**Project Title:** Electric field assisted Thermo-catalytic Decomposition with Regeneration: Comparisons with ReaxFF Atomistic simulations

**FOA Area of Interest:** 1B – Electromagnetic Energy-Assisted Approaches to Convert Fossil Fuels to Low-Cost Hydrogen


**Investigators**

Prof. Randy Vander Wal (PI)

Prof. Adri van duin (Co-PI)

Dr. Margaret Kowalik (Co-I)

James Heim II (Graduate student)

&

Dr. Alison Metz (Program Manager)

NETL_DOE

Contact:
Phone: 814-865-5813
Email: ruv12@psu.edu


**Review Meeting**
April 23rd, 2024

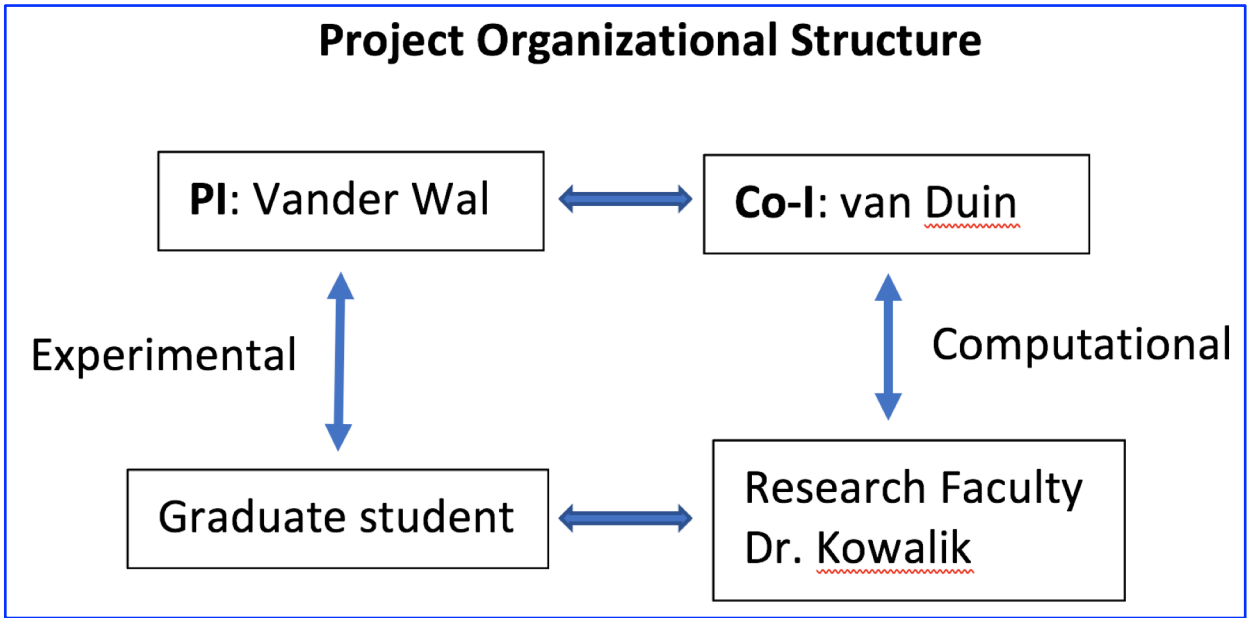
**Project Organization and Structure:** Roles and Responsibilities of Participants:

Dr. Vander Wal as PI is directing the overall project, manage project personnel, oversee and track budgets, tasks, schedule and be responsible for project deliverables.

Dr. van Duin as Co-PI is providing training in the use of the ReaxFF reactive force field methods – and in connecting ReaxFF results to experiments.

Dr. Kowalik as Co-I is performing simulation development and result assessment.

James Heim II is setting up experimental apparatus and performing tests.



# Technical Background / Motivation for the Project

- Presently hydrogen production is ~ 50 MMT per year worldwide

- ~ 10 MMT of this in the U.S., primarily produced (> 95%) via steam methane reforming [1].

<u>Steam reforming of methane (SMR), the present industrial practice, produces</u>

- 3.7 kg $CO_2$ (equiv.)/kg of net hydrogen [2]
- consumes 19.8 liters of water per kg of hydrogen [3].

*And requires*

- sulfur removal prior to processing,
- downstream high and low temperature water gas-shift reactions,
- CO removal,
- cleanup of residual $CO_2$ and $H_2S$

*in order to generate a usable $H_2$ stream*.

[1]. The International Energy Agency: $H_2$ Economy Overview & Report https://www.iea.org/hydrogen2019/
[2]. Marbán, G., Valdés-Solís, T. (2007). Towards the hydrogen economy? *Int. J. of Hydrogen Energy*, *32*(12), 1625-1637. *See also,* Abbas, H. F., Daud, W. W. (2010). Hydrogen production by methane decomposition: a review. *Int. Journal of Hydrogen Energy*, *35*(3), 1160-1190.
[3]. Spath, P. L., and Mann, M. K., Life cycle assessment of hydrogen production via natural gas steam reforming. (2001). Technical Report NREL/TP-570-27637.

# Technical Advantages of Thermo-catalytic decomposition vs. SMR

- TCD does not generate $CO/CO_2$ byproducts or consume water resources.
- No need for water-gas-shift and $CO_2$ removal stages.
- Eliminates need along with stock desulphurization and steam generation.
- Energy requirement for methane cracking (37.8 kJ/mole of $H_2$) is less than that for steam reforming (63.3 kJ/mole of $H_2$) [6].
- Life-cycle assessments [7] and techno-economic analyses [6] are positive.
- Non-catalytic decomposition requires temperatures ~ 1200 ℃.
- With catalyst decomposition can be accomplished in the range 850 – 900 ℃ [8].

[6]. Thermo-catalytic $CO_2$-free production of hydrogen from hydrocarbon fuels U.S. DOE Hydrogen Program Review. U.S.: 2002. NREL/CP-610-32405. [7]. Life cycle assessment of processes for hydrogen production. Environmental feasibility and reduction of greenhouse gases emissions. Int. J. of Hydrogen Energy, 34(3), 1370-1376. [8]. Review of methane catalytic cracking for hydrogen production. Int. J. of hydrogen energy, 36(4), 2904-2935.

# Problem Statement

- $H_2$ may be generated from natural gas by thermo-catalytic decomposition (TCD) or gasification of coal.
- In TCD the reaction rate decreases with time.
- Required temperatures for gasification are high.
- For TCD and regeneration reactions – can an external E-field change the reaction rate? If so, is this due to a change in number of active sites or a change in mechanism and activation energy?

**Approach:** Connect active sites with kinetic rates to differentiate these possibilities and resolve E-field role(s) by reference to atomistic simulations.

# Project Objectives

Project objectives will connect kinetic rates with active sites for thermo-catalytic (TCD) of natural gas and regeneration reactions of $CO_2$ oxidation of TCD carbon and $H_2O$ gasification of coal under an applied E-field with parallel ReaxFF-based molecular dynamics simulations for comparisons.

**Objectives:**

1. Measure active sites parametrically with reaction conditions.

2. Determine reaction rates as function of reaction conditions.

3. Evaluate activation energies for comparison to active site number and type.

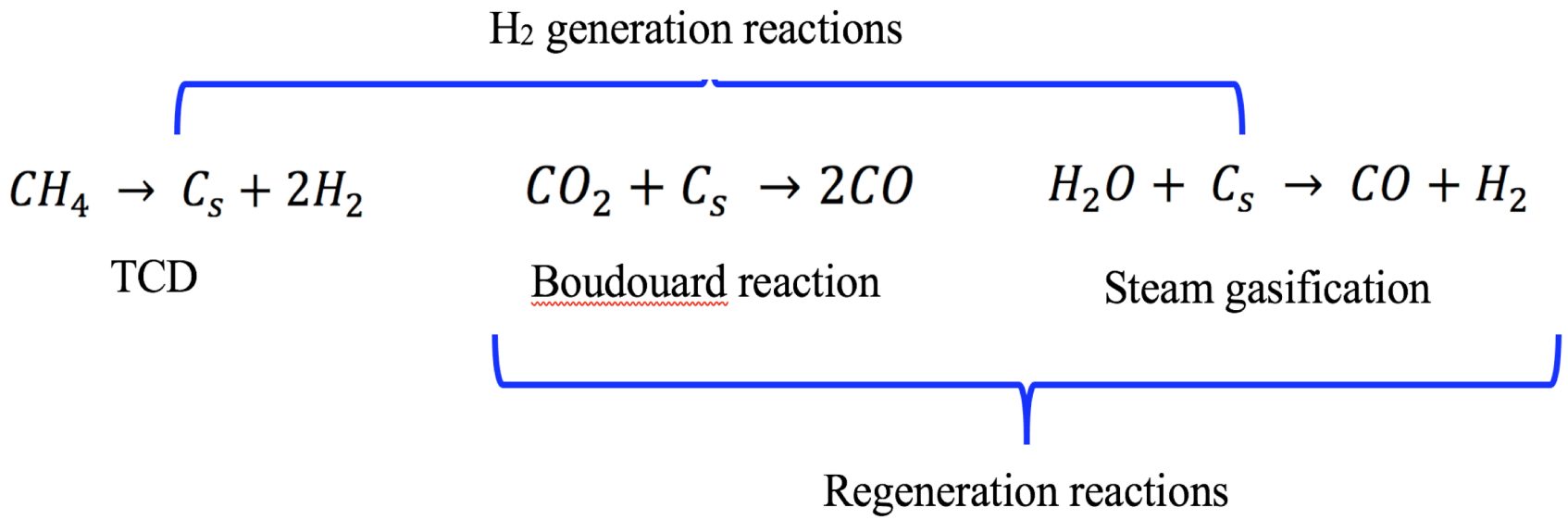
4. Develop atomistic simulations for TCD and regeneration reactions for applied E-fields.

# Experimental Approach – Reactions, Rates and Active Sites

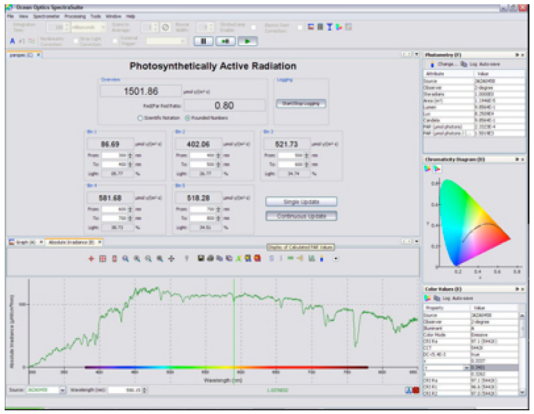
- TCD carbon deposition rate will be measured.

- Regeneration will be conducted using $CO_2$ for CO generation and with $H_2O$ for gasification.
- (establishing applicability to a coal fed process).

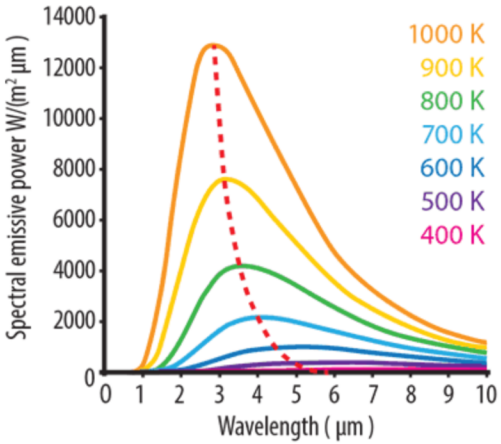
- Regeneration rates will be monitored by products using calibrated analysis methods.

