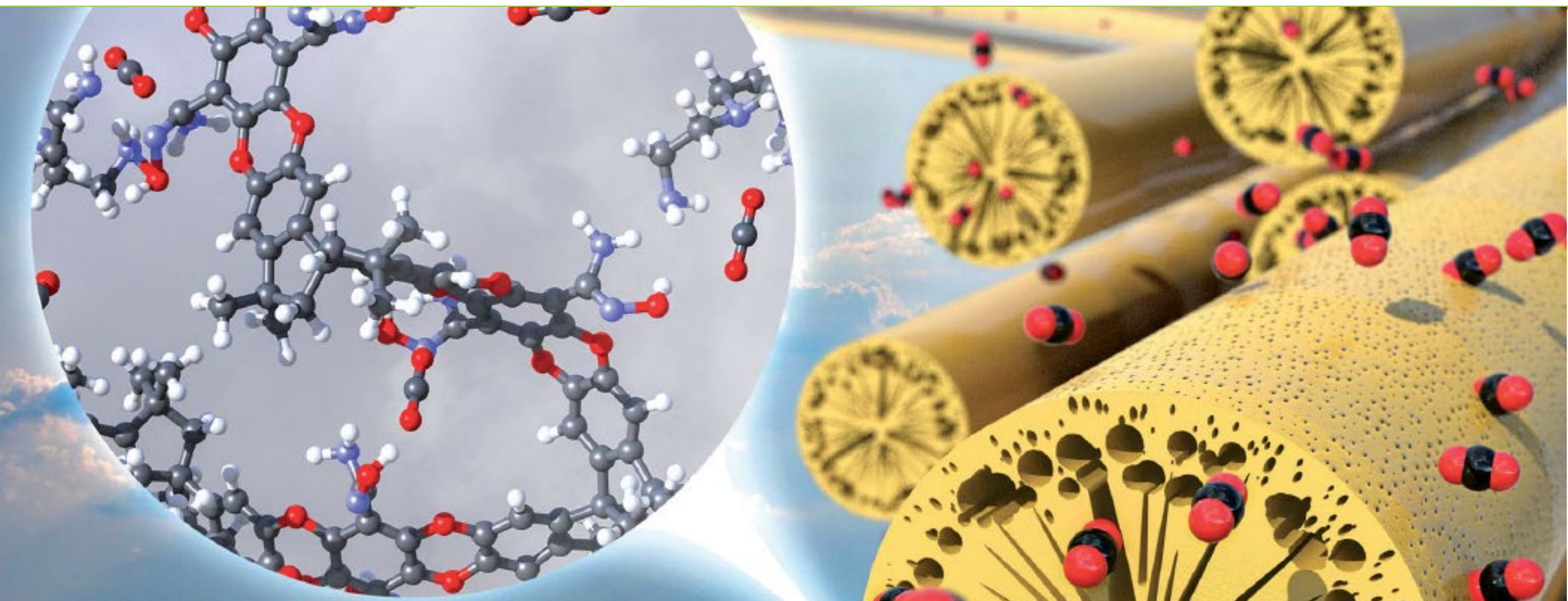


Amine Degradation Experiments on a Polymer Supported Molecular Amine DAC Sorbent

2024 FECM / NETL Carbon Management Research Project Review Meeting

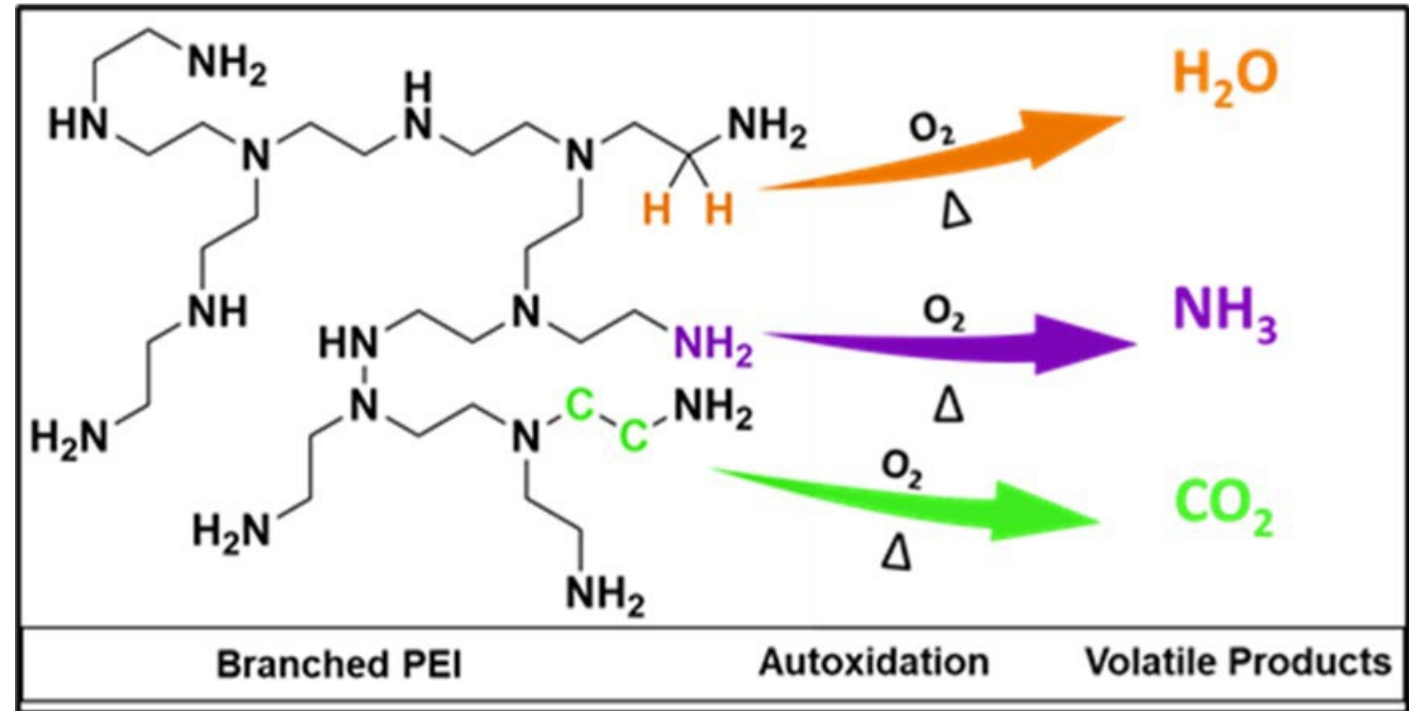
Jan Steckel, NETL



Amine Degradation in Porous Sorbents

Overview of Solid Sorbent Lifetime Impacts

