# Hard Soft Acid Base Mismatches for Hydrogen Activation

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## Project Purpose Summary:

Global reliance on fossil fuels including coal, oil, and gas exacerbates the effects of climate change. Rising temperatures and extreme heat will raise American emergency healthcare costs by nearly \$1 billion.[1] Fossil fuel combustion in electricity, manufacturing, transportation, and food production, accounts for 75% of global greenhouse gas emissions, the heat-trapping effect underlying the climate crisis.[2] Fuel combustion is a nonrenewable single-step process, resulting in the production of $CO_2$ and $H_2O$ (figure. 1). Fuel cycles can be renewable if they are carbon neutral and photosynthesis is a great model (figure. 2). Photosynthesis is renewable as it converts $CO_2$ and $H_2O$ into energy-dense fuels like glucose. Replacing fossil fuel combustion with renewable cycles mitigates extreme heat, which threatens public health, projecting 28,000 annual deaths in U.S. cities by 2090, especially among working-class, low-income, disabled, young, and elderly populations.[3]

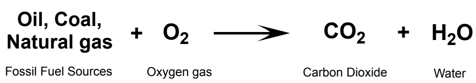



**Figure. 1** Combustion of Fossil fuels resulting in carbon dioxide emission.

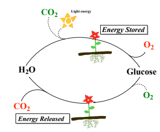



**Figure. 2** Photosynthetic, carbon neutral cycle

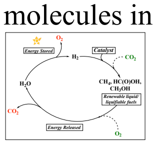
## Project Goals and Preliminary Results:

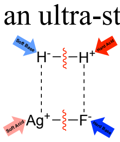
The Tate lab uses a gas-to-liquid fuel cycle to mimic the carbon-neutral process of photosynthesis (figure. 3). We focus on a key step in the fuel cycle, activating $H_2$ through splitting the molecule into $H^+$ and $H^-$. Similar to plants breaking water into $H^+$ ions to produce their glucose fuel, we split $H_2$ into ions using synthetic catalysts for a subsequent reaction with $CO_2$. In the gas-to-liquid fuel cycle, $H_2$ from water reacts with $CO_2$ to form an energy-dense renewable fuel, with catalysts activating $H_2$ to facilitate the bonding of $H^+$ and $H^-$ with $CO_2$.

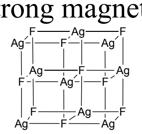
Our work applies the Hard-Soft Acid-Base (HSAB) theory, predicting acid-base interactions based on size, charge, and polarizability.[4] Hard acids form strong ionic bonds to hard bases, while soft acids form strong covalent bonds to soft bases. In the HSAB theory, the $H_2$ molecule is a hard-soft mismatch: $H^-$ is a soft base favoring covalent bonds, while $H^+$ is a hard acid preferring ionic bonds, resulting in a weak bond, one easily broken when each ion pairs with its HSAB complement (figure. 4). We focus on combining the soft acid, silver, ($Ag^+$) with the hard base, fluoride ($F^-$), forming an HSAB mismatch. According to our mismatch hypothesis, this proposed Ag-F catalyst has strong potential to activate $H_2$. However, the Ag-F catalyst tends to form a crystalline structure, unideal for catalysts; to prevent crystallization and promote catalysis, we use an organic support to isolate individual Ag-F bonds (figure. 5). Key results of my project this summer include the development of a reliable synthetic pathway for the construction of an organic molecular scaffold that supports discrete HSAB mismatches such as Ag-F (figure. 6).[5] We are continuing to explore the ability of these isolated Ag-F mismatches to activate $H_2$ and facilitate the formation of energy-dense fuels like formic acid, an input for sustainable aviation fuel according to the U.S. Department of Energy.[6]

## Methods:

My project relies strongly on nuclear magnetic resonance (NMR) spectroscopy, a technique similar to magnetic resonance imaging (MRI) diagnostics, that probes the absorption of radio waves by molecules in an ultra-strong magnetic field to determine details of molecular structure.





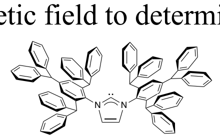


**Figure. 3** $CO_2$ neutral gas-to-liquid fuel cycle **Figure. 4** Hard-Soft Acid Base Mismatch Catalyst Design **Figure. 5** Crystalline structures of Silver-Fluorine **Figure. 6** Organic Support: IPr#

**Faculty Mentor: Brandon Tate**

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[1] Jessica Ordóñez-Lancet, Jasia Smith, Cathleen Kelly, *Climate Change is Subjecting More Americans to Unbearable Extreme Heat*, Center for American Progress Action Fund, https://www.americanprogress.org/article/climate-change-is-subjecting-more-americans-to-unbearable-extreme-heat/.
[2] United Nations Climate Action, *Causes and Effects of Climate Change*, United Nations, https://www.un.org/en/climatechange/science/causes-effects-climate-change.
[3] Jessica Ordóñez-Lancet, Jasia Smith, Cathleen Kelly, *Climate Change is Subjecting More Americans to Unbearable Extreme Heat*, Center for American Progress Action Fund, https://www.americanprogress.org/article/climate-change-is-subjecting-more-americans-to-unbearable-extreme-heat/.
[4] Ralph G. Pearson, Hard and Soft Acids and Bases, *Journal of the American Chemical Society* **1963**, *85*, 3557.
[5] Qun Zhao, Guangrong Meng, Guangchen Li, Carol Flach, Richard Mendelsohn, Roger Lalancette, Roman Szostak, and Michal Szostak, *IPr#—Highly Hindered, Broadly Applicable N-Heterocyclic Carbenes*, The Royal Society of Chemistry **2021**, 3-4.
[6] Bioenergy Technologies Office, *New Research Pathway Uses Renewable Electricity to Product Formic Acid from Carbon Dioxide*, U.S. Department of Energy, https://www.energy.gov/eere/bioenergy/articles/new-research-pathway-uses-renewable-electricity-produce-formic-acid-carbon.