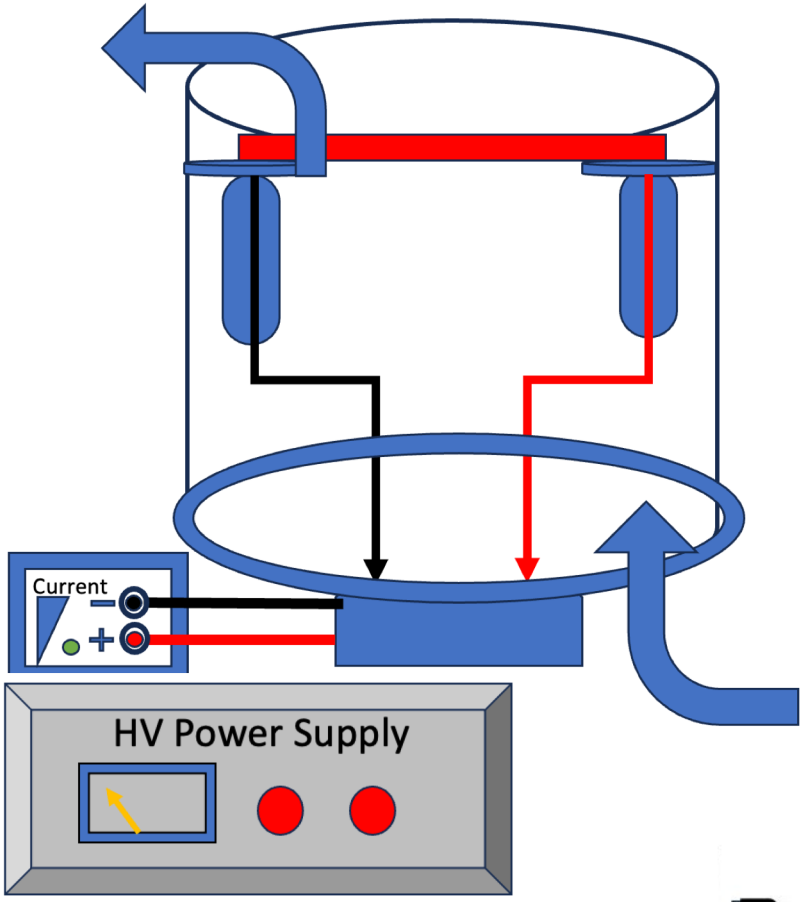


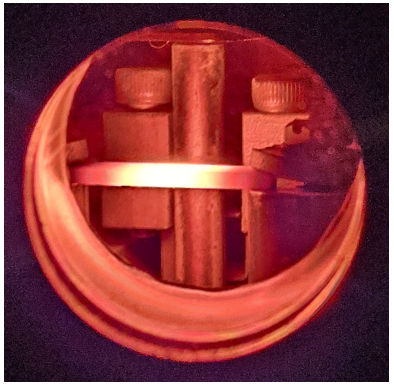
# Joule based Heating

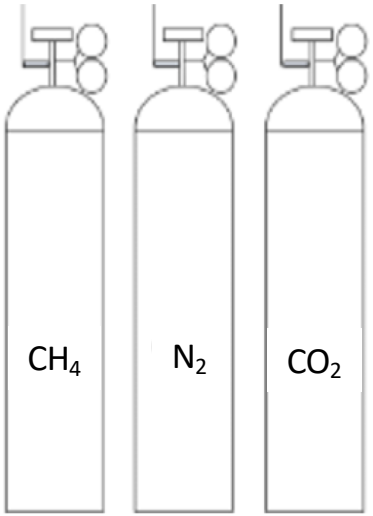



Black body spectrum



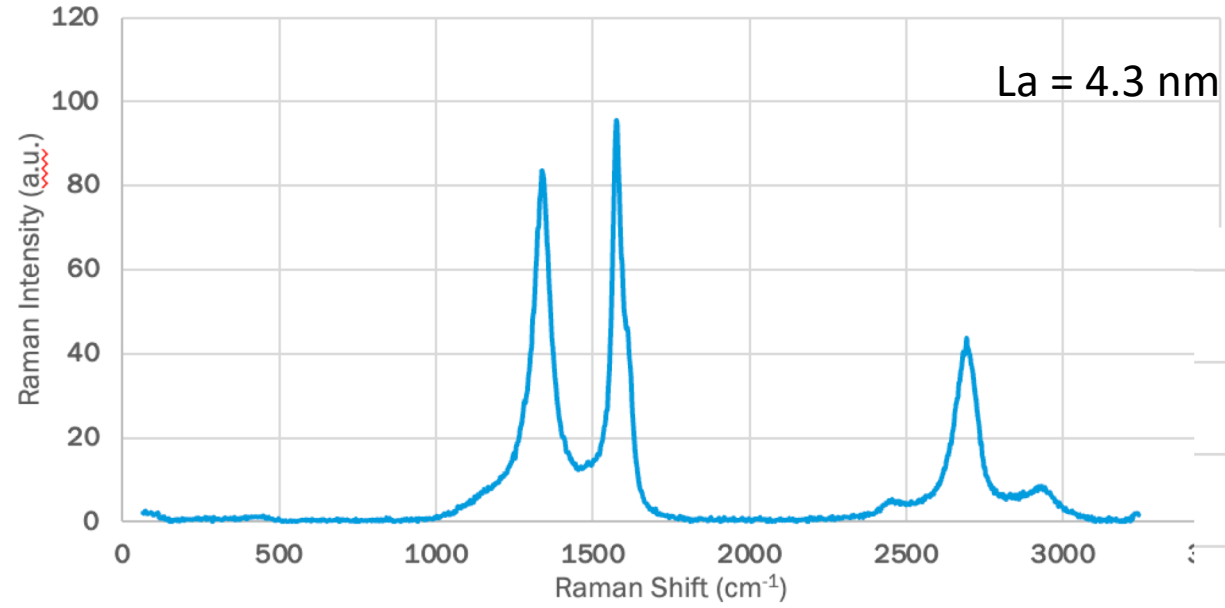



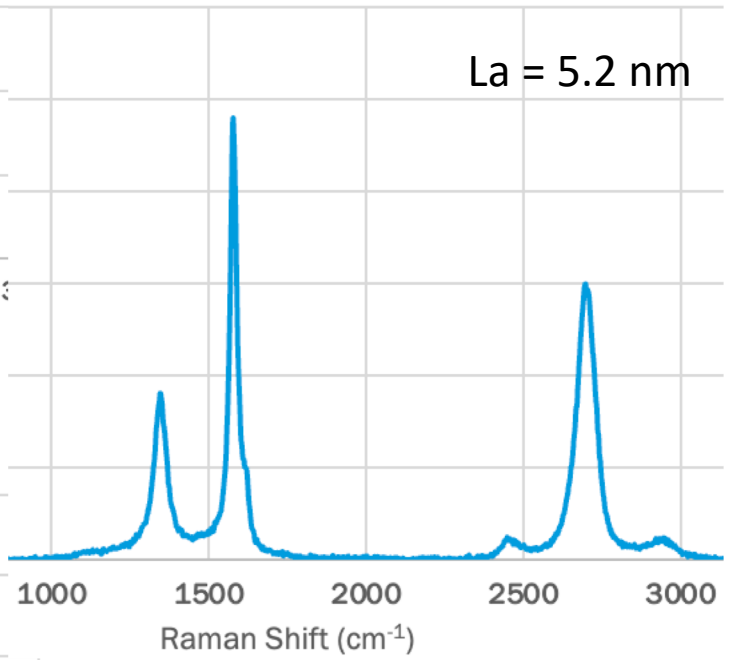


$$T = H/C_p \approx I^2R = V^2/R$$

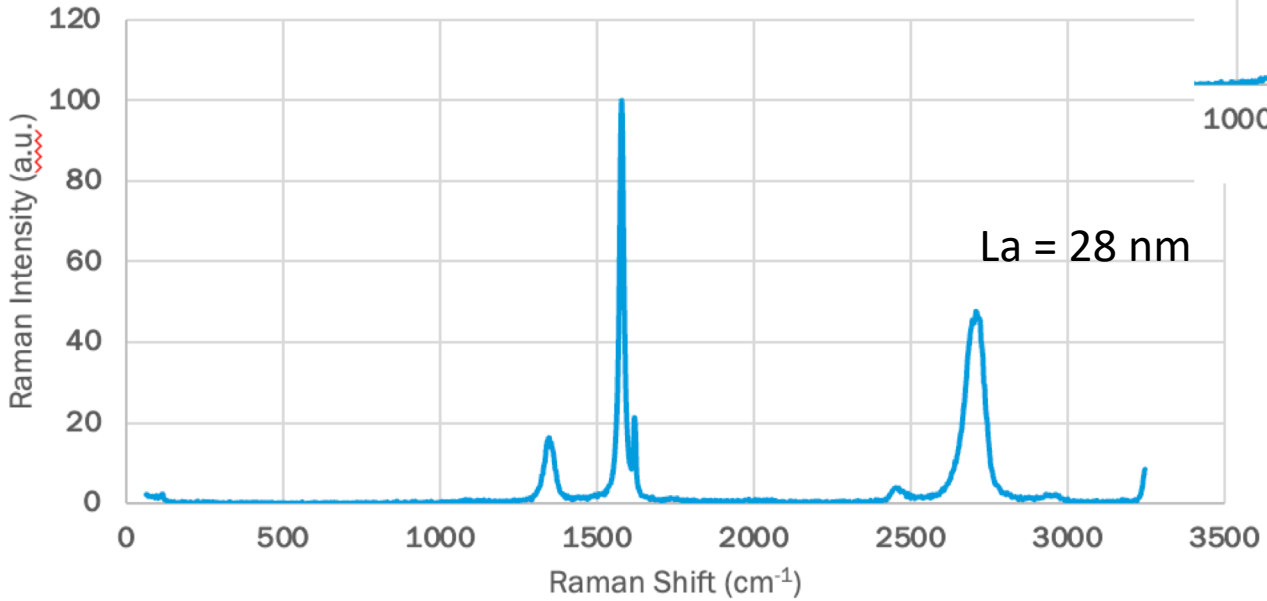
$CO_2$ Gasification – Joule heating: 1,000 ℃