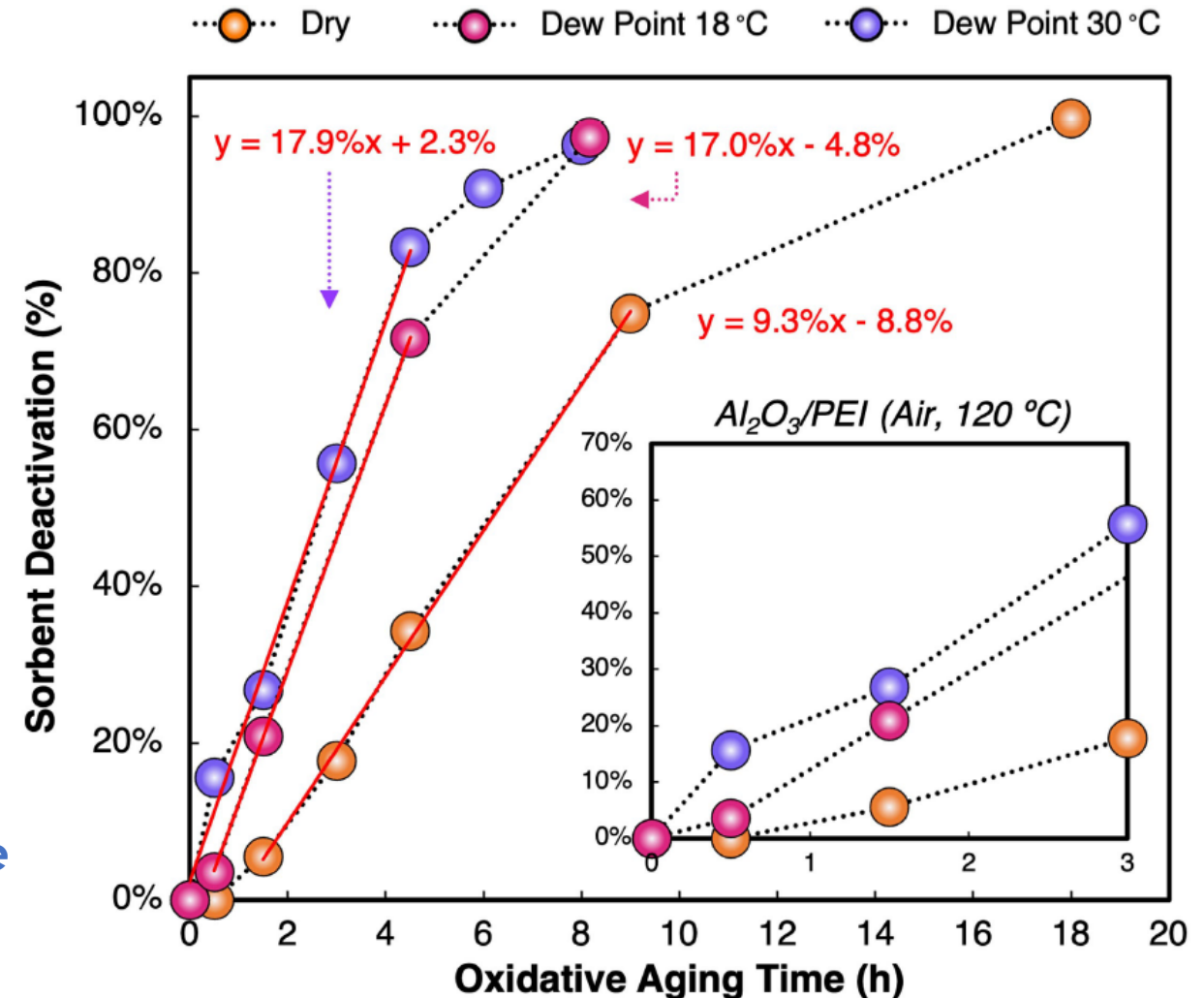
- Amine degradation: breakdown of sorbent performance
- The **cost of DAC increases** as sorbent lifetime decreases.
- Amine degradation leads to
 - The need for sorbent contactor replacement or recycling
 - Possible release of harmful contaminants (**organic nitrogen compounds** and/or ammonia)



