Project Description
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Projects

1. U.S. Department of Energy, Office of Science, Basic Energy Sciences, *Computational Chemistry of Biofuel Functional Group Effects for Sustainable Transportation Energy*

- includes collaboration opportunity with National Laboratories
- interdisciplinary impact: physical chemistry + computer science/algorithm development

2. National Science Foundation, Chemical Measurements and Imaging Program, *Data Science and Machine Learning for Spectral Analysis to Advance Chemical Sciences*

- includes collaboration opportunity with National Laboratories
- interdisciplinary impact: spectroscopy for energy applications + machine learning/data science

Broader Impact and Scientific Motivation

Building a clean and equitable energy economy and mitigating anthropogenic contributions to climate change is a top priority of the Biden Administration, which in a recent White House report titled *U.S. Innovation to Meet 2050 Climate Goals* [1] identifies advanced biofuels as a 'cross-cutting innovation' part of a carbon-neutral fuels strategy incorporated into the Inflation Reduction Act that can contribute to climate goals by mitigating emissions from transportation. Sustainable biofuels and e-fuels are an integral part of the three core strategies put forth by the Biden administration in the recent report *The U.S. National Blueprint for Transportation Decarbonization* [2] produced as a joint strategy by DOE, DOT, and EPA to transform transportation and address all sources of transportation emissions and achieve the vision of a clean, safe, secure, accessible, affordable, equitable, and decarbonized transportation system. In addition, ‘sustainable fuels’ is identified as one of five ‘critical fundamental scientific topics for basic energy research’ with ‘potentially significant impacts on future US innovation and technology development’ in a 2021 report by the BESAC Subcommittee on International Benchmarking titled *Can the U.S. Compete in Basic Energy Science? Critical Research Frontiers and Strategies* [3].

Machine learning applications to problems in the chemical sciences is growing exponentially [4] and provides a means for accelerating the pace of progress on issues related to energy sustainability, climate modeling, and identification of species in the interstellar medium. Because of the reliance on large datasets spanning numerous parameters, coordination with experimental and modeling tools to provide input for machine learning is essential. With sufficient training sets of data, the identification of new combinations of mathematical and statistical models is required to produce machine learning tools with broad applicability.

References

[1] White House, "U.S. Innovation to Meet 2050 Climate Goals", 2022.
[2] White House, "The U.S. National Blueprint for Transportation Decarbonization: A Joint Strategy to Transform Transportation", 2023.
[3] Cynthia Friend, U.S. Department of Energy, BESAC Subcommittee on International Benchmarking, "Can the U.S. Compete in Basic Energy Science? Critical Research Frontiers and Strategies", 2021.
[4] Nongnuch Artrith, Keith T. Butler, François-Xavier Coudert, Seungwu Han, Olexandr Isayev, Anubhav Jain, Aron Walsh, "Best practices in machine learning for chemistry", *Nature Chemistry*, 13 (2021) 505-508.

Project 1 – Department of Energy

Computational Chemistry of Biofuel Functional Group Effects for Sustainable Transportation Energy

Resonance-stabilization is common in radicals produced during biofuel oxidation and lowers the energy of molecular intermediates central to chain-branching mechanisms. However, despite the ubiquity, the role of resonance-stabilization on reaction pathway selectivity of radicals during low-temperature oxidation remains unclear stemming, in part, from a lack of theoretical chemical kinetics models. Unsaturated biofuel molecules, such as prenol, contain allylic and/or benzylic hydrogen, the C–H bond energies for which are significantly lower than for alkylic sites, which facilitates intramolecular H-abstraction in organic peroxy radicals (ROȮ) undergoing isomerization to hydroperoxy-substituted carbon-centered radicals, ȮOOH. Subsequent decomposition barriers of ȮOOH are higher as a result of resonance-stabilization, which creates a 'trapping effect' that may disfavor unimolecular reaction and, instead, facilitate reaction with O_2 including second-O_2-addition. Moreover, for unsaturated alcohol biofuels, including 2-phenylethanol, *iso*-prenol, and prenol, resonance-stabilized radical reactions compete with prototypical alkyl oxidation reactions, and the effects of substituent size and proximity on the balance of reactions remains entirely unknown.

The research project involves an extensive theoretical effort centered on fundamental chemical kinetics and thermochemistry of resonance-stabilized ȮOOH radicals. The scientific driver is to produce new insight derived from high-level theoretical models to describe the oxidation of three species in which resonance-stabilization is a central feature: prenol, iso-prenol, and 2-phenylethanol, which are relevant biofuels for next-generation combustion applications that support reducing the carbon footprint of transportation.

Project 2 – National Science Foundation

Data Science and Machine Learning for Spectral Analysis to Advance Chemical Sciences

Data-enabled computational science such as machine learning (ML) remains a critical component to ongoing development of sustainable energy technologies for transportation, which relies extensively on understanding fundamental chemical mechanisms of elusive radicals that are central to next-generation biofuel combustion. Success of this effort is predicated on the ability to identify multi-functional intermediates, including substituted cyclic ethers, organic hydroperoxides, and other complex species. Isomer-resolved vacuum ultraviolet (VUV) spectroscopy is a cutting-edge tool to detect such species either via differential absorption or via photoionization coupled with mass spectrometry. However, these techniques rely on well-controlled measurements of reference spectra for isolated species, and many important intermediates are unobtainable via chemical synthesis due to issues with separation, purification, or stability. To circumvent this issue and to uncover chemical insight on biofuel oxidation chemistry among other scientific areas such as photochemistry, this proposal employs high-resolution VUV measurements of absorption spectra and, in collaboration with National Laboratory researchers, synchrotron-based photoionization measurements to provide new data for the development of new machine learning methods.

The primary goal of the data science aspect of this project is produce new machine learning tools that identify features in the spectra in order to enable identification of multi-functional species. Combining new machine learning methods with measurements in the VUV will produce new tools that can be used by other researchers to yield chemical kinetics insight about these important intermediates or to improve understanding of photochemistry via dissociation dynamics. For this project, we will train and use several promising machine learning methods for identifying functional groups and other molecular motifs: (1) deep neural networks, (2) boosted decision trees and (3) support vector machines. This work develops new data-enabled machine learning tools to innovate the analysis and interpretation of molecular structure from vacuum ultraviolet spectroscopy measurements to address lingering inabilities for detecting elusive, multi-functional intermediates that are relevant to tropospheric chemistry, combustion chemistry, and other areas.