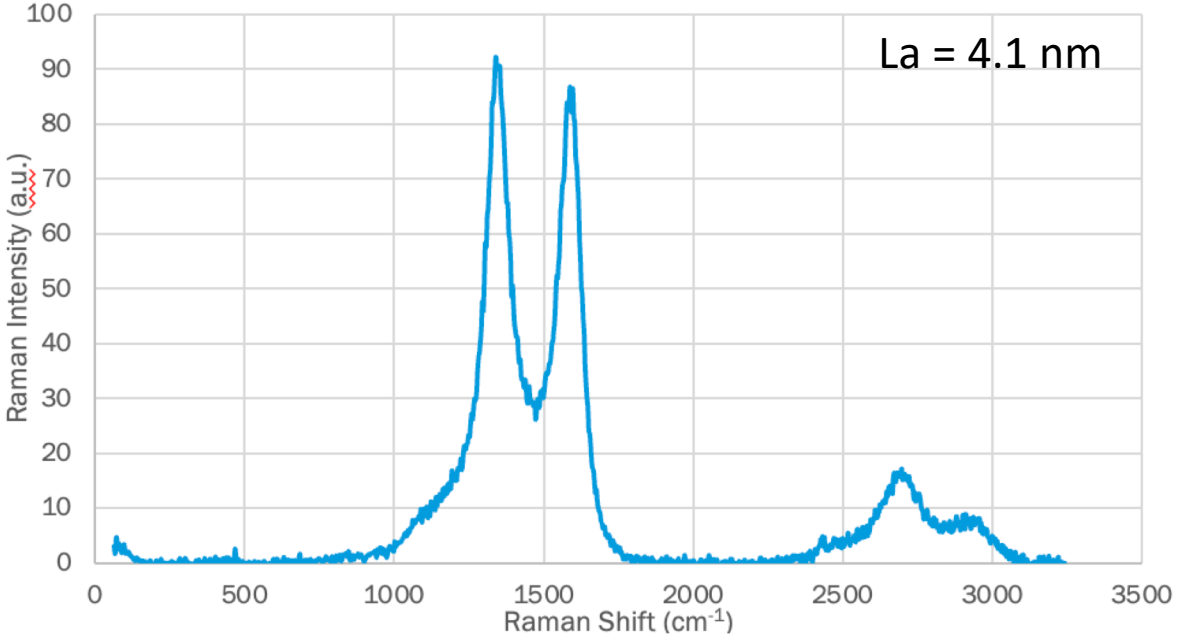

Pristine Graphite



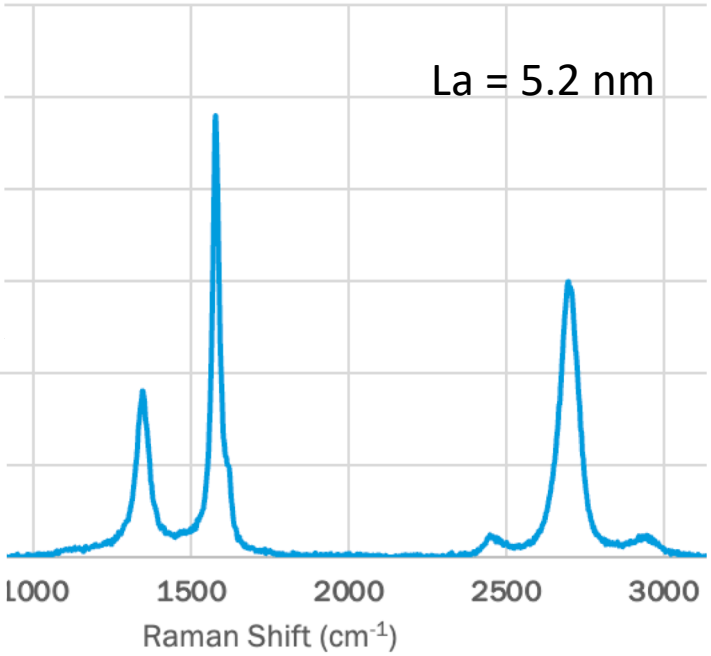

$CO_2$ Gasification – Furnace heating: 1,000 ℃



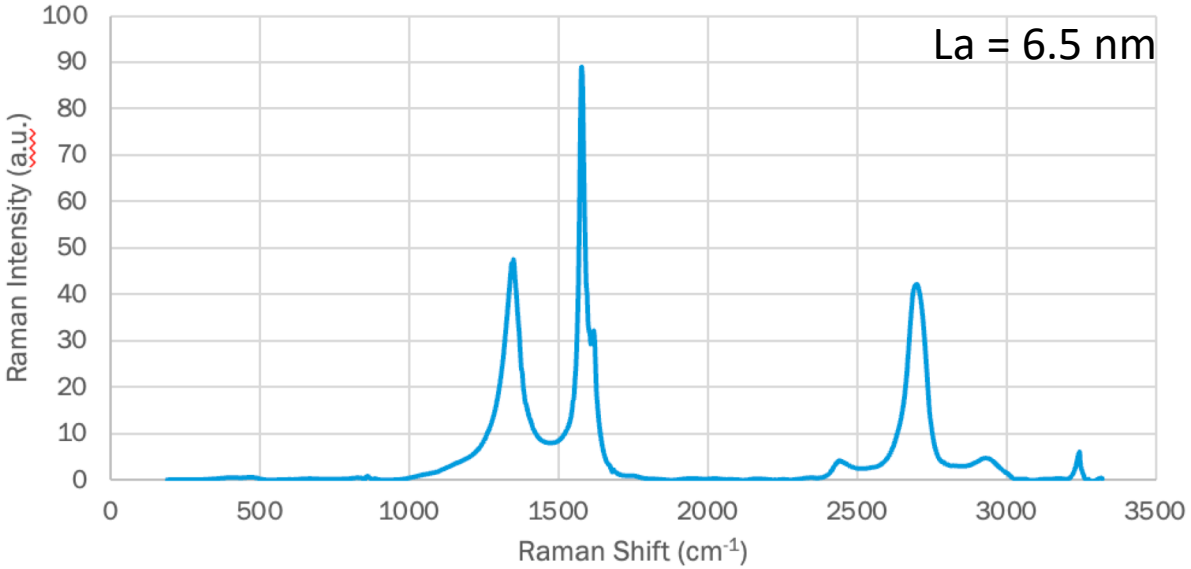
TCD 10% SNG: 1,000 ℃



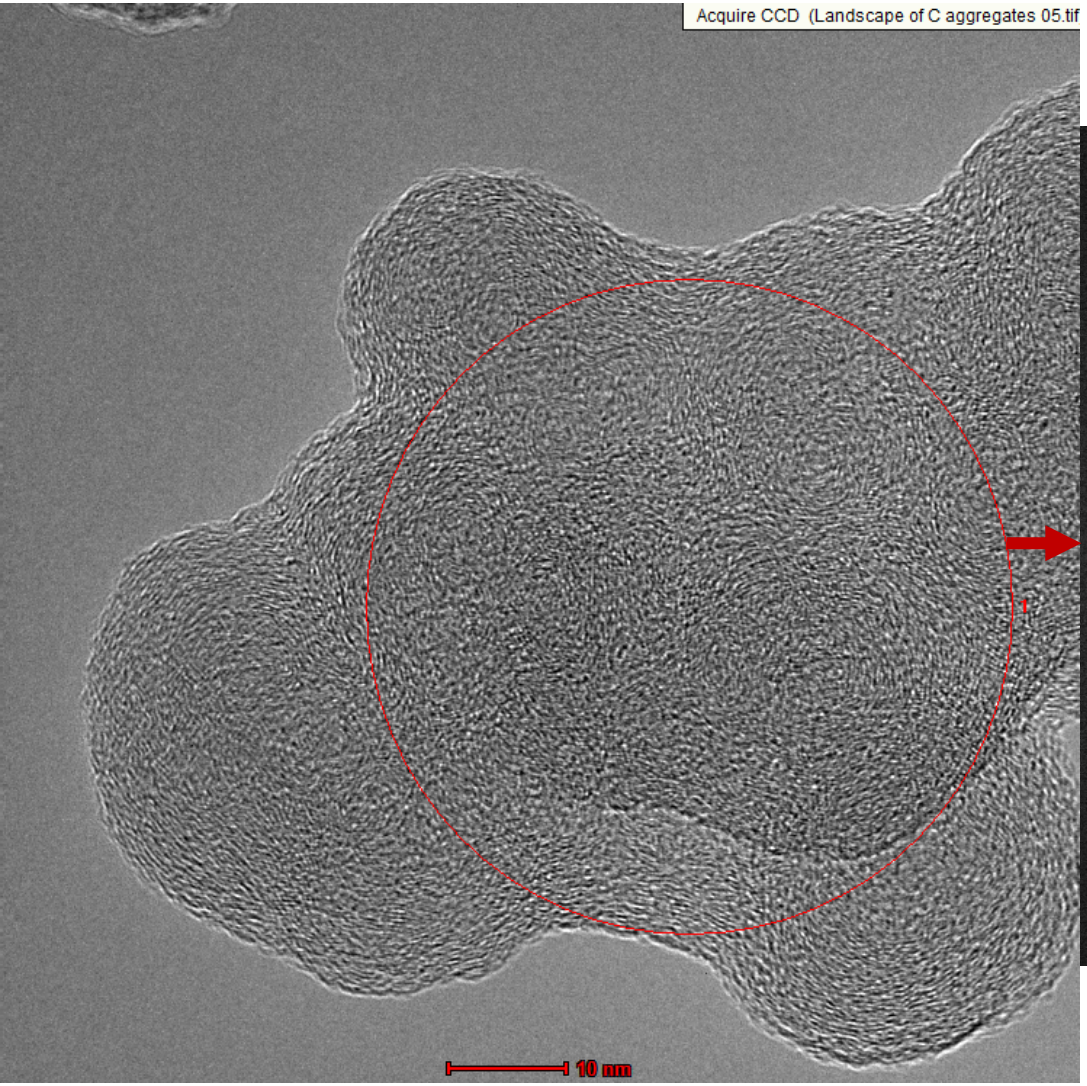

Pristine Graphite

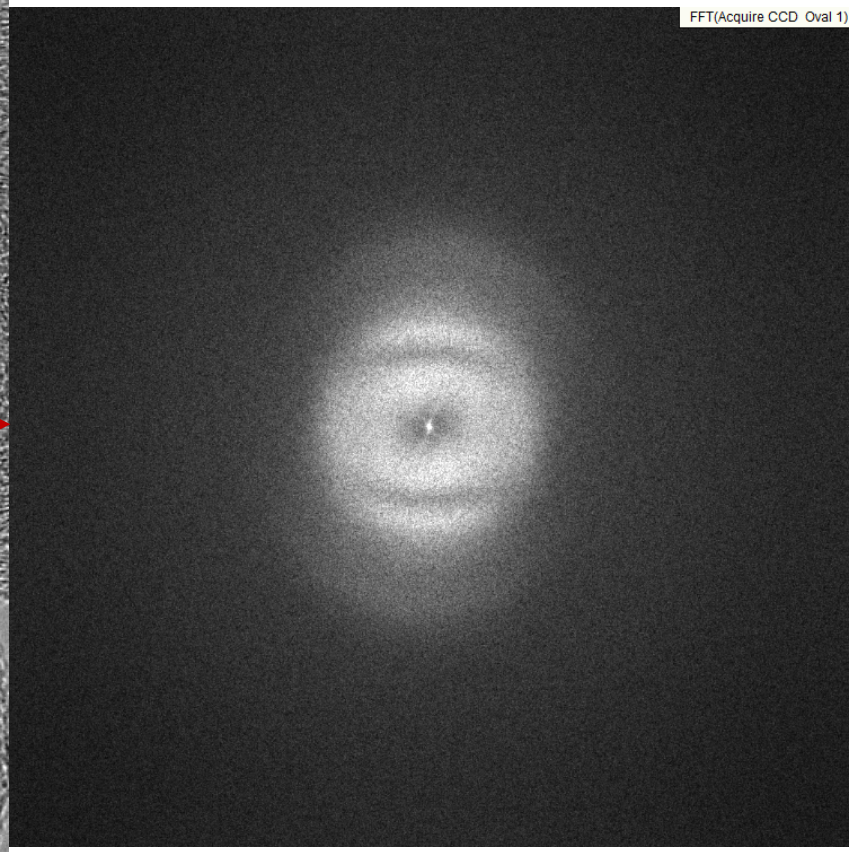


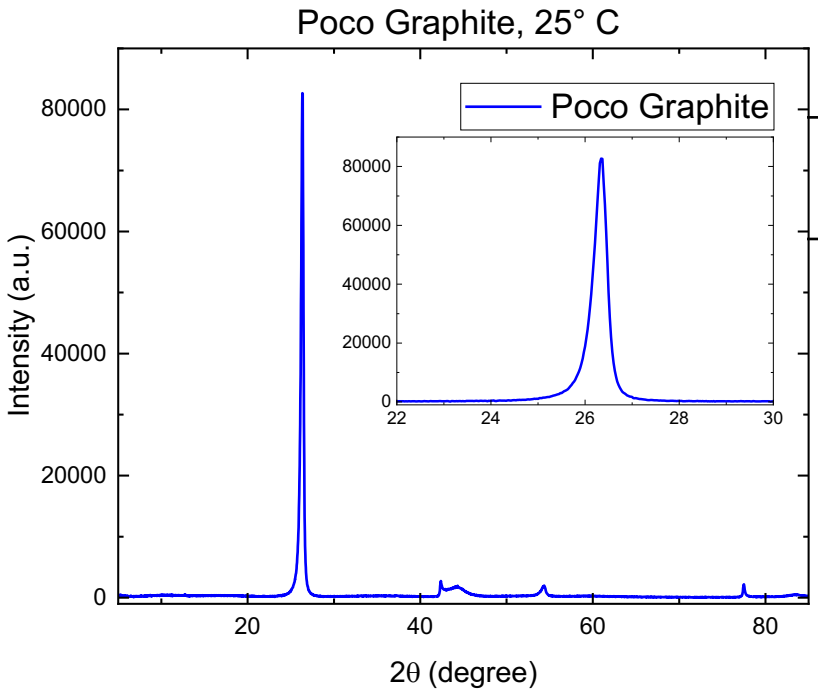

TCD 10% SNG 1,000 ℃ – Gasification $CO_2$: 950 ℃



# HRTEM Image and SAED of TCD Carbon under Joule-Based Heating



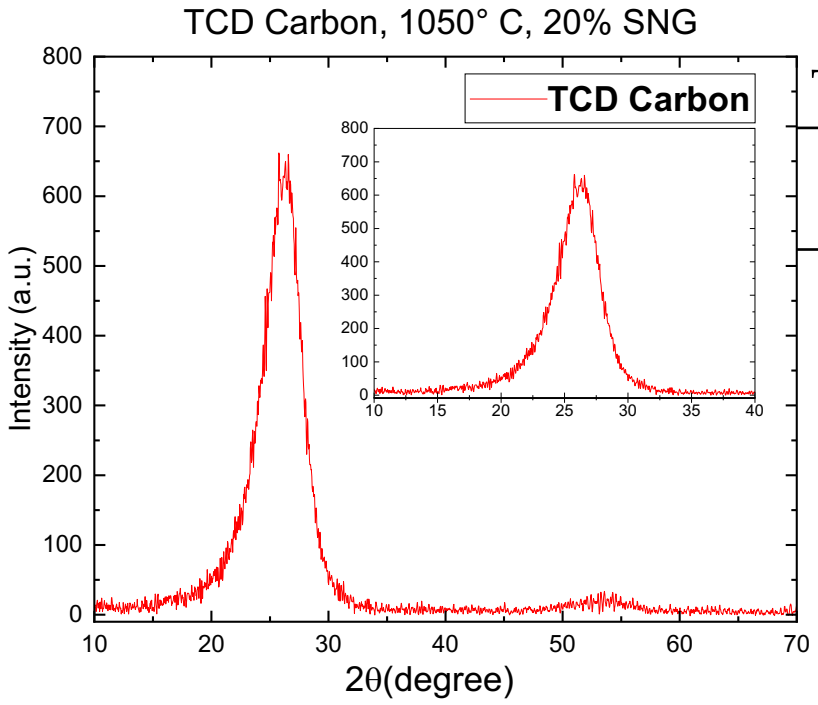






## Poco Graphite, 25° C

| Planes | d (Å) | Angle (2ɵ) | La (Å) | Lc (Å) |
|---|---|---|---|---|
| 002 | 3.378 | 26.36 | | 218.6 |
| 100 | 2.130 | 42.40 | 967.4 | |
| 110 | 1.230 | 77.55 | 741.1 | |

Furnace




## TCD Carbon (no EF), 1050° C, 20% SNG

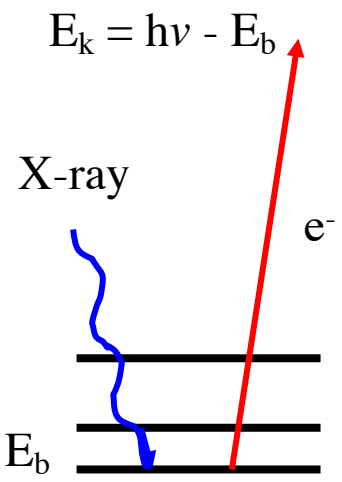
| Planes | d (Å) | Angle (2ɵ) | La (Å) | Lc (Å) |
|---|---|---|---|---|
| 002 | 3.3701 | 26.43 | | 20.7 |

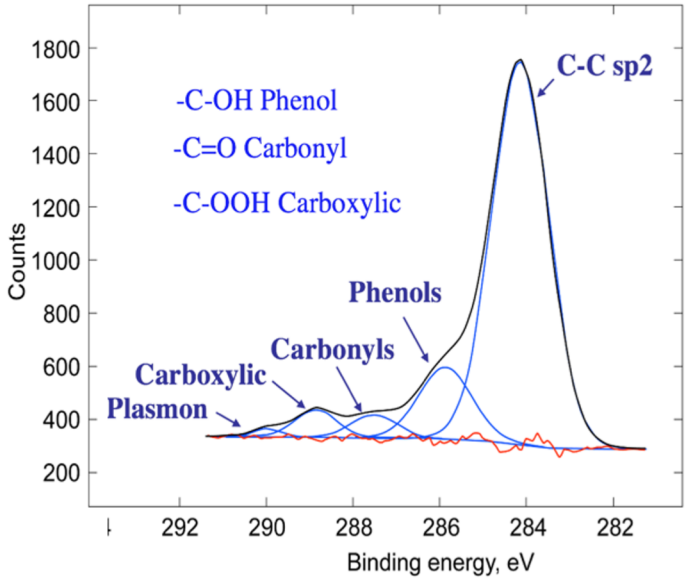
# Active Sites

- XPS has 3 key advantages for active site determination when coupled with chemisorption, compared to TPD – the more commonly used technique.

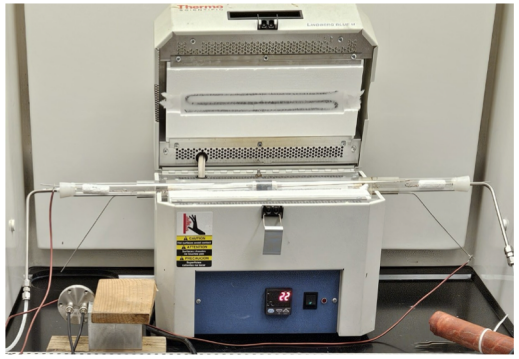
- Quantitative for oxygen content (at.%)
- Better sensitivity (~ 0.1%)
- Directly measures chemisorbed oxygen rather than derivative reaction products (CO and $CO_2$)

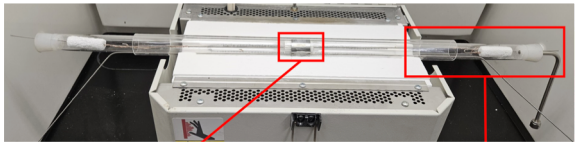
- Differentiates oxygen groups, which otherwise can be scrambled by interconversion during the high temperature ramp used in TPD.



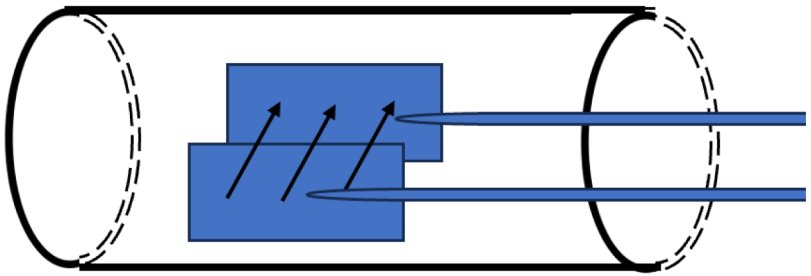



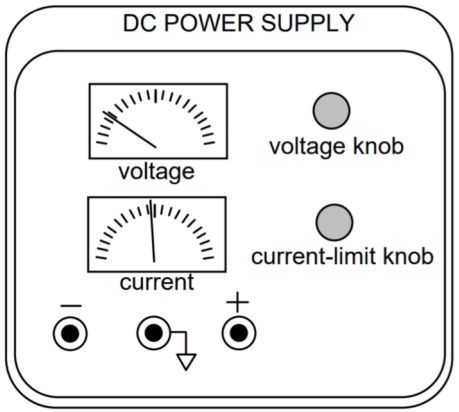
# High Voltage E-field Configurations

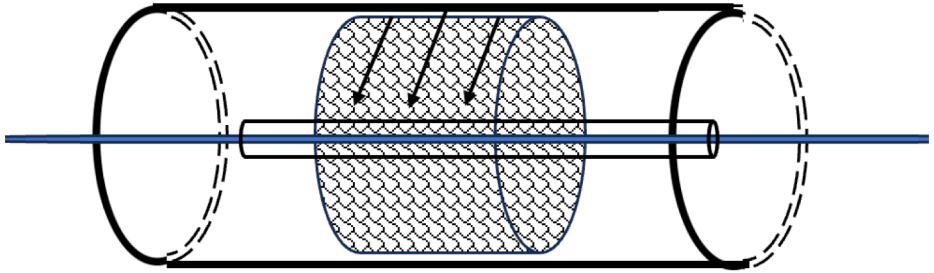


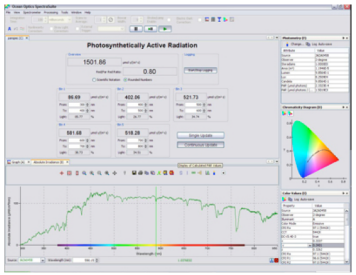


$E = V/d$

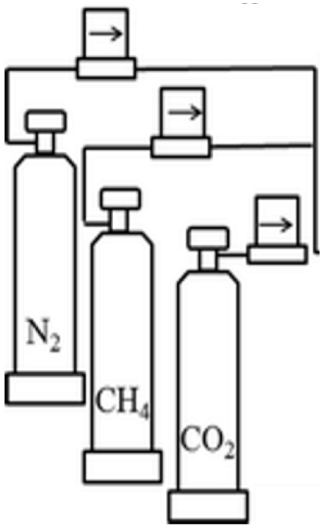






$E = V/r \ln(a/b)$



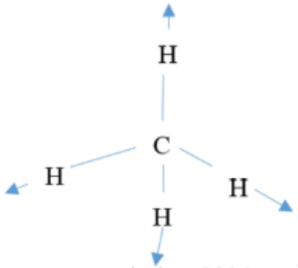
Radial and parallel field configurations

# FTIR Gas Analysis

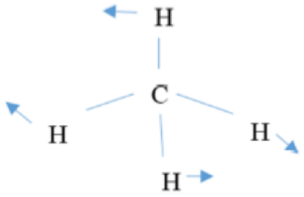
CH4 45%, 22.5%, 11.25%, 5.625%, 2.8125%, 1.40625% Balance: Ar

**Symmetry: $T_d$ Symmetry Number σ = 12**

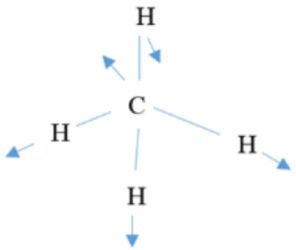
| Sym. Species | No | Approximate type of mode | Selected Freq. Value | Rating | Infrared Value | Phase | Raman Value | Phase |
|---|---|---|---|---|---|---|---|---|
| $a_1$ | 1 | Sym str | 2917 | A | ia | | 2917.0 | gas |
| e | 2 | Deg deform | 1534 | A | 1533 | ia gas | 1533.6 | |
| $f_2$ | 3 | Deg str | 3019 | A | 3018.9 | gas | 3019.5 | |
| $f_2$ | 4 | Deg deform | 1306 | C | 1306.2 | gas | | |