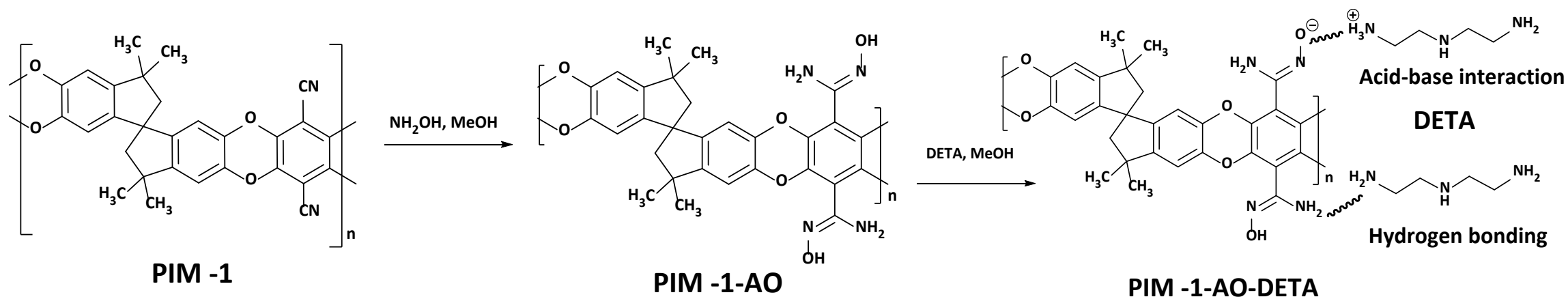
Published Works Focus on PEI

Mechanism of Oxidative Degradation

- **Polyethylenimine (PEI)** is a commonly used amine for DAC sorbents
- Deactivation of the sorbent tracked via relative loss in CO₂ adsorption
- Accelerated oxidative deactivation was evaluated with dry and humid aerobic (21% O₂) atmosphere at 120 °C
- Dry oxidation exhibited a sigmoidal profile with an initial induction period of ~2h
 - **Indicative of formation of carbon-centered radicals.**
 - **Subsequent rapid oxidative degradation due to radical reaction.**



PIM-1-AO as an Anchor for Amines



Amines considered:

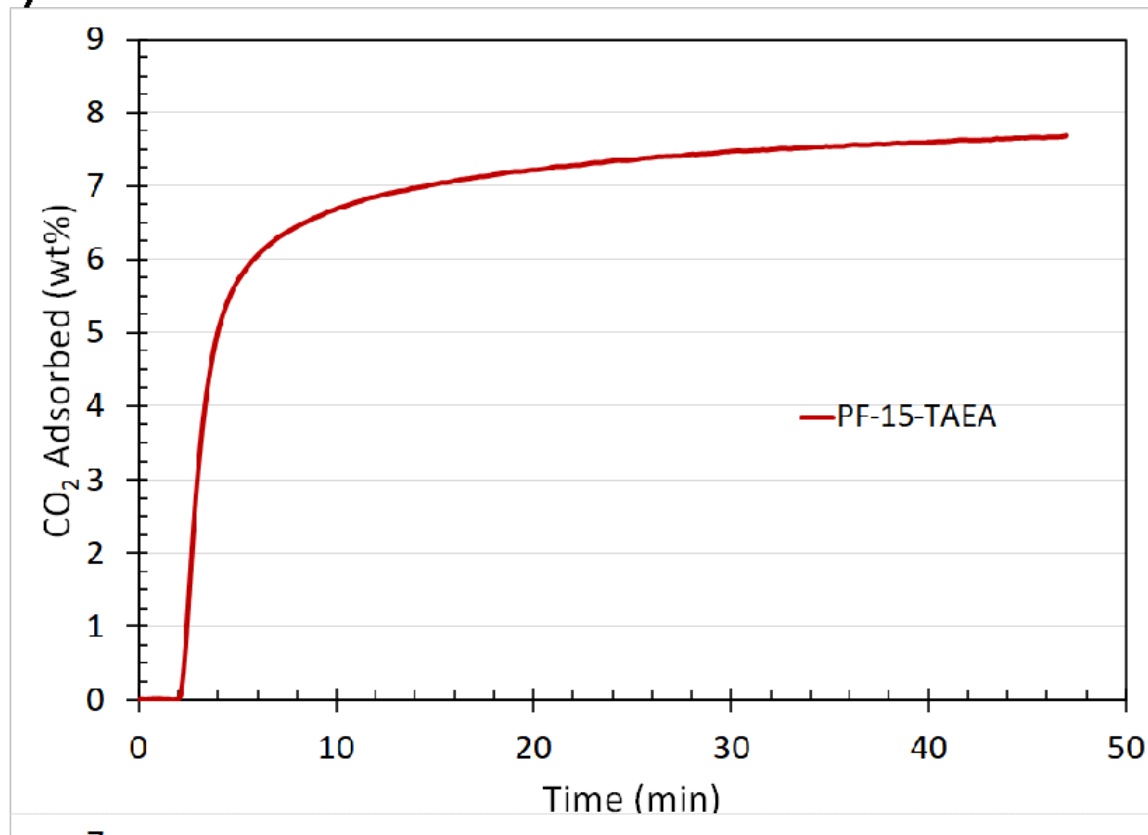
- Diethylenetriamine (DETA)
- Tris(2 aminoethyl)amine (TAEA)
- Tetraethylenepentamine (TEPA)
- Tris(2 aminopropyl)amine (TAPA)

