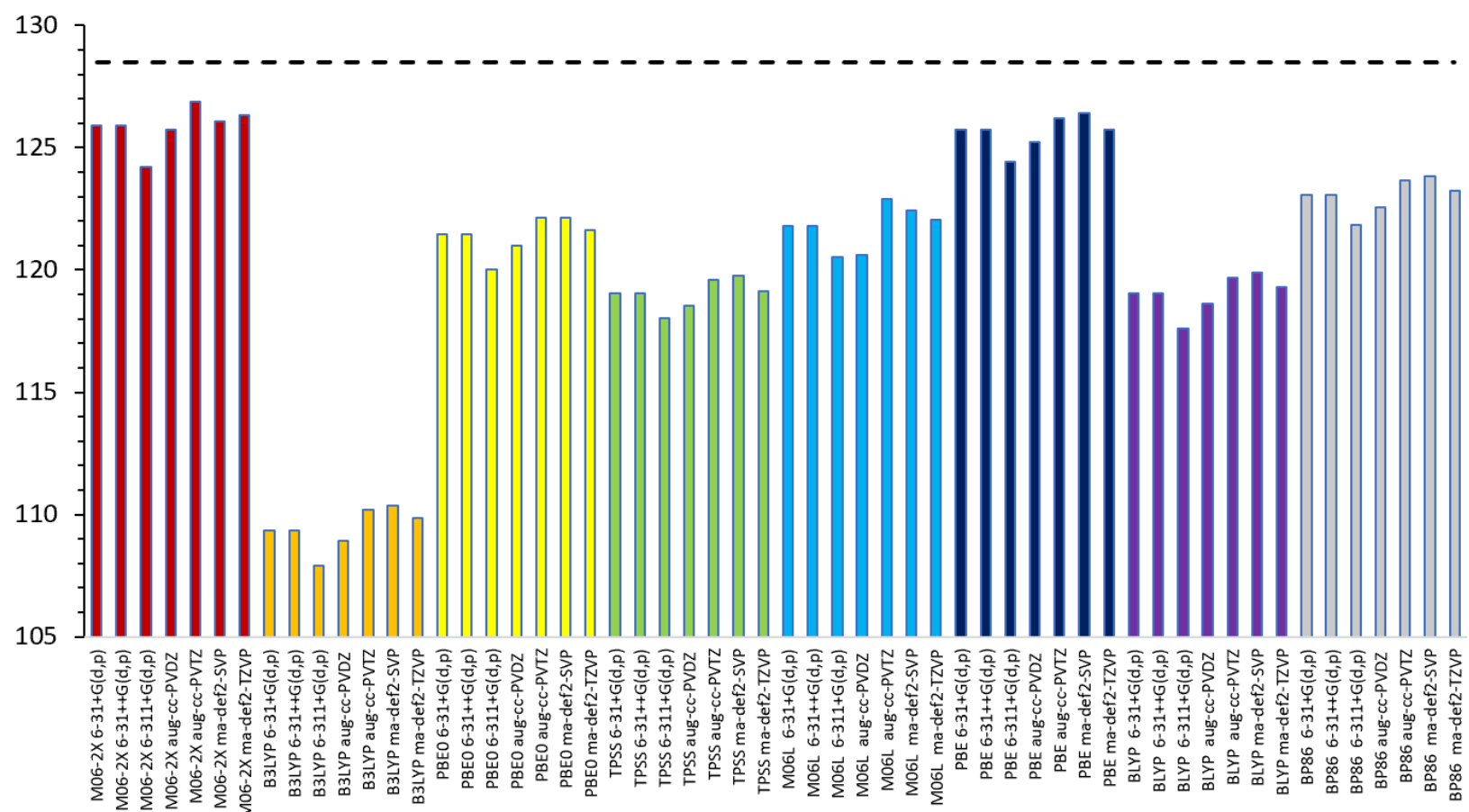
Scheme 1: PFAS containing products and representative PFAS compounds<sup>4</sup>

- PFAS degradation via **nonthermal plasma**, is cost effective and efficient and nonthermal plasma generates several **reactive intermediates** including electrons that could be utilized for electron upconversion and catalysis if **base** is present.