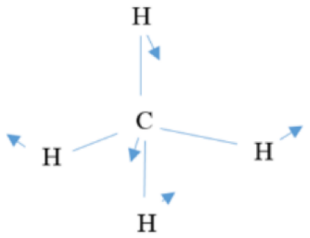

$\nu_1$ ($A_1$) at 2914 $cm^{-1}$



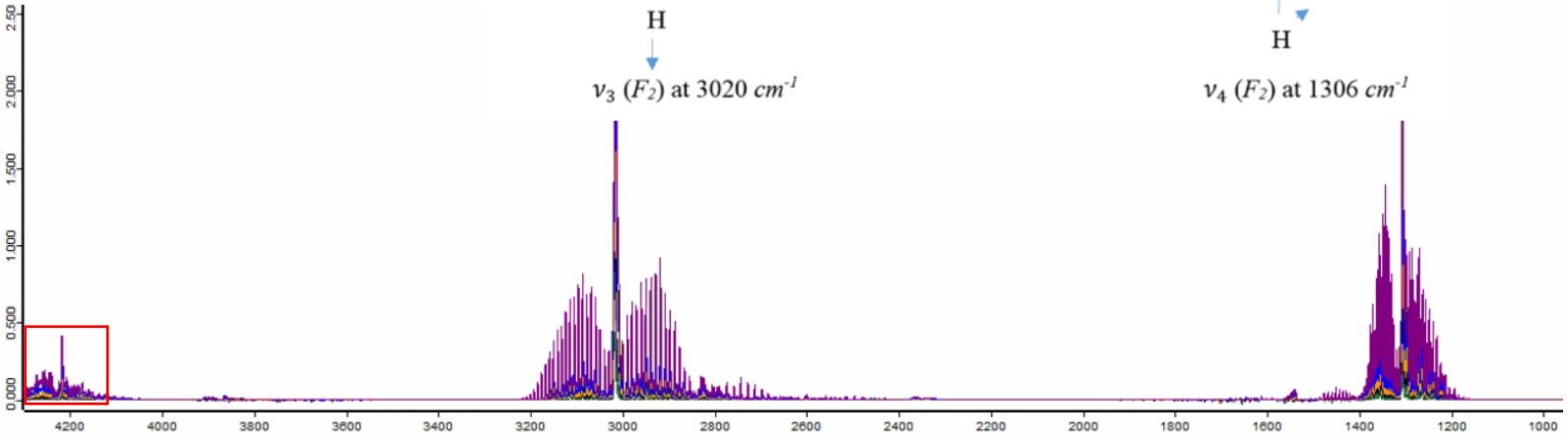

$\nu_2$ ($E$) at 1526 $cm^{-1}$




$\nu_3$ ($F_2$) at 3020 $cm^{-1}$

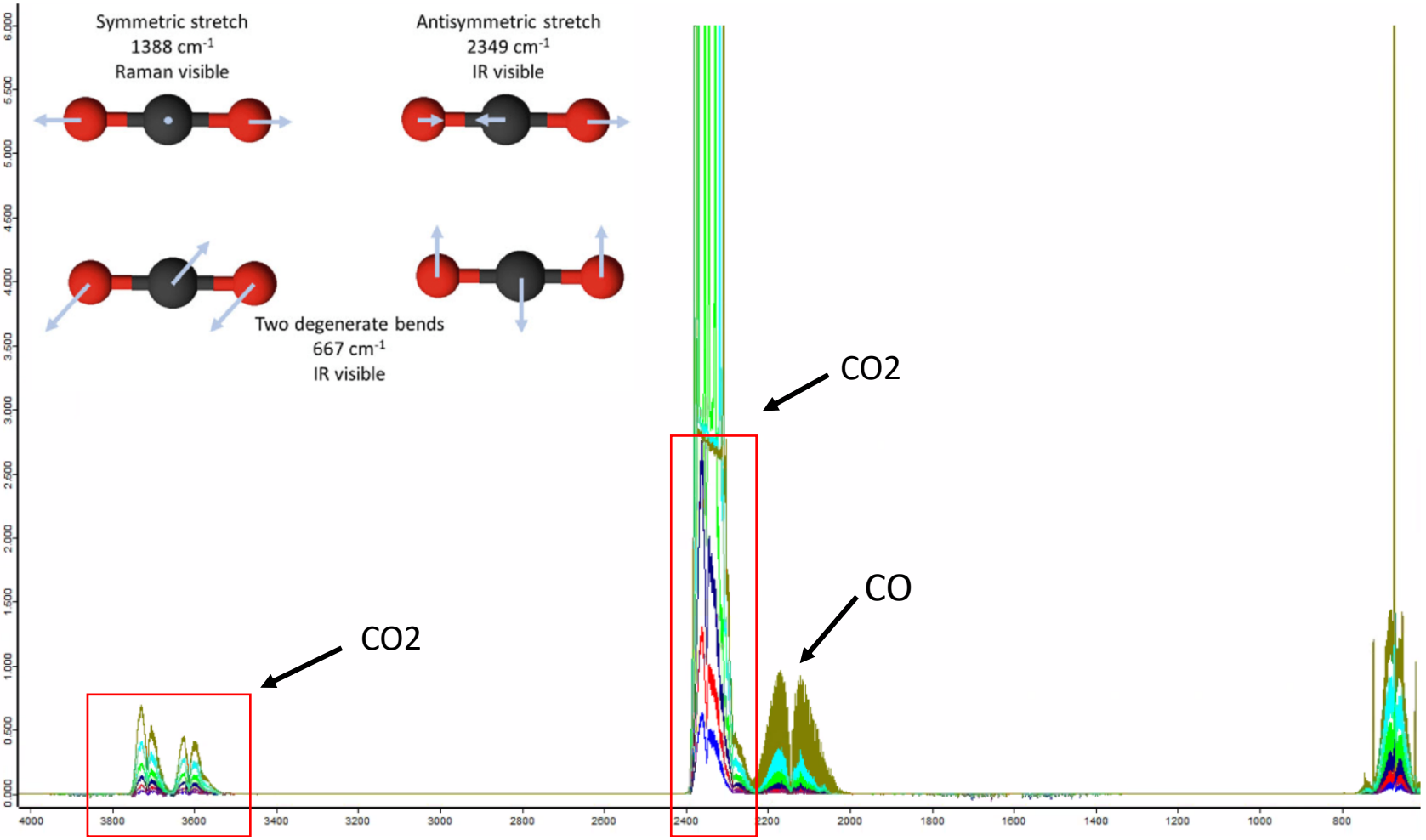



$\nu_4$ ($F_2$) at 1306 $cm^{-1}$



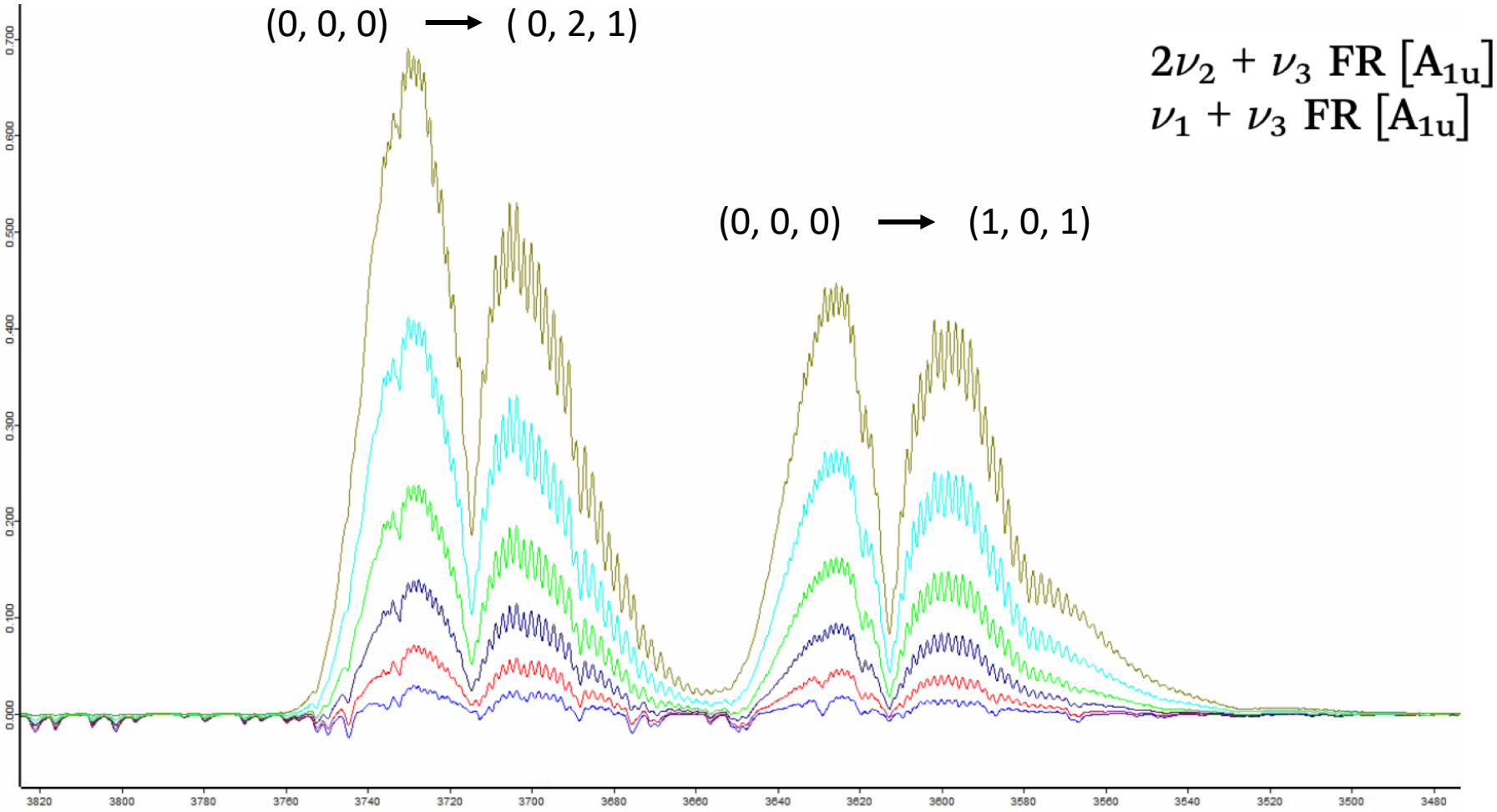
# FTIR Gas Analysis

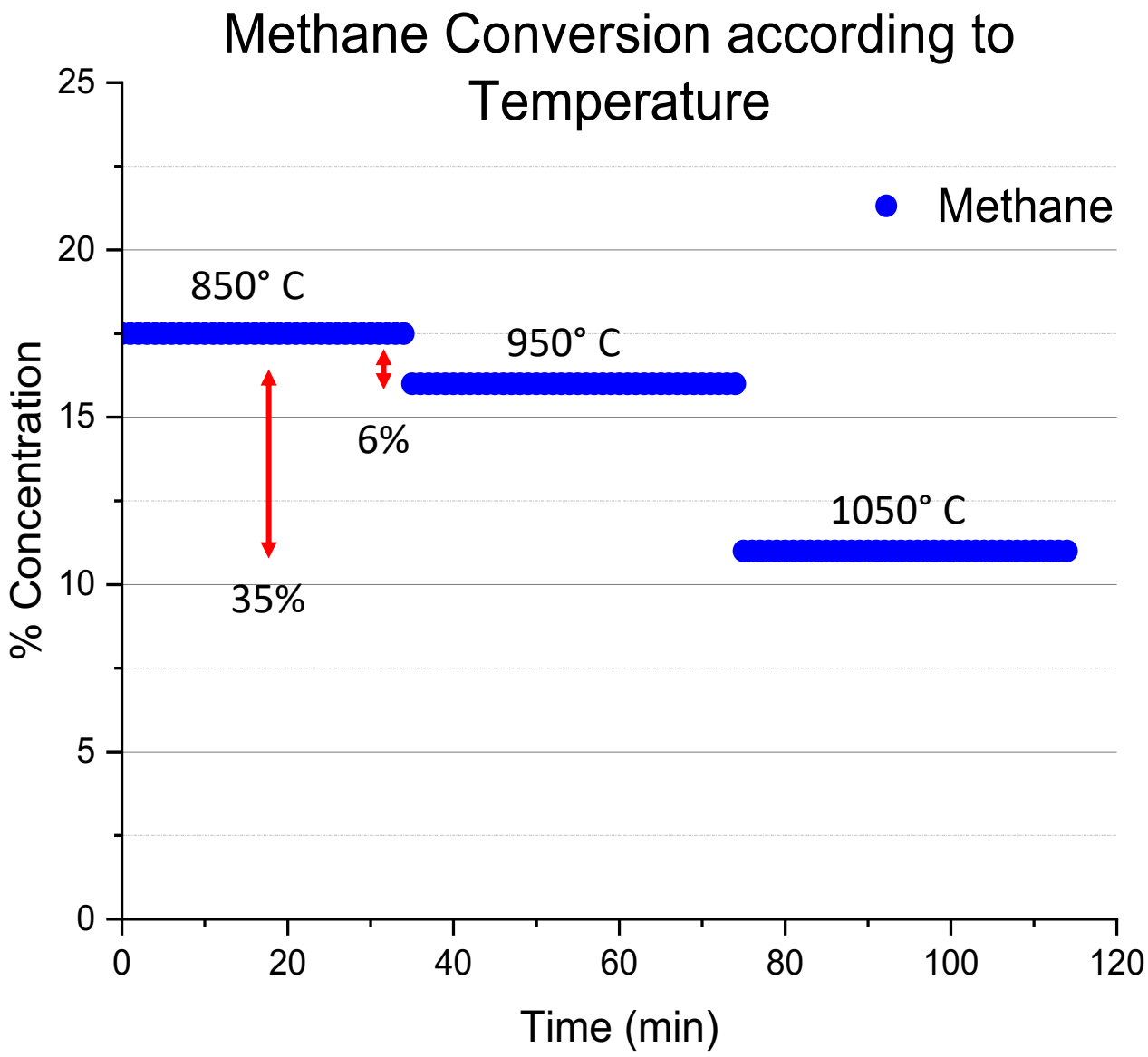
CO2 & CO: 45%, 22.5%, 11.25%, 5.625%, 2.8125%, 1.40625% Balance: Ar



# FTIR Gas Analysis

CO2 & CO: 45%, 22.5%, 11.25%, 5.625%, 2.8125%, 1.40625% Balance: Ar

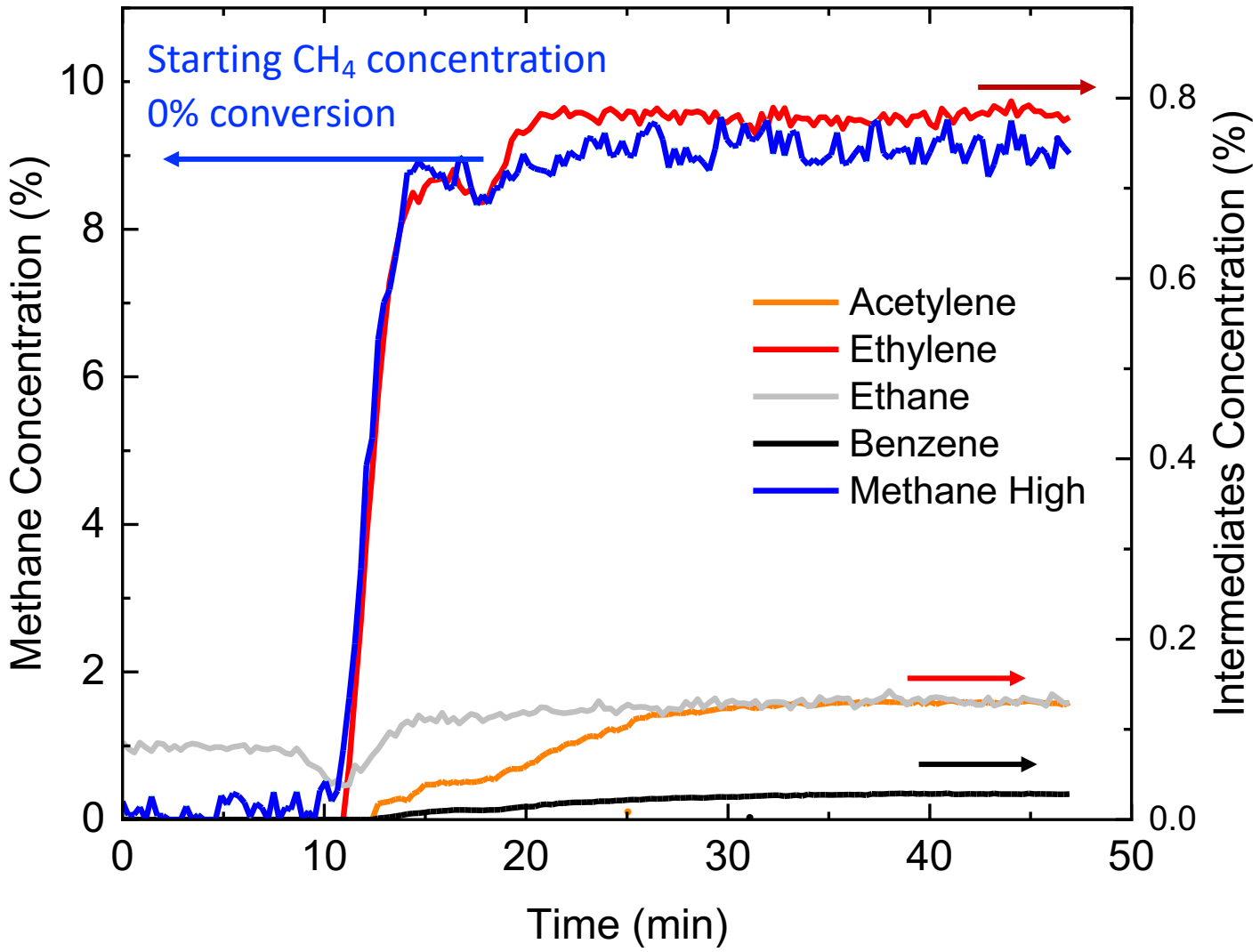




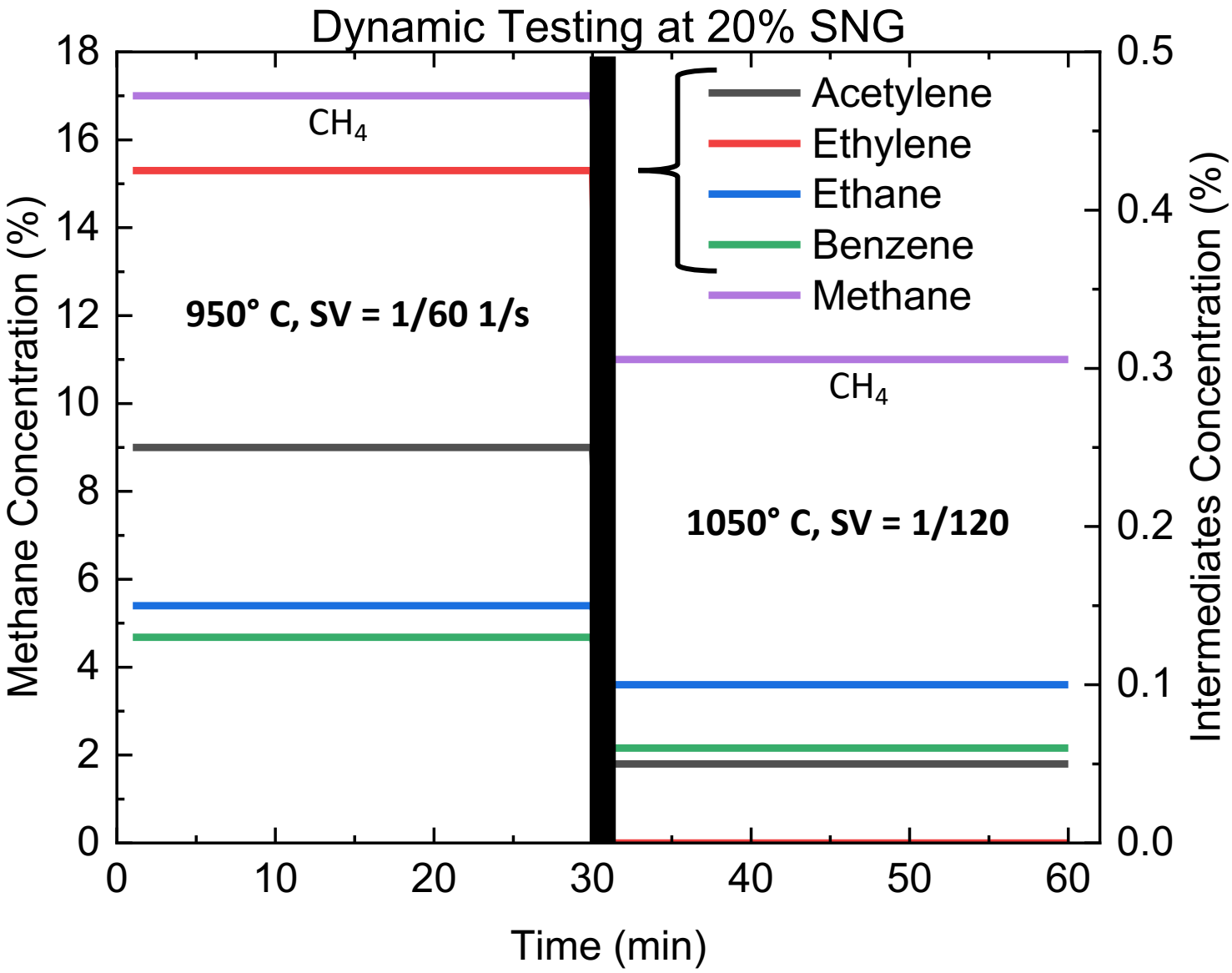

- Constituents of SNG cylinder:
  - 85% methane
  - 10% ethane
  - 5% propane
- With a 20% SNG dilution, Unreacted methane
- (or zero conversion) is ~17%
- **Methane conversion at various temperatures**:
  - 850° C = ~0%
  - 950° C = ~6%
  - 1050° C = ~35%

$E_a$ = 247 kJ/mole

# Natural Gas Component Specific TCD

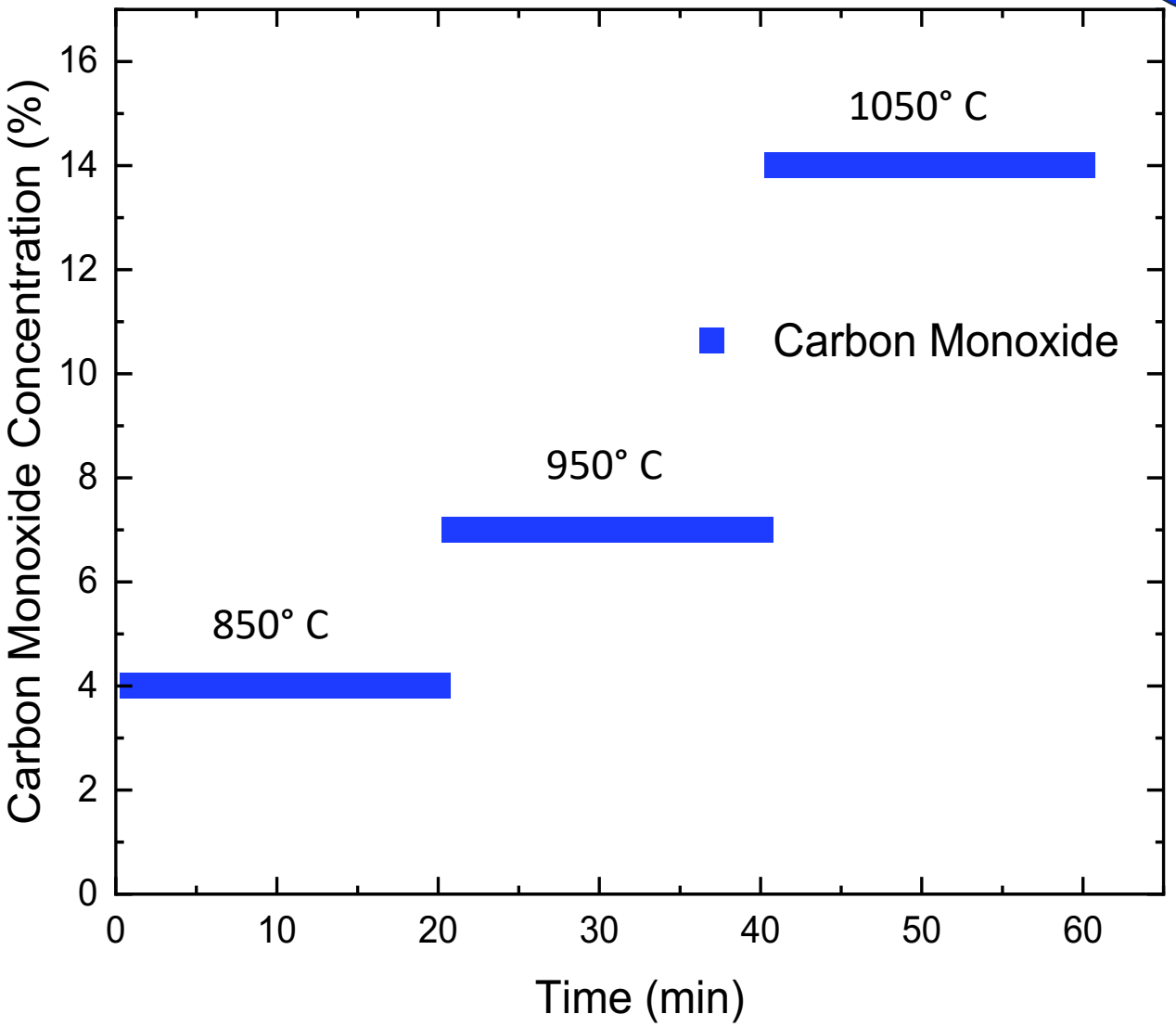


# Temperature and Space Velocity Comparisons



## Gasification by 50% $CO_2$ at 850, 950 and 1,050 ℃

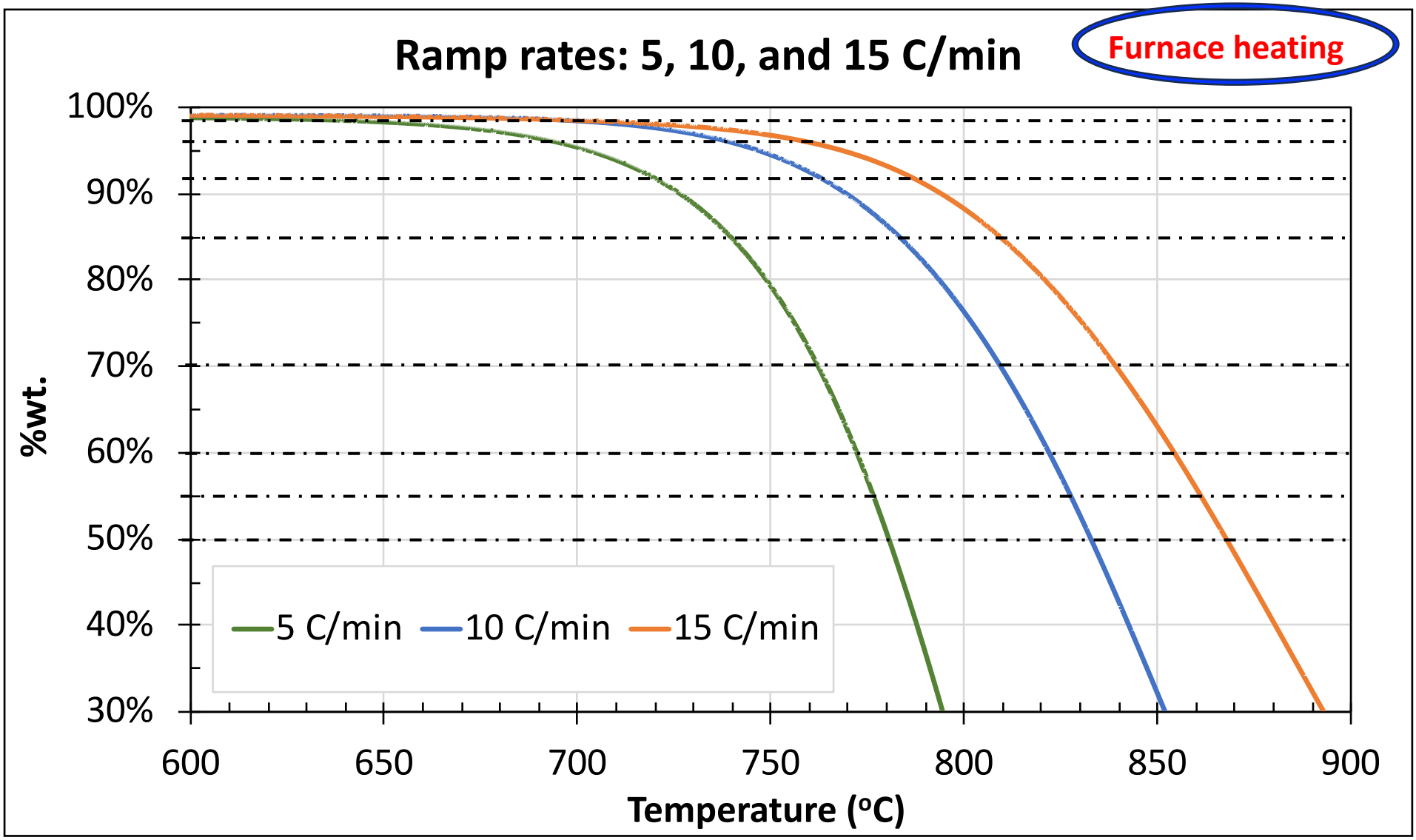
Joule heating




By Arrhenius analysis, $E_a \approx 80$ kJ/mole.

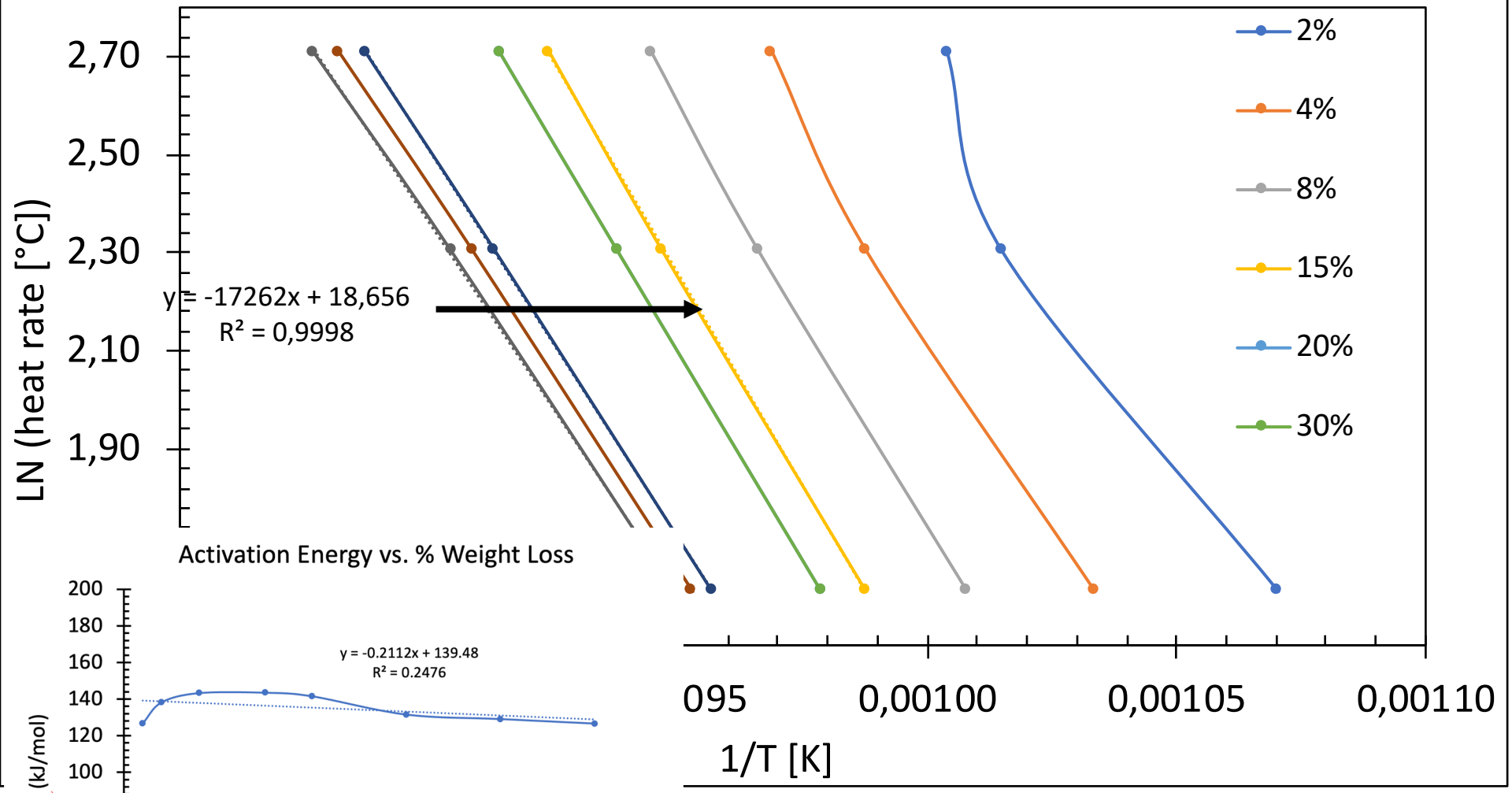
$C + CO_2 \rightarrow 2\,CO$

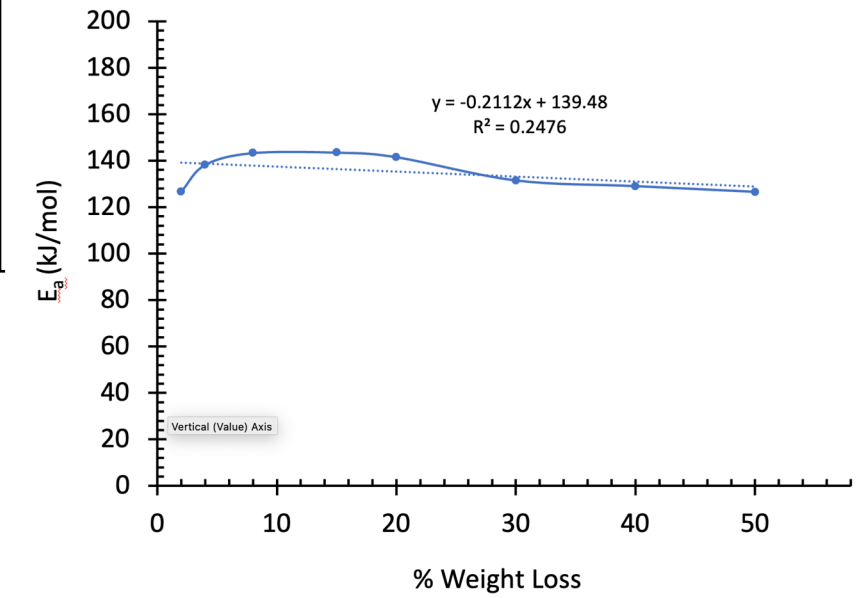
# Comparative Gasification Kinetic Analysis by $CO_2$