PIM-1-AO TAEA - NETL-Developed Polymer Sorbent for DAC

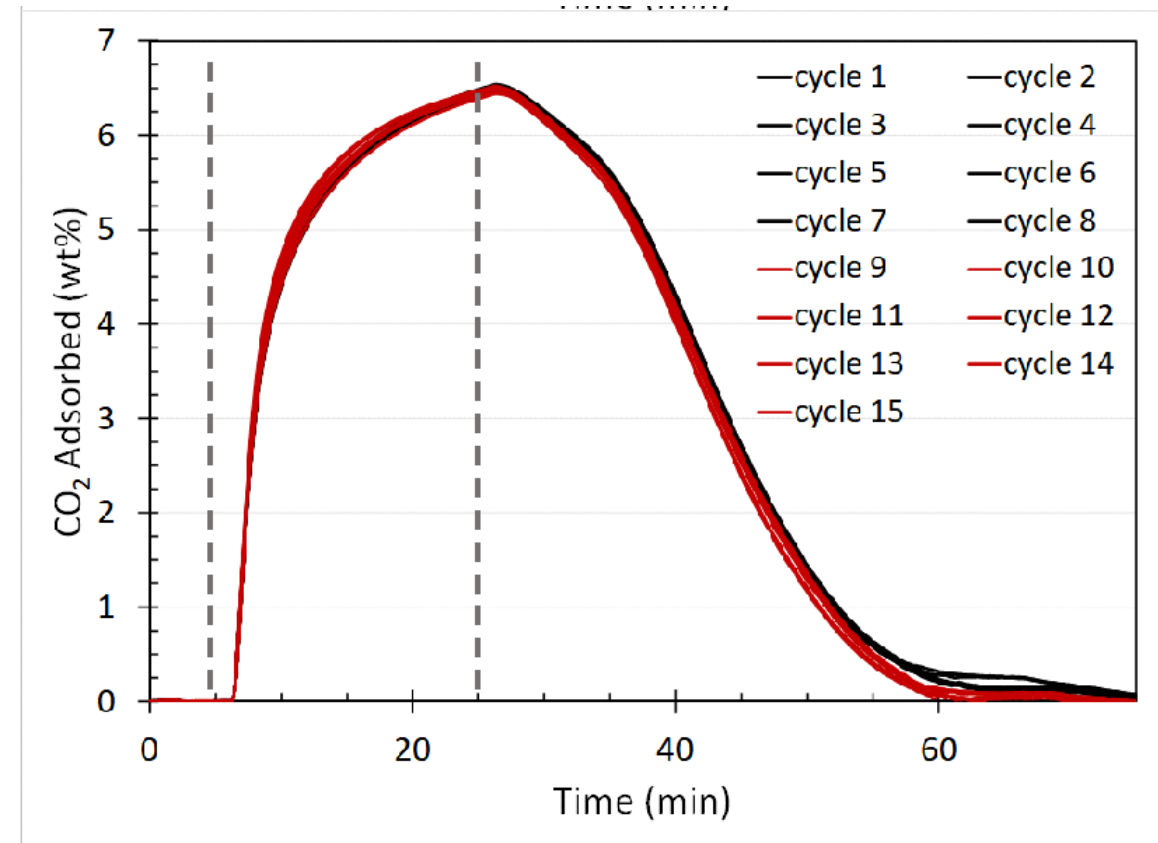


- Based on an amidoxime-functionalized version of PIM-1 polymer (**high surface area**)
- PIM-1-AO is soluble in several common solvents
- Fibers or other form factors are produced from the material directly; no additives needed
- **The sorbent lifetime of this material has not been investigated**
- **Study the mechanism of degradation by forcing these materials to degrade – subject them to harsh conditions**

CO₂ Uptake in Flowing Gas



CO₂ uptake in PF-15-TAEA measured in flowing gas at a total pressure of 100 mbar, 25°C. The switch from pure N₂ to 10%CO₂/90%N₂ occurs at 2 min.



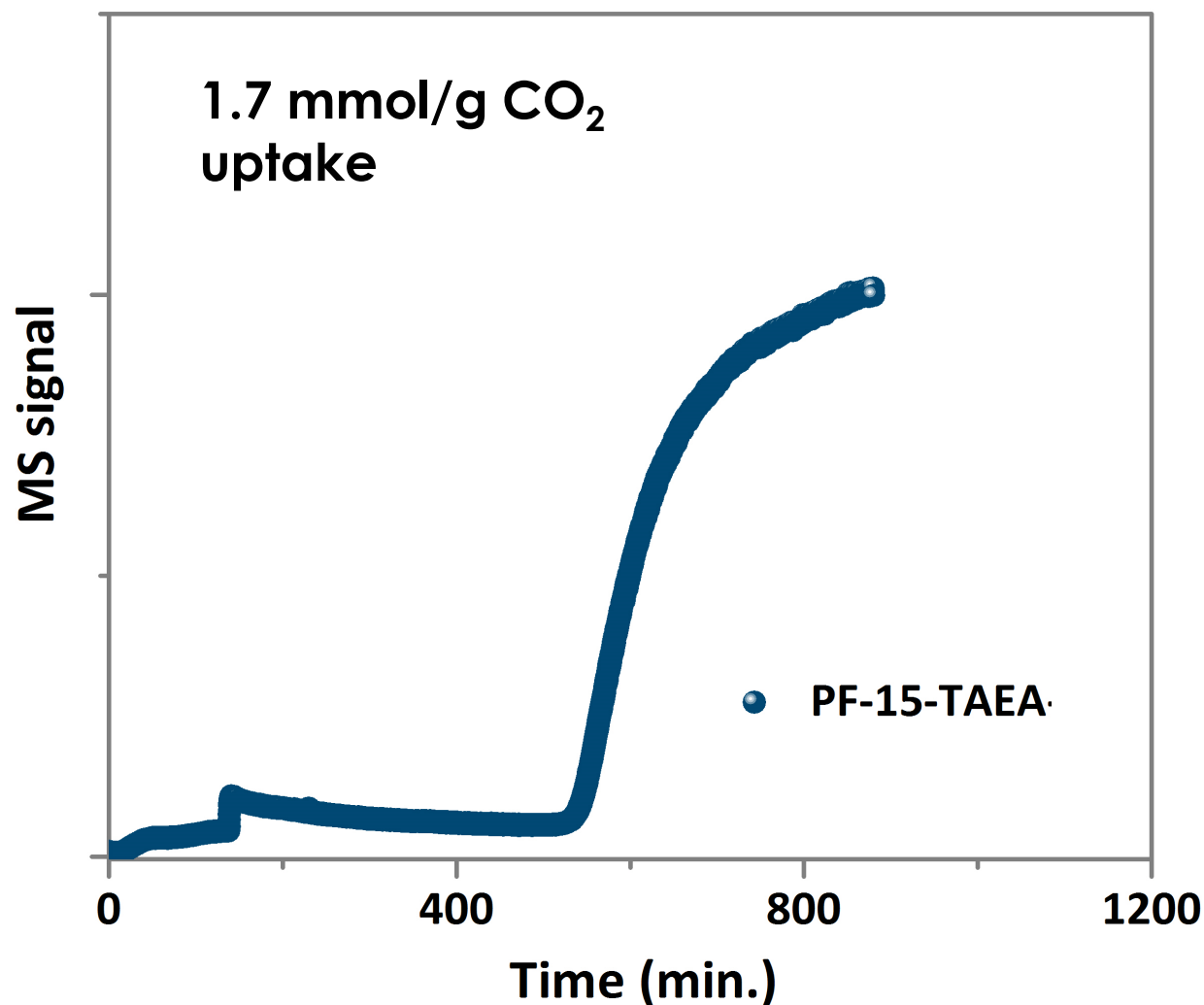
Adsorption / desorption cycles in flowing gas at a total pressure of 1bar. Conditions: (1) pure N₂, 25°C; (2) 10%CO₂/90%N₂; (3) temperature ramp in pure N₂ at 3°C/min to 70-75°C (black) or 75-80°C (red).