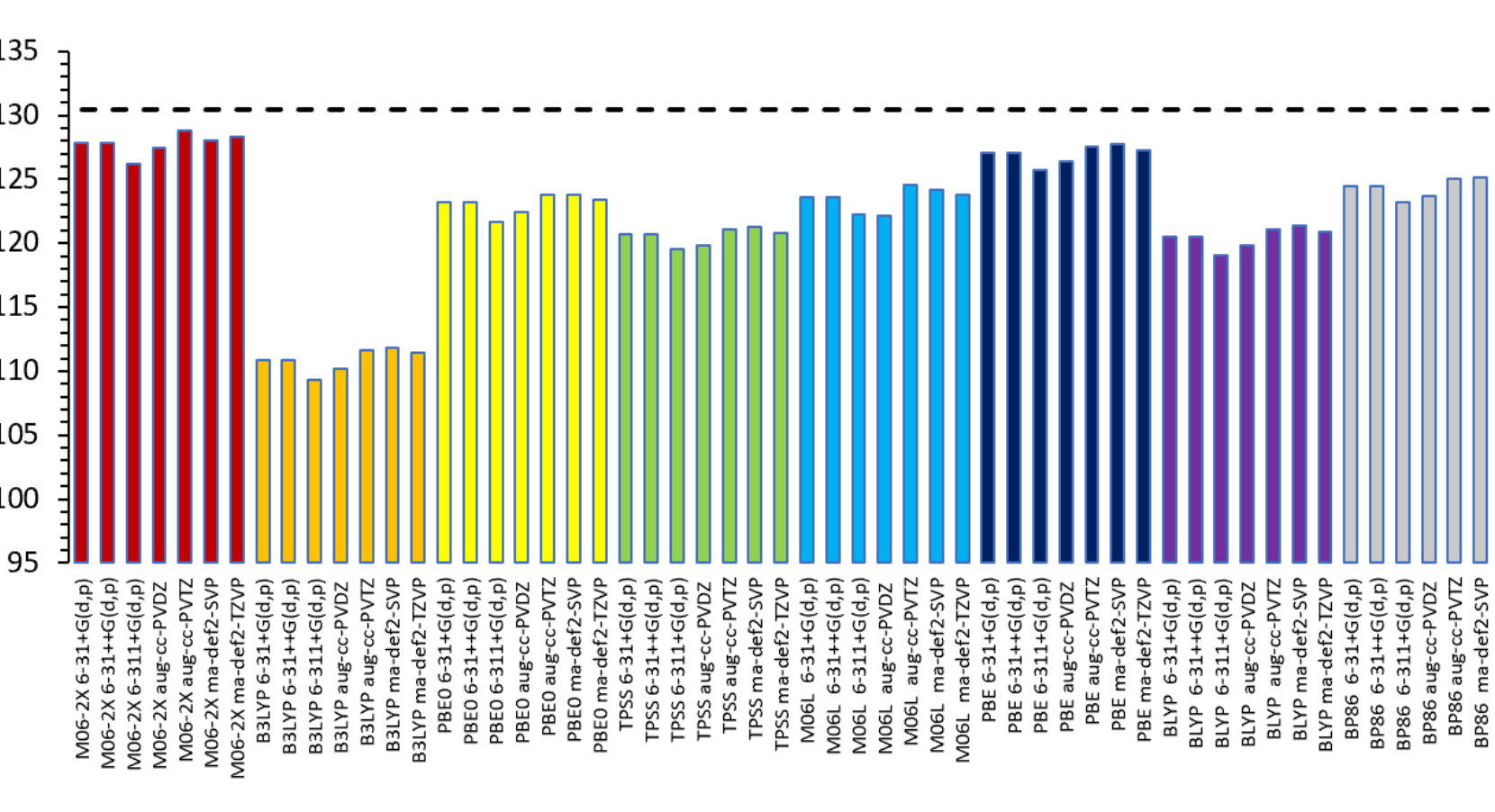


Scheme 2: Achieving electron upconversion, nonthermal plasma reactor, and reactive intermediates formed