Ramp rate compared at iso-conversional levels.

# Carbon TGA Gasification Kinetics




$E_a$ = 143.5 kJ/mol

Activation energy decrease by ~ 2-fold under Joule based heating versus thermal furnace.

# Experimental Summary

### High voltage E-field Configuration

1. Methane decomposition kinetics and activation energy analysis.
2. Component selective TCD wherein only C2 and C3 components undergo TCD while methane remains unchanged in concentration.

### Joule based Heating

1. Structural analysis by Raman spectroscopy of gasified graphite under Joule based heating with reference comparison to furnace heating at 1,000 ℃ under 50% $CO_2$ in inert carrier.
2. Structural analysis by Raman spectroscopy of TCD carbon using synthetic natural gas (SNG) with comparison to partial gasification of the same, by $CO_2$.
3. Gasification kinetic analysis by $CO_2$, determining the activation energy for the Boudouard reaction producing CO. *Preliminary analysis indicates a significant reduction of the activation energy by Joule heating relative to furnace heating via TGA.*
4. Comparative XRD analysis for TCD carbon relative to graphite.

# Next steps

- TCD and regeneration reaction kinetics (gasification – $H_2O$ and reverse Boudouard – $CO_2$ will be evaluated as a function of applied E-field strength, and polarity.

- Active sites and kinetic dependence upon reactive gases (methane, natural gas, $CO_2$, $H_2O$) mapping will continue.

- The nano- and micro-structure of TCD produced carbons wil be further analyzed for E-field differences.

- Further measurements under Joule based heating and high field configurations – supplemented by thermal transfer.

# Connections Between Experiments and Simulations

- Activation energy and kinetic metrics will test the hypothesis of the E-field changing the gasification and TCD reaction mechanisms.

- Simulations will provide feedback to experiments for TCD/gasification conditions for E-field effects upon carbon nanostructure / active sites.

- Simulations will explore conditions whereby activation energies and kinetics are changed in TCD/regeneration by an applied E-field.

# Computational Approach: ReaxFF Atomistic Simulations

- ReaxFF combines a bond order/bond distance relationship with a polarizable charge description along with bond-order dependent 3- and 4-body interactions.

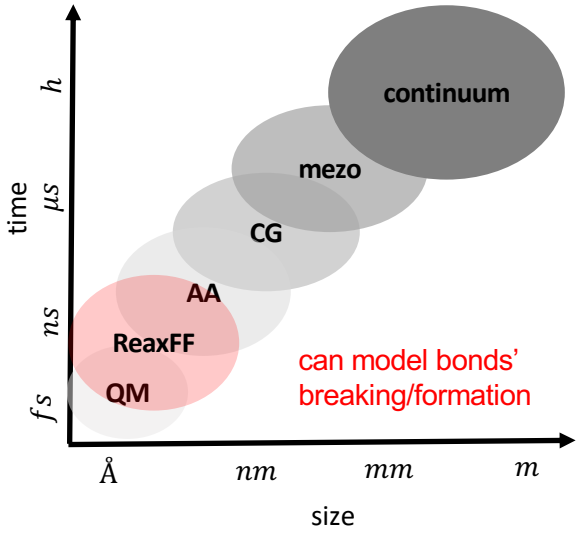
- Accurately reproduce reaction energies and barriers, by comparison to DFT-calculations.

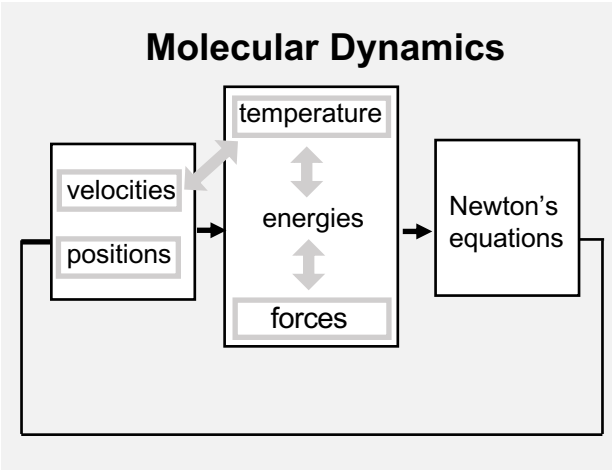
- The force field description includes bonded and non-bonded interactions.

- Of particular relevance is the polarizable charge description in ReaxFF.

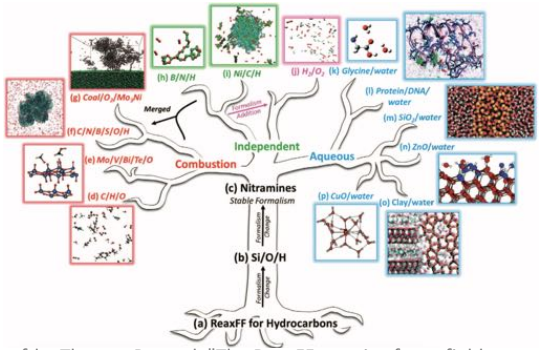
# ReaxFF/eReaxFF Molecular Dynamics

Molecular Dynamics: deterministic method to model atoms' interactions.



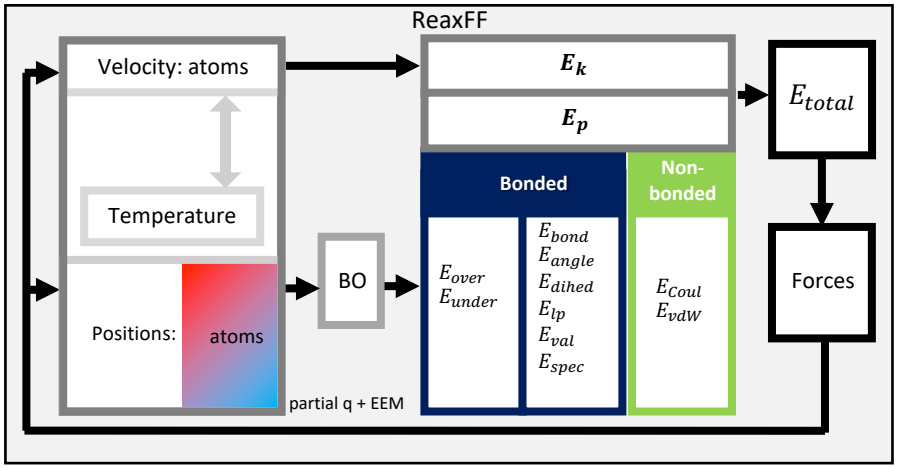



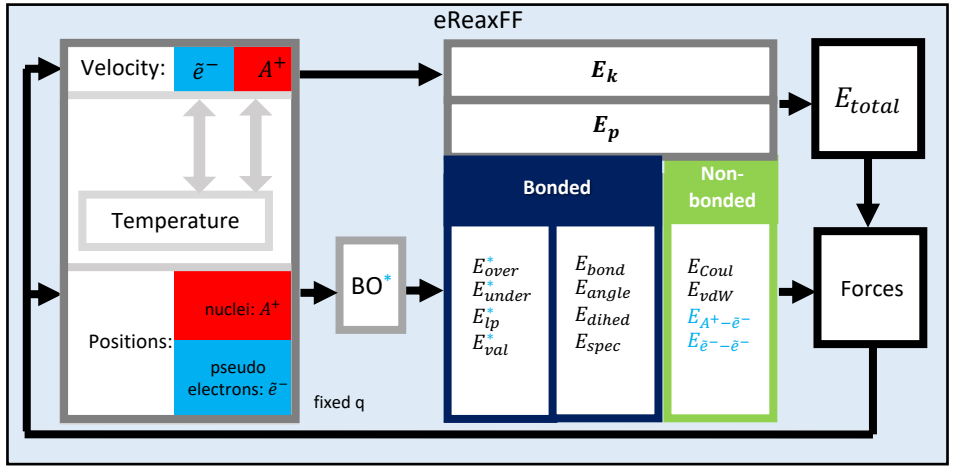

ReaxFF development tree




Senftle, Thomas P., et al. "The ReaxFF reactive force-field: development, applications and future directions." *npj Computational Materials* 2 (2016): 15011

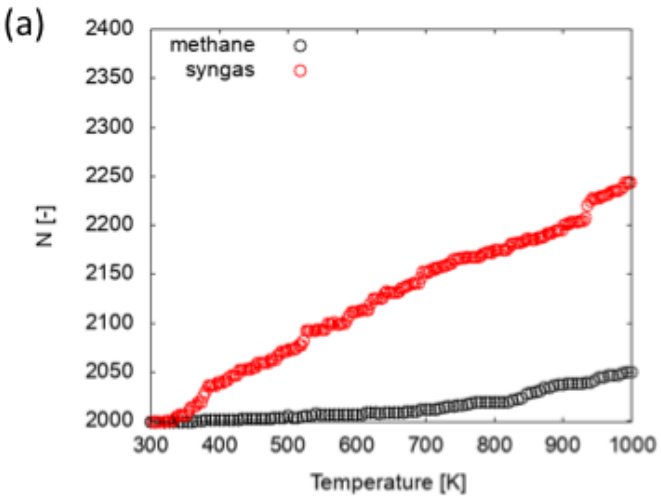
ReaxFF is an example of the bond order method.
Bond order between two atoms depends on: distance between them and on the local environment.

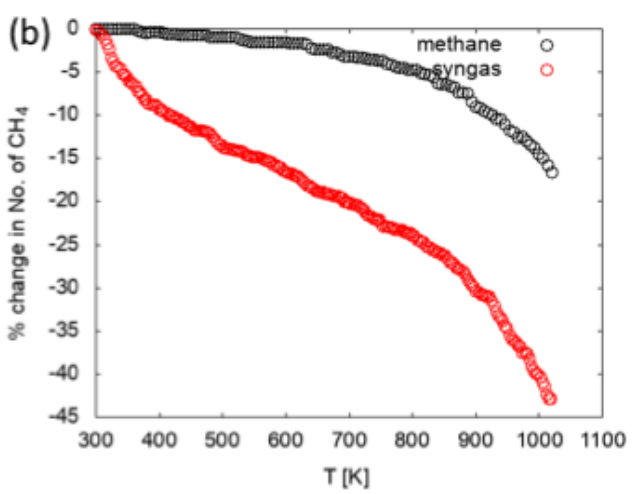


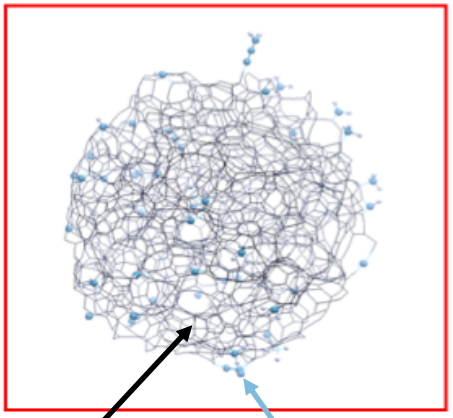
# ReaxFF Activation Energies

The same trend for activation energy difference for methane vs SNG (methane/ethane/propane with 85/10/5ratio) as in experiment ($E_a^{methane} > E_a^{SNG}$).



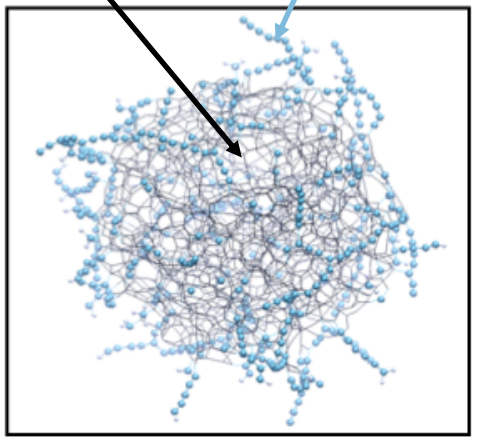



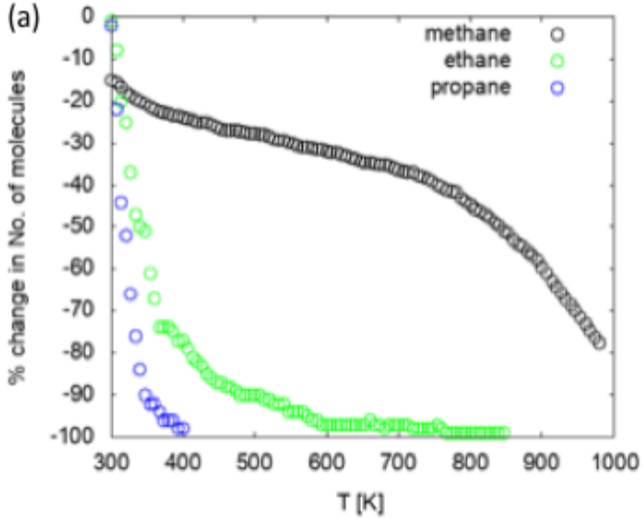

Final structures

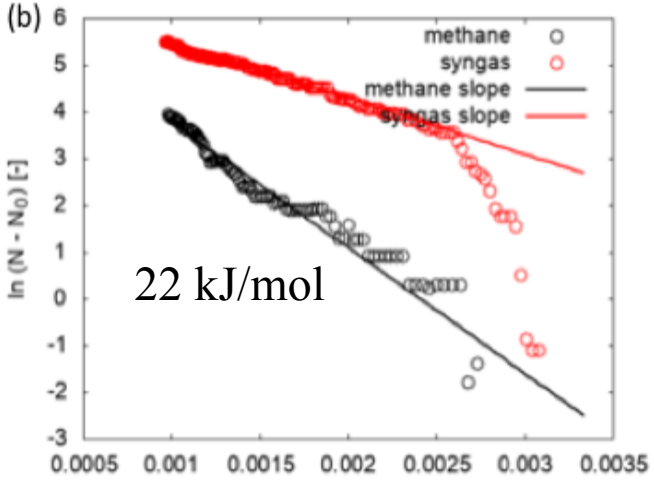


initial carbon nanostructure

gas-originated carbon





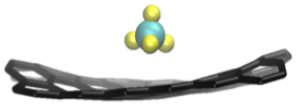



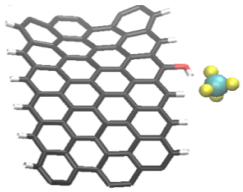

$E_a^{methane} = 22\ ^{kJ}/_{mol}$ $E_a^{SNG} = 10\ ^{kJ}/_{mol}$

[1]