Breakthrough Analysis: Porous Wet-Spun Fibers

DAC Conditions

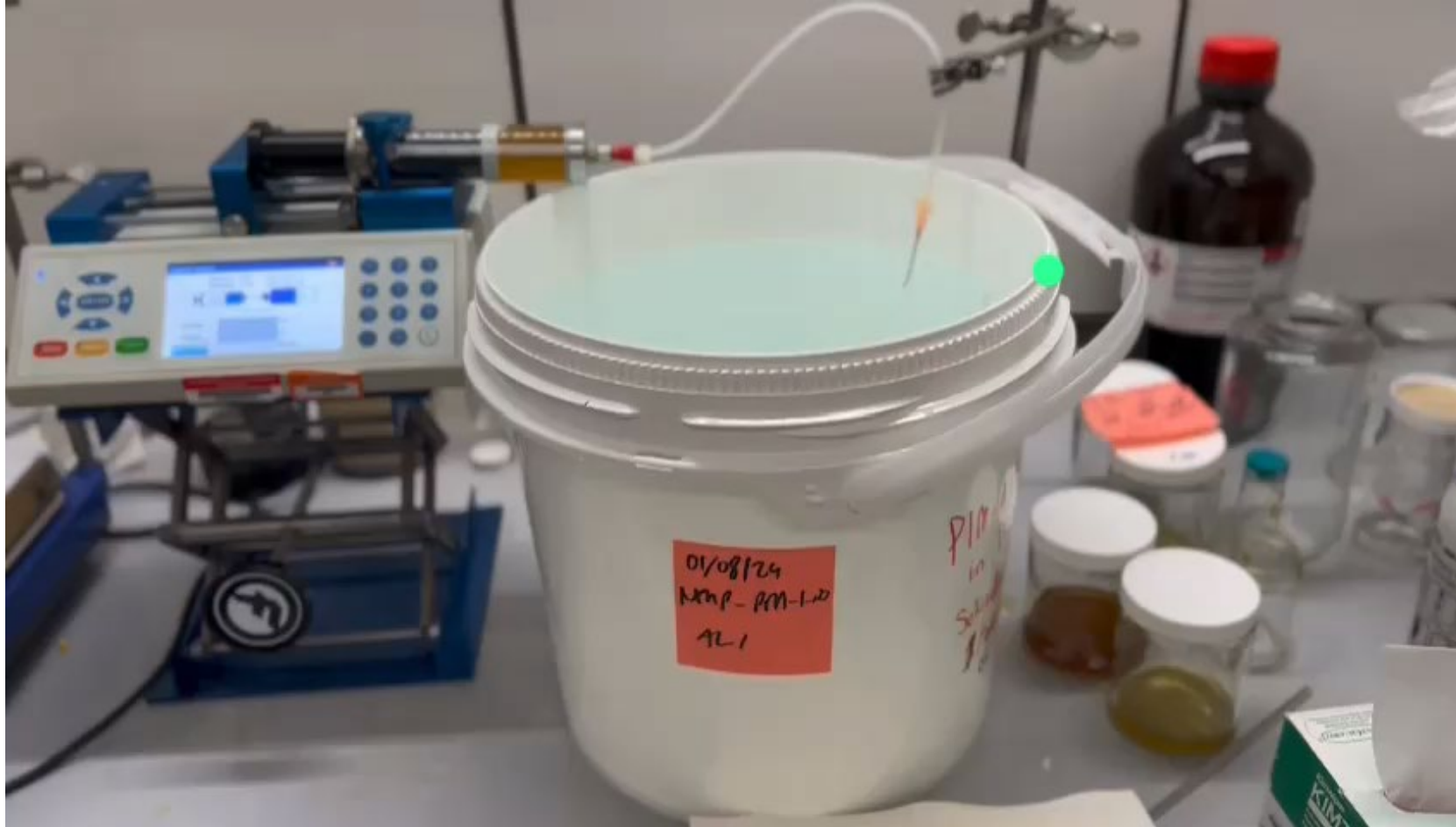
400 ppm CO₂
concentration, 10% O₂,
10% He, balance N₂, and
50 % RH at 25 °C
Regenerated at 75 °C

1.5 mmol/g
400 ppm CO₂
concentration, 10% O₂,
10% He, balance N₂,
and 50 % RH at 25 °C
Regenerated at 50 °C