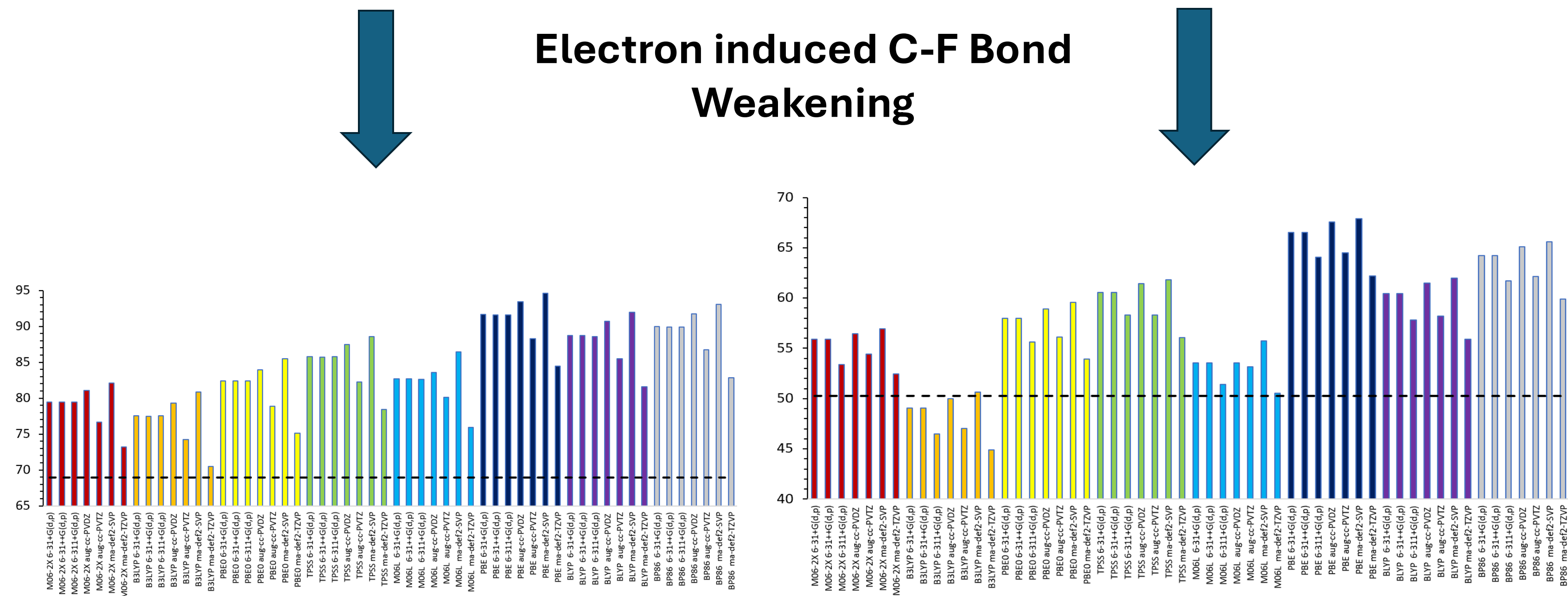
- Since **PFAS** are persistent and difficult to degrade, our research aim is to find the best way to most efficiently model electron induced degradation. Our hypothesis is that the M06-2X level of theory should work best to model **PFAS**, as it has proven successful in prior studies.
- The knowledge gap in this study is how nonthermal plasma degrades **PFAS** via electron upconversion powered catalysis.



**Figure 1:** CF3-SO3H C-F single point bond dissociation energies in kcal/mol in water with different levels of theory and DLPNO-CCD(T) aug-cc-PVTZ/CBS indicated with a dashed line optimized at the M06-2X 6-31+G(d,p) level of theory.



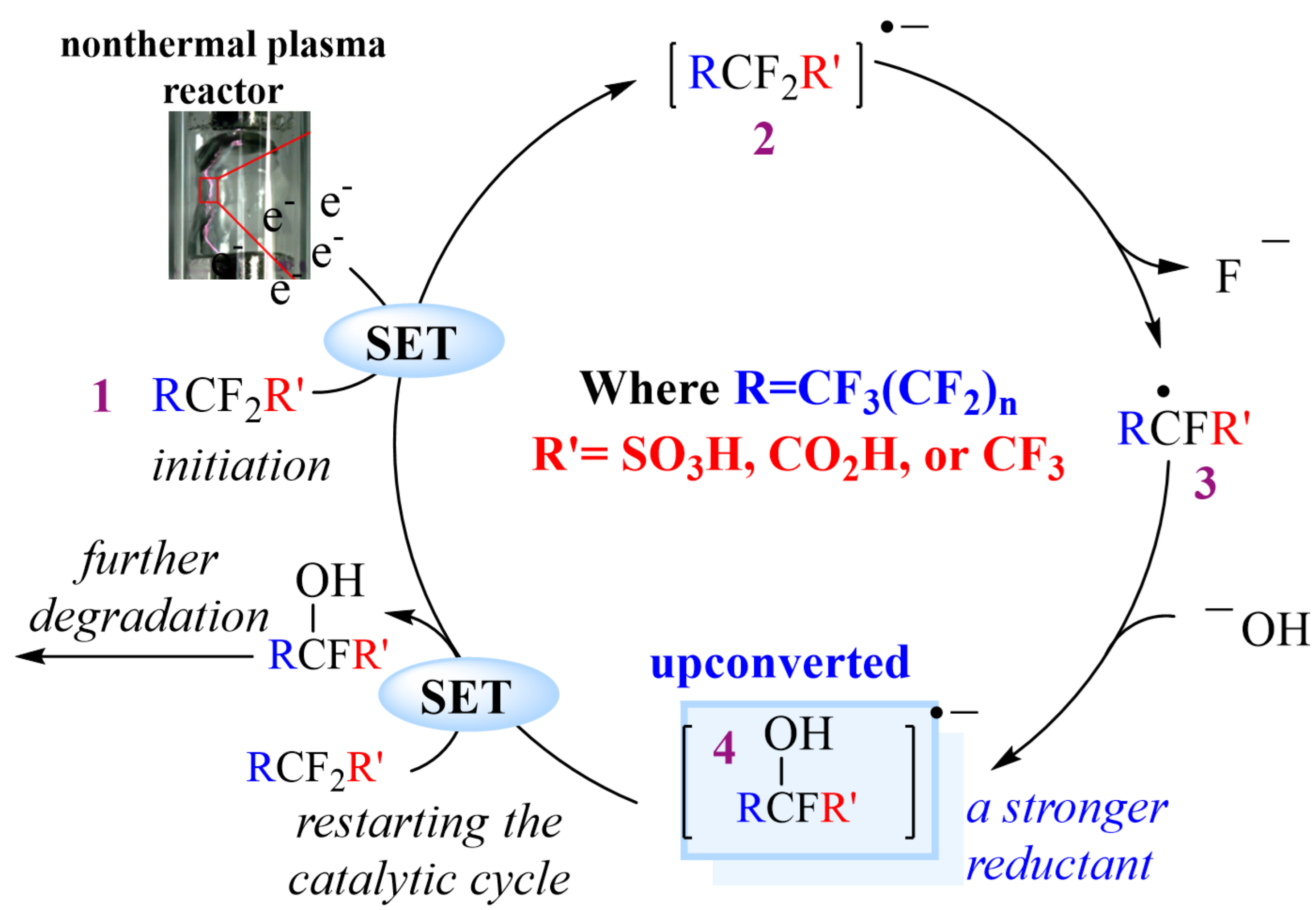
**Figure 2:** CF3-SO3-ANION C-F single point bond dissociation energies in kcal/mol in water with different levels of theory and DLPNO-CCD(T) aug-cc-PVTZ/CBS indicated with a dashed line optimized at the M06-2X 6-31+G(d,p) level of theory.