# ReaxFF vs DFT data

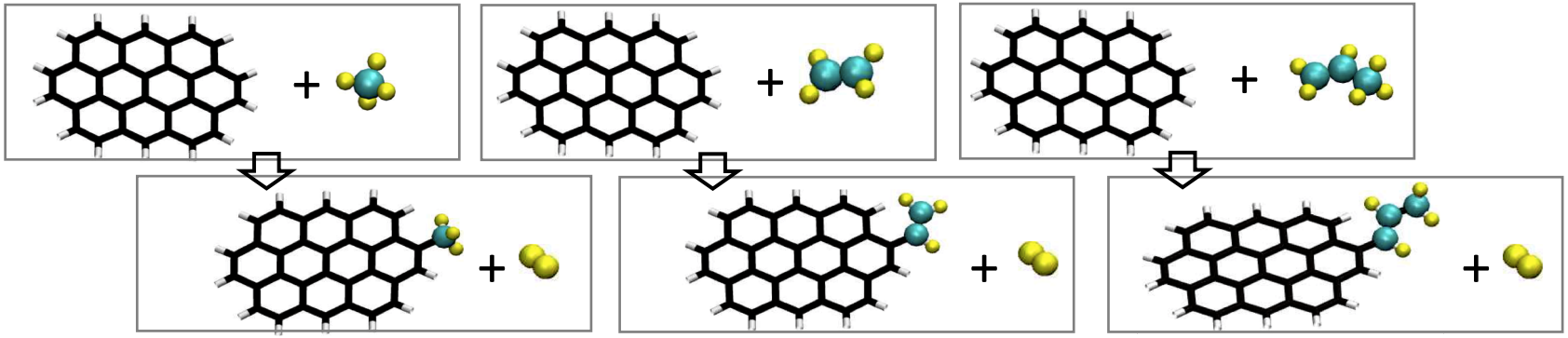
Good agreement for the binding energies calculated based on the ReaxFF and DFT.





| ReaxFF | **5.7 kcal/mol** | **1.3 kcal/mol** | **2 kcal/mol** |
|---|---|---|---|
| DFT | 4.8 kcal/mol [1]<br>5.3 kcal/mol [2] | 0.96-1.9 kcal/mol[3] | 5-16 kcal/mol [3] |

Some of the formation energies might be modify to closer reproduce DFT.



| ReaxFF | **3.9 kcal/mol** | **1.25kcal/mol** | **-1.56 kcal/mol** |
|---|---|---|---|
| DFT | -13.4 kcal/mol | -4.6 kcal/mol | -3.9 kcal/mol |

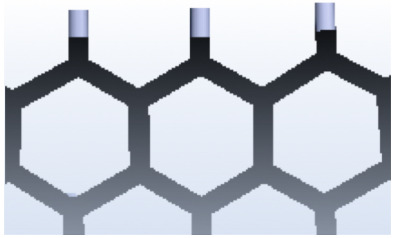
[1] Koskinen, P et al. 2008, Self-Passivating Edge Reconstructions of Graphene, Physical Review Letters 101, 115502.
[2] Anithaa, V.S. and Vijayakumar, S., 2018. Effect of side chain edge functionalization in pristine and defected graphene-DFT study. *Computational and Theoretical Chemistry*, *1135*, pp.34-47.

# eReaxFF vs DFT data

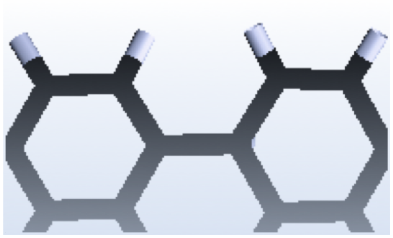
A good agreement for the edge chemistry of graphene for the eReaxFF and DFT [1] data.

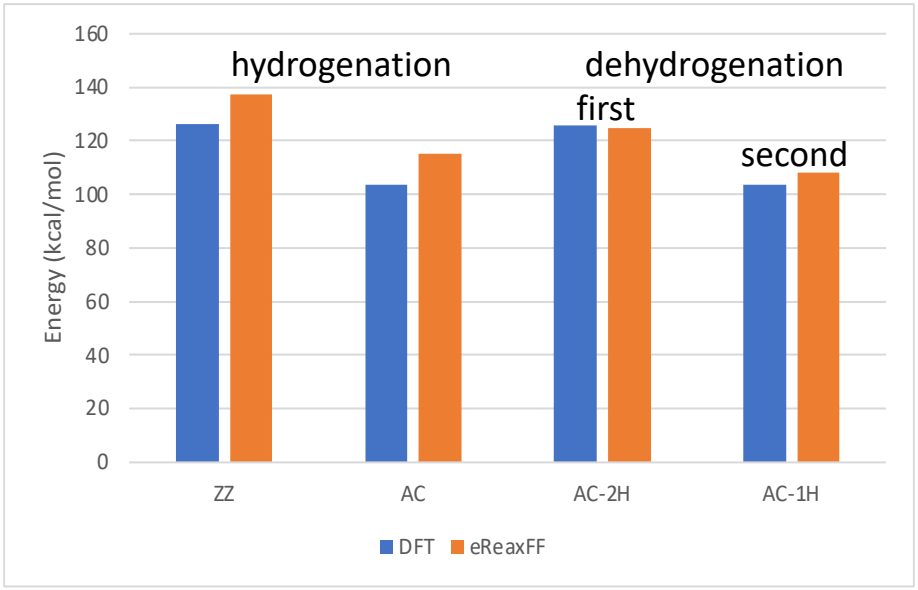
graphene edge types

Zigzag (ZZ)



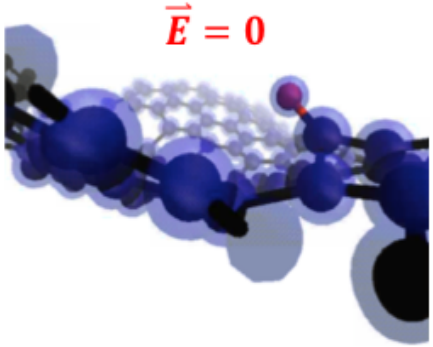
Armchair (AC)

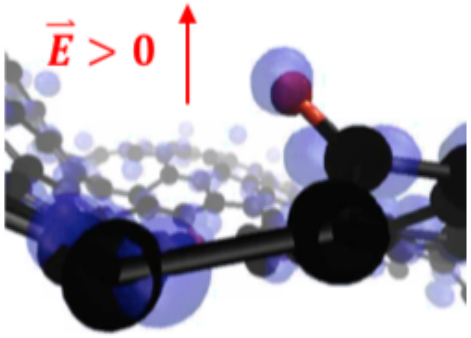


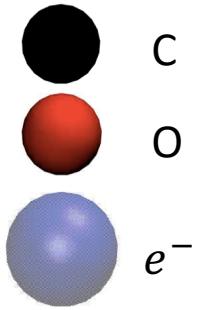



[1] Koskinen, P et al. 2008, Self-Passivating Edge Reconstructions of Graphene, Physical Review Letters 101, 115502

It is possible to model local polarization of the functional groups in a presence of external electric field.

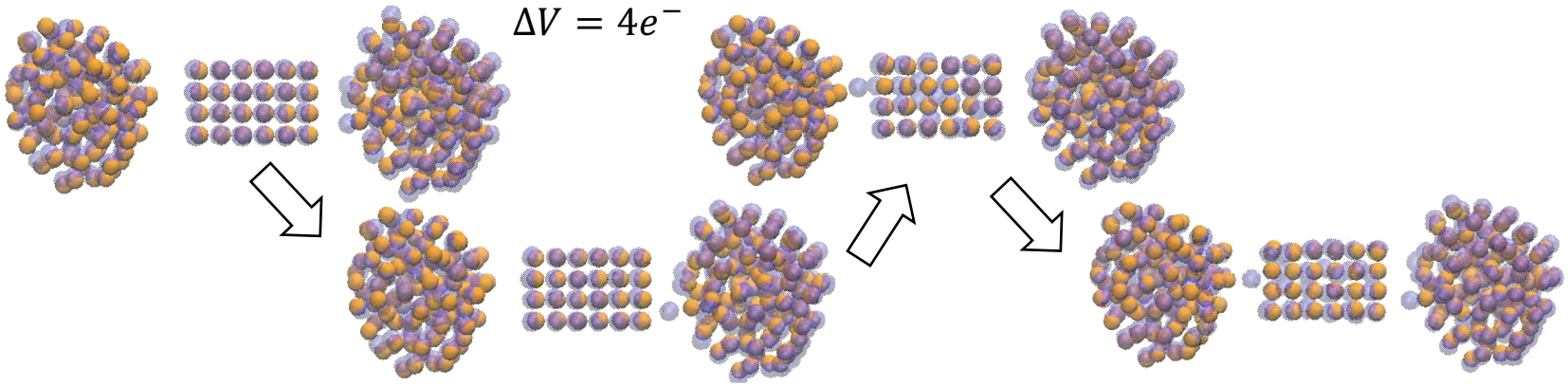


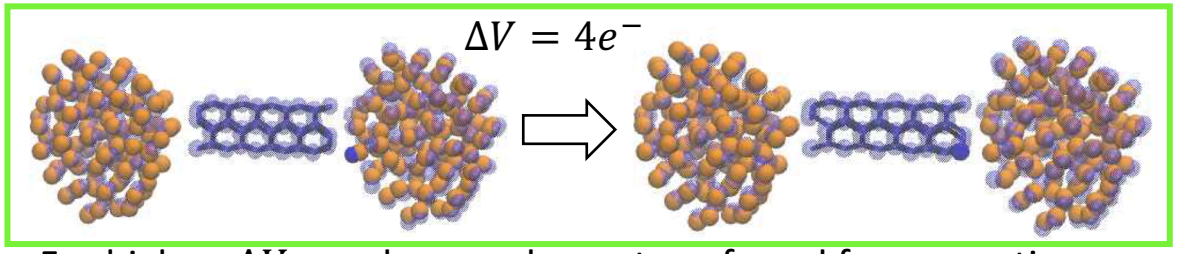



# eReaxFF development towards Joule heating modelling

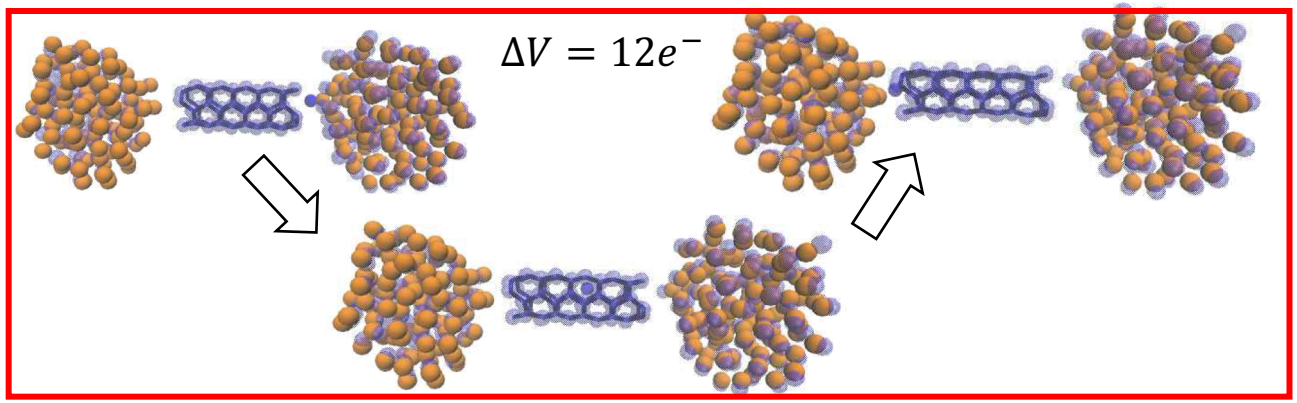
We observe multiple charge transfer between copper electrodes for the copper conducting element even for small $\Delta V$.



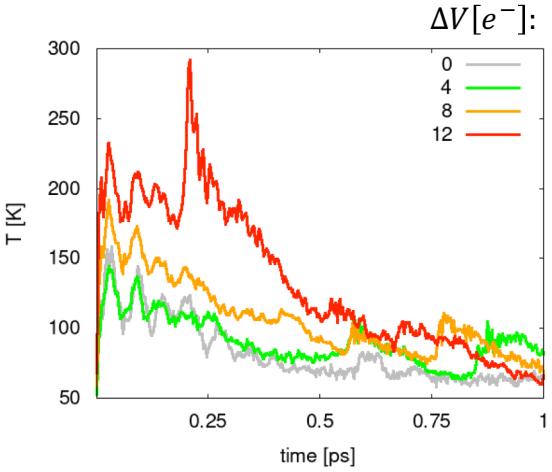

We observe only one charge transferred from copper electrode to carbon conducting element for small $\Delta V$, which localizes at the edge of CNT.




For higher $\Delta V$ we observe charge transferred from negative copper electrode through CNT to positive one.

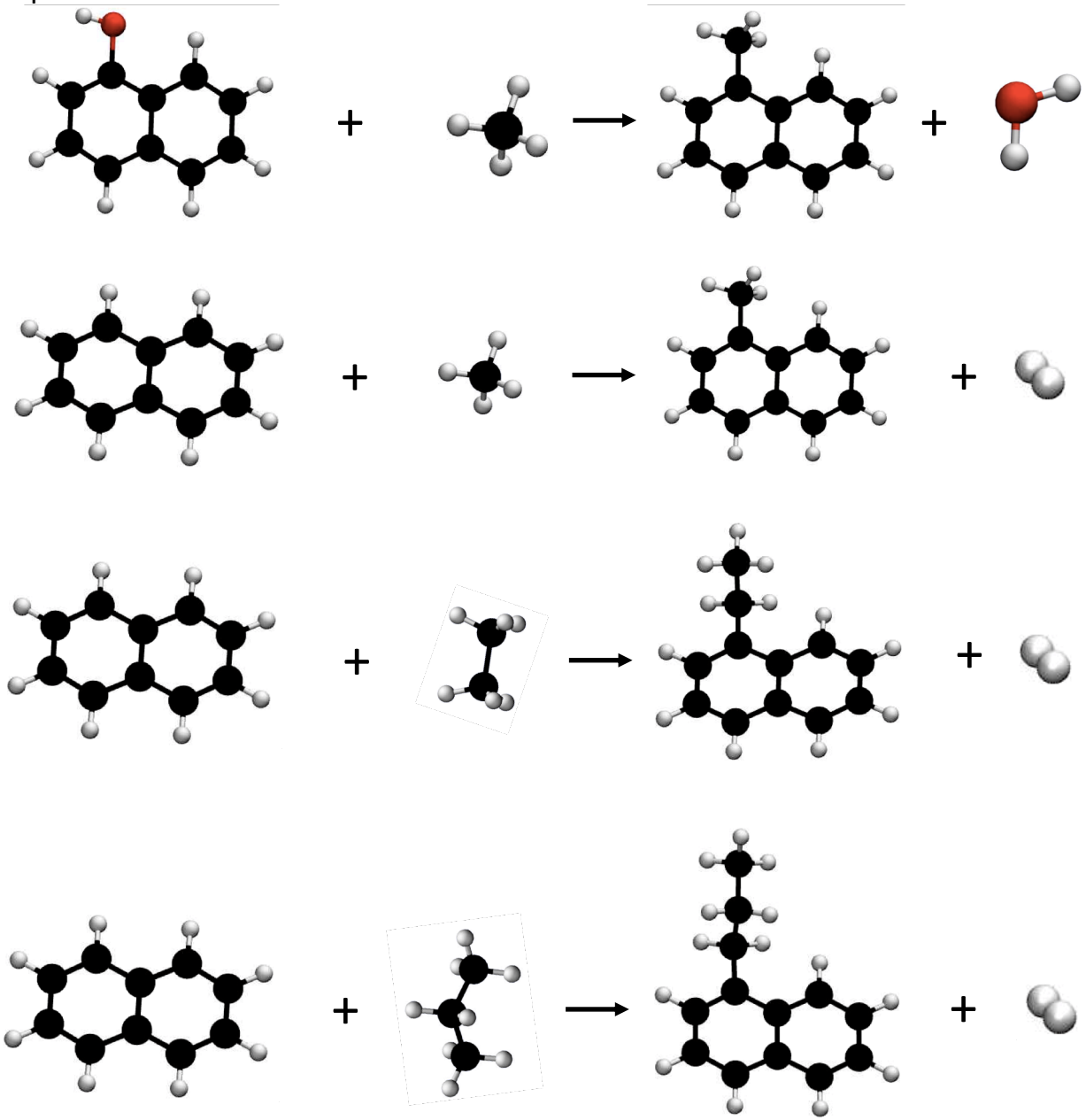



We observe a spike in the temperature profile due to charge transfer.