Structured porous adsorbent forms

Wet Spun Fibers: scaled up from ~1g batch to ~20 g batch

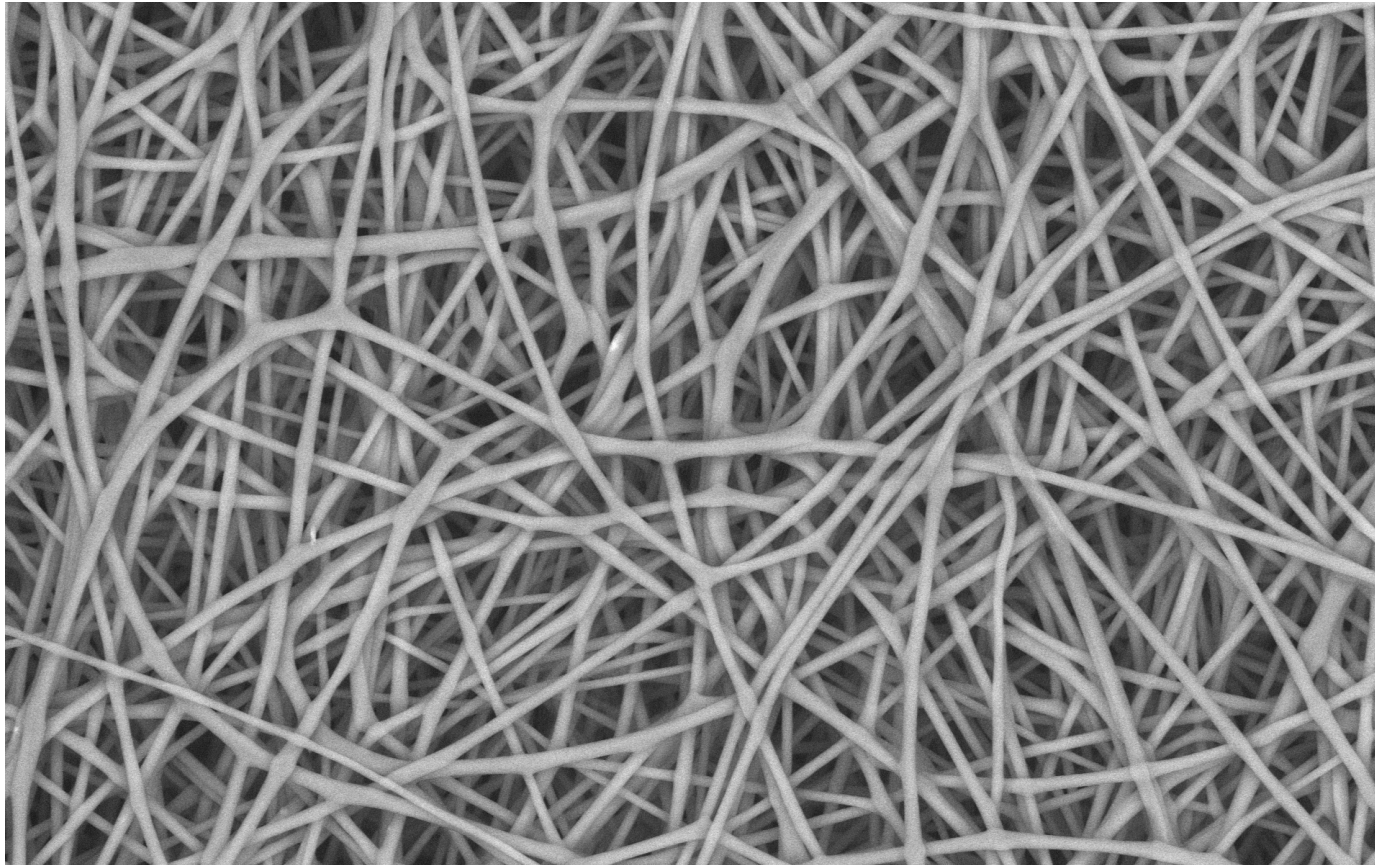


diameter of fibers: 1 mm



Structured porous adsorbent forms

Electrospun Flat Sheets (30 x 5 cm)



diameter of fibers: 2 micron

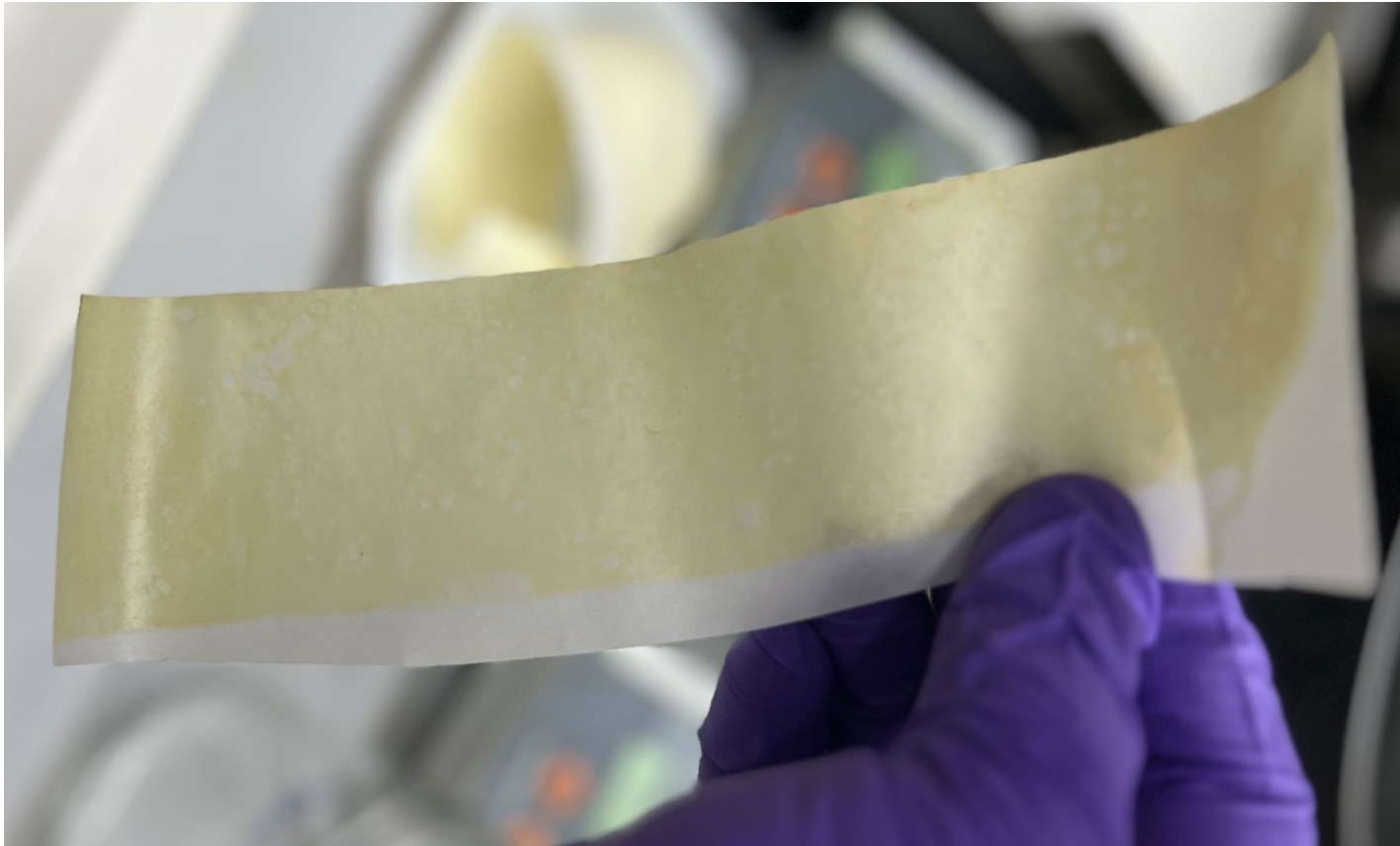


Structured porous adsorbent forms

Hand Cast Porous Flat Sheets

Uptake ~ 1.3 mmol/g under humid DAC conditions with 70°C regeneration

Uptake ~ 1.1 mmol/g under humid DAC conditions with 50°C regeneration



Structured porous adsorbent forms

~10 m long flat sheet (large-scale knife casting instrument)



*Uptake ~1.7 mmol/g under humid DAC conditions with 70°C regeneration (prelim)



DAC Center Aging

DAC Center Allows for Controlled Accelerated Aging Conditions



Lab scale

systems for novel solvent and sorbent
material assessment
(~0.1 kg CO₂/day)

- Focused on material properties and longevity
- Multi-gas measurements with amounts of materials greater than typical lab scale
- Able to accommodate all common materials (powder, granular, fiber, structured)
- Automated for extended, multi-cycle testing

For the accelerated aging experiments, we used the lab scale unit to hold the material for 7 days at specific harsh conditions.



Uptake Loss – DAC Center Aging - Dry

Breakthrough Analysis (BTA) Provides a Measure of CO₂ Uptake

- Pristine (un-aged) sample:
 - CO₂ capacity: **1.40** mmol/g
- Aged under N₂ 420 ppm CO₂ Dry 75°C
 - After 4 days: CO₂ capacity: **1.36** mmol/g
 - After 7 days: CO₂ capacity: **1.37** mmol/g
- Aged under N₂ 420 ppm CO₂ 20% O₂ Dry 75°C
 - After 3.5 days: CO₂ capacity: **0.70** mmol/g
 - After 7 days: CO₂ capacity: **0.43** mmol/g



Diminished CO₂ uptake capacity after aging with O₂

Uptake Loss – DAC Center Aging - Humid

Breakthrough Analysis (BTA) Provides a Measure of CO₂ Uptake

- Pristine (un-aged) sample:
 - CO₂ capacity: **1.40** mmol/g
- Aged under house air, (420 ppm CO₂) 40-50% RH, 75°C
 - After 3.5 days: CO₂ capacity: **0.39** mmol/g
 - After 7 days: CO₂ capacity: **0.14** mmol/g



Presence of humidity increases the rate of oxidative degradation

NMR Results for Aging

Solid State NMR Analysis (University of Pittsburgh)

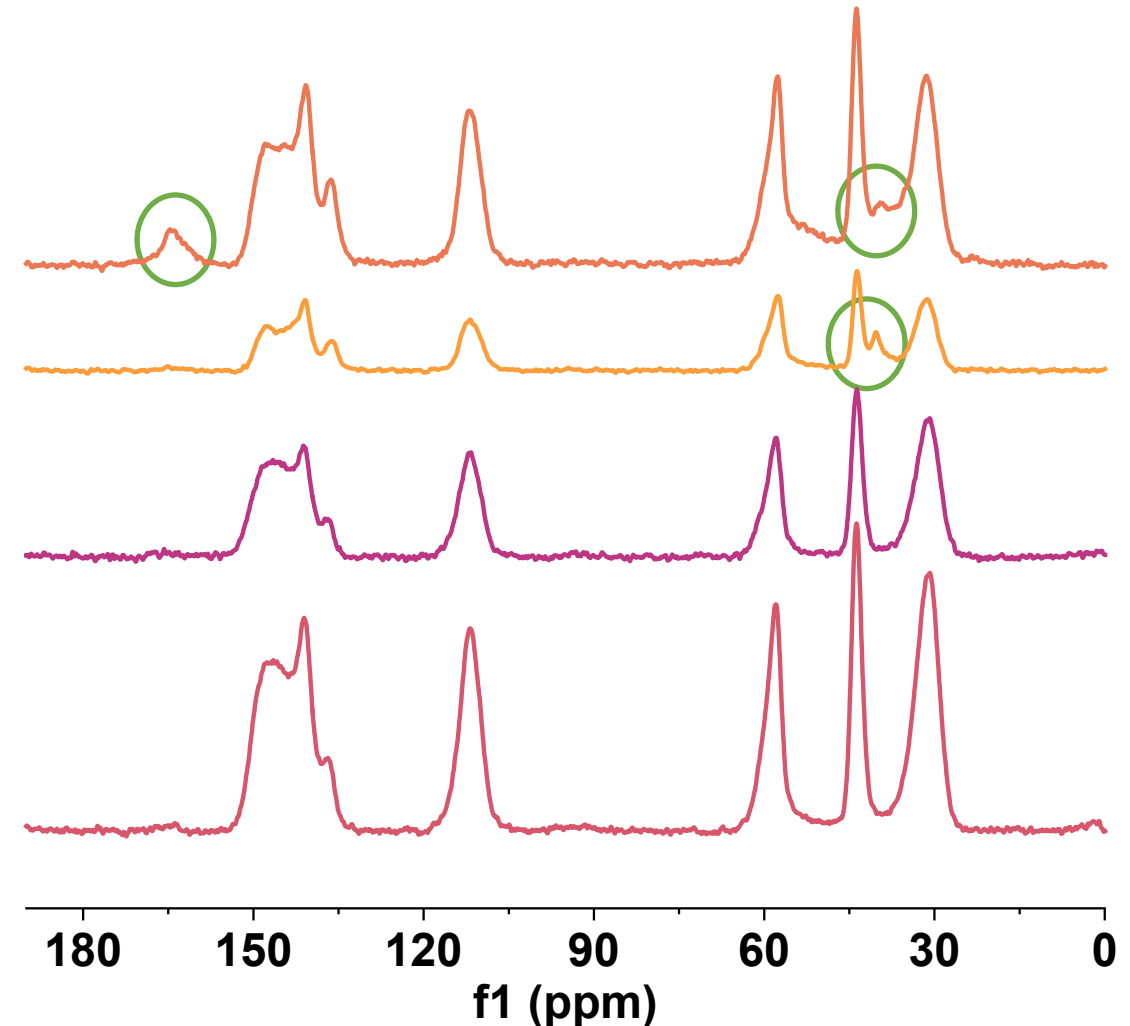
- TAEA Tris(2-aminoethyl)amine
- Aging in oven, 70°C, RH ambient
- Peak around 160 ppm **increasing**, associated with degradation
- Peak near 39-40 ppm corresponds to the C near the NH₂ group. **Decreasing** with aging.
- Natural abundance of ¹³C is very low, leading to a **low signal to noise ratio**. We are investigating synthesizing the ¹³C or ¹⁵N versions of the amines.