**Figure 3:** CF3-SO3H-RADICAL-ANION C-F single point bond dissociation energies in kcal/mol in water with different levels of theory and DLPNO-CCD(T) aug-cc-PVTZ/CBS indicated with a dashed line optimized at the M06-2X 6-31+G(d,p) level of theory.

**Figure 4:** CF3-SO3-RADICAL-DIANION C-F single point bond dissociation energies in kcal/mol in water with different levels of theory and DLPNO-CCD(T) aug-cc-PVTZ/CBS indicated with a dashed line optimized at the M06-2X 6-31+G(d,p) level of theory.

## Proposed Electrocatalytic Cycle for Degradation of PFAS with Base Present



## Methods

- Basis of Research:** PFAS benchmark and electrocatalytic cycle for degradation was investigated.
  - Find the best ways to effectively and efficiently degrade PFAS with nonthermal plasma.
- Programs:** FSU supercomputer, Gaussian 16, and ORCA 5.0.4 to model and analyze PFAS molecules and their enthalpy and free energy of their bond dissociation energies (BDE).
  - Conformer-Rotamer Ensemble Sampling Tool (CREST) program
    - Search for the best conformation of neutral molecules and radicals that yielded the most optimal results.
    - Simulated the best conformations to work with.
- Single Point Energy:** optimized the geometry of these conformations using the M06-2X functional with a basis set of 6-31+G (d,p) as a level of theory for density functional theory (DFT) calculations.
  - Allowed for most efficient way to calculate the thermodynamics of PFAS molecules.
  - Calculated single point energies with various levels of theory to determine the BDE for perfluorosulfonic acid and carboxylic acids.
    - Coupled-cluster singles and doubles theory (DLPNO-CCSDT) with 6-31+G (d,p) and 6-31++g (d,p) basis sets were used.
    - Gave the best turnout in calculating single point energies.
- Interpreting Data:** Linux and Excel were used to convert these findings into a legible format and analyzed which levels of theory had the least amount of deviation from CCSDT.

## Results and Conclusions

- Average deviations from the benchmark level DLPNO CCSD(T)/CBS (the “gold standard”), and M06-2X had the lowest deviation compared to other functionals.
- For negatively charged species there was significant deviation from DLPNO-CCSD(T), however it looks like the M06-2X 6-31++G(d,p) level of theory was a decent double zeta level of theory which is in agreement with previous studies<sup>2</sup>.
- Electrons clearly weaken C-F bonds as can be seen in the benchmark.
- If base is added to the reactor, it is possible to initiate a catalytic degradation cycle and our preliminary computations show that this reaction is favorable and the hydroxylated radical anions are upconverted.

## References

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## Acknowledgements

- We are grateful to the Donors of ACS Petroleum Research Fund and National Science Foundation (NSF CHE-2102579) for partial support of this work.
- This material is partially based upon support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Award No. DE-SC-0025438