# ReaxFF vs eReaxFF vs DFT

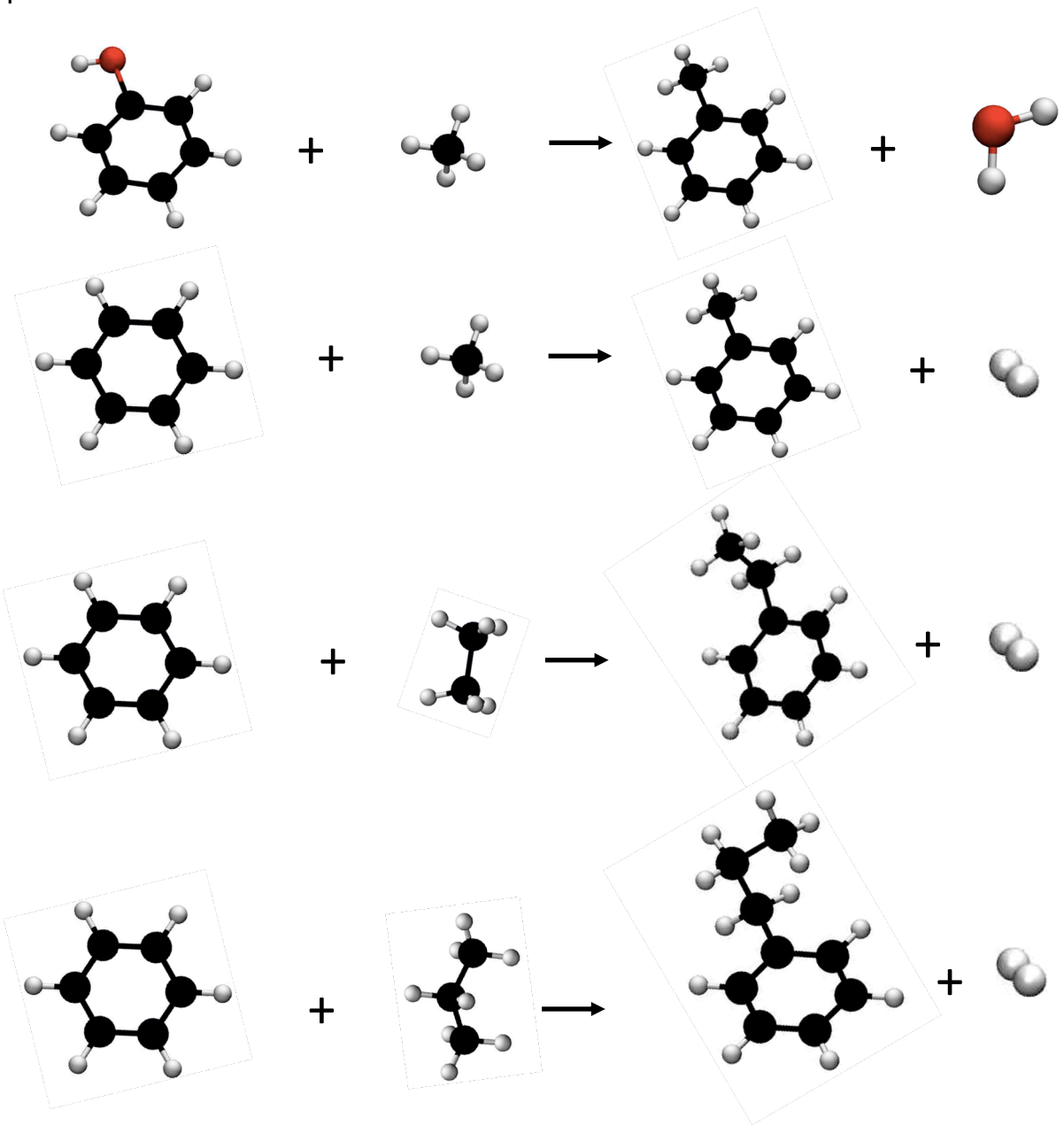
Some changes in the parameter set are still neededfor ReaxFF/eReaxFF closer reproduce DFT data.



| ReaxFF [kcal/mol] | eReaxFF [kcal/mol] | DFT [kcal/mol] |
|---|---|---|
| -5.19 | | -2.25 |
| 3.54 | 22.05 | 17.77 |
| -0.095 | 28.62 | 15.22 |
| 1.4 | 33.5 | 17.89 |

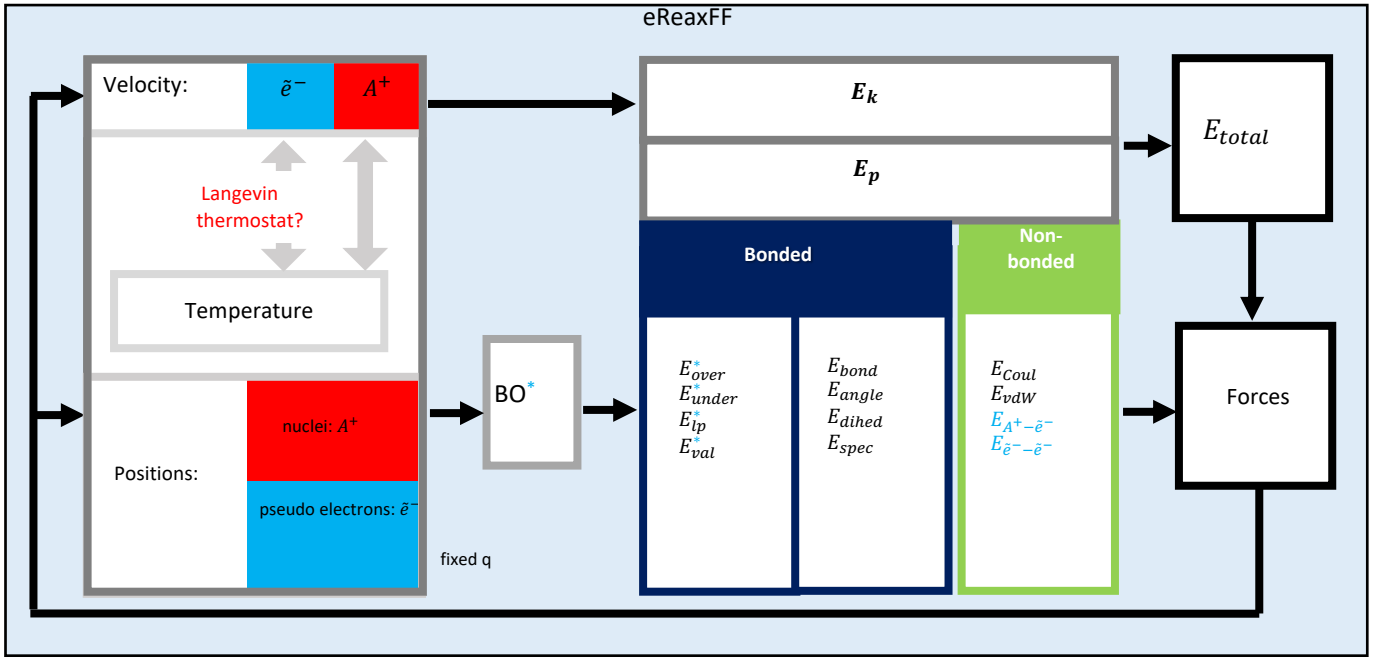
# ReaxFF vs eReaxFF vs DFT

Some changes in the parameter set are still neededfor ReaxFF/eReaxFF closer reproduce DFT data.



| ReaxFF [kcal/mol] | eReaxFF [kcal/mol] | DFT [kcal/mol] |
|---|---|---|
| -7.8 | | 2.68 |
| 3.03 | 21.56 | 17.04 |
| -0.27 | 28,44 | 29.83 |
| 1.98 | 32.92 | 16.77 |

# Challenges and Future Work




- To consider reactions with phenol/carbonyl/carboxylic groups;
- To compare the reaction rates for systems with/without E-field to identify a possible atomistic mechanism responsible for lowering the activation energies in the presence of E-field.

# Modeling and Simulation Conclusions

1) Tested the ReaxFF capability to identify a difference in the CH4 vs SNG activation energy;

2) Compared CH4 binding energies for current versions of eReaxFF and ReaxFF to the DFT data.

3) Demonstrated the eReaxFF capability to model electron cloud polarization in the presence of an external electric field.

4) Tested a possible difference in charge conductance characteristic for copper vs carbon-based material in correlation with local change in temperature.

# Success Criteria and Outcomes

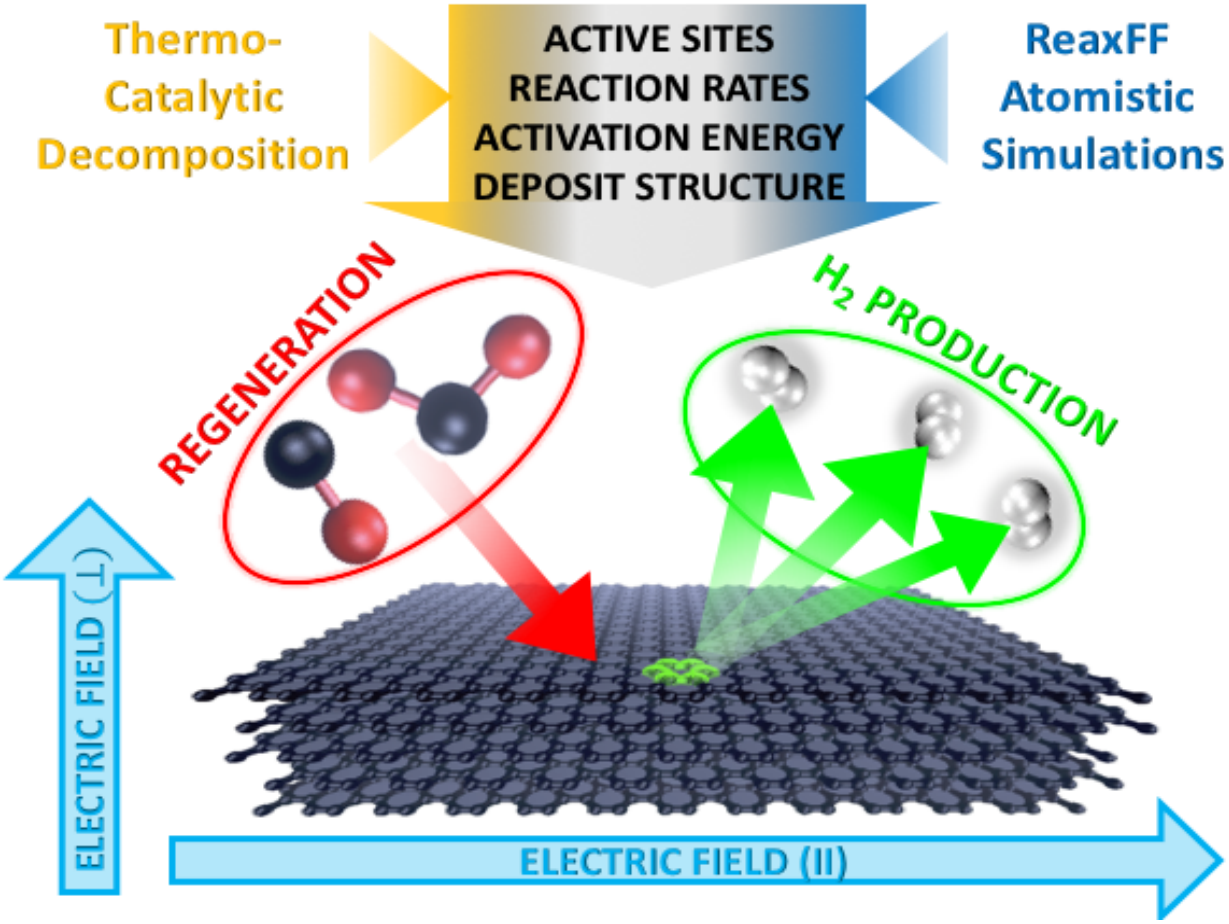
**The following questions are applicable to both TCD and (oxidative) regeneration, highlighting their reciprocal nature, and the underlying fundamental role of active sites and E-field enhancement mechanism of carbon surface reactions.**

1. **As baseline, how do active site number and rate vary with time during TCD and regeneration?**
2. **Can active site number and rate be controlled by an applied E-field the carbon nanostructure?**
3. **Can simulations predict and experiments validate conditions wherein regeneration is not needed, i.e., where active sites are (autocatalytically) re-created?**

**Project success criteria and outcomes will be answers to each of these research questions.**

**As overall outcome, measurement of active sites and predictions by simulations will provide mechanistic insights for carbon surface reactions relevant to both TCD and regeneration reactions. Beyond the relation between reaction rate and active sites, the primary question of whether the E-field affects active site number and/or type will be addressed for these carbon surface reactions.**

# Summary




*This study addresses potential changes in the reaction kinetics and mechanism for TCD and gasification reactions under an applied E-field.*

| **Project Timeline:** Task & Milestones† | **Assigned** | **Year 1 Quarter** | | | | **Year 2 Quarter** | | | | **Year 3 Quarter** | | | | **Year 4 Quarter** | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Task Name** | **Persons** | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Task 1.0 – Rev. Project Mgt. Plan | PI, Co-I | | | | | | | | | | | | | | | | |
| Task 2.0 TCD | PI, GS, AVD & MK | | | | | | | | | | | | | | | | |
| Milestone 1 | | | | | | | | | | | | | | | | | |
| Milestone 2 | | | | | | | | | | | | | | | | | |
| Milestone 3 | | | | | | | | | | | | | | | | | |
| Milestone 4 | | | | | | | | | | | | | | | | | |
| Milestone 5 | | | | | | | | | | | | | | | | | |
| Milestone 6 | | | | | | | | | | | | | | | | | |
| Milestone 7 | | | | | | | | | | | | | | | | | |
| Task 3.0 Regeneration with $CO_2$ | | | | | | | | | | | | | | | | | |
| Milestone 8 | | | | | | | | | | | | | | | | | |
| Milestone 9 | | | | | | | | | | | | | | | | | |
| Task 4.0 Gasification with $H_2O$ | | | | | | | | | | | | | | | | | |
| Milestone 10 | | | | | | | | | | | | | | | | | |
| Milestone 11 | | | | | | | | | | | | | | | | | |
| Task 5.0 – Final Report | | | | | | | | | | | | | | | | | |
| Milestone 12 | | | | | | | | | | | | | | | | | |