PF-15-TAEA
11 days

PF-15-TAEA
Fresh

PF-15-Control
11 days

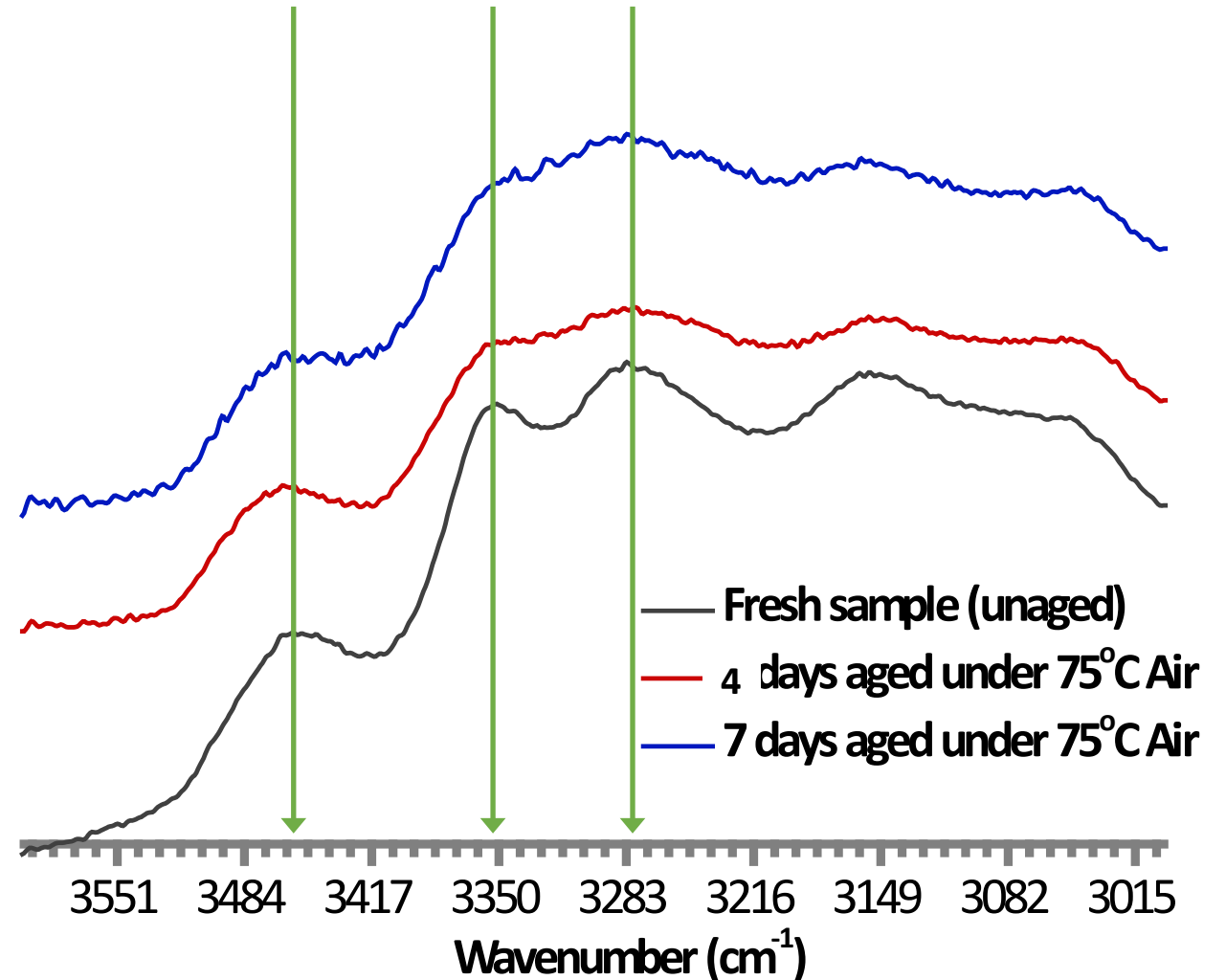
PF-15-Control
Fresh



Spectroscopic Results for Aging

Fourier Transform Infrared (FT-IR) Spectroscopy Provides Information About Chemical Changes

- N-H stretch for amidoxime amine
 - Broad peak near 3450 cm^{-1}
 - Does not disappear with aging
- N-H stretch for alkyl amine
 - Peaks at $3283, 3350\text{ cm}^{-1}$
 - Disappear with aging
- Aging leads to **loss of the alkyl amine group** but not the amidoxime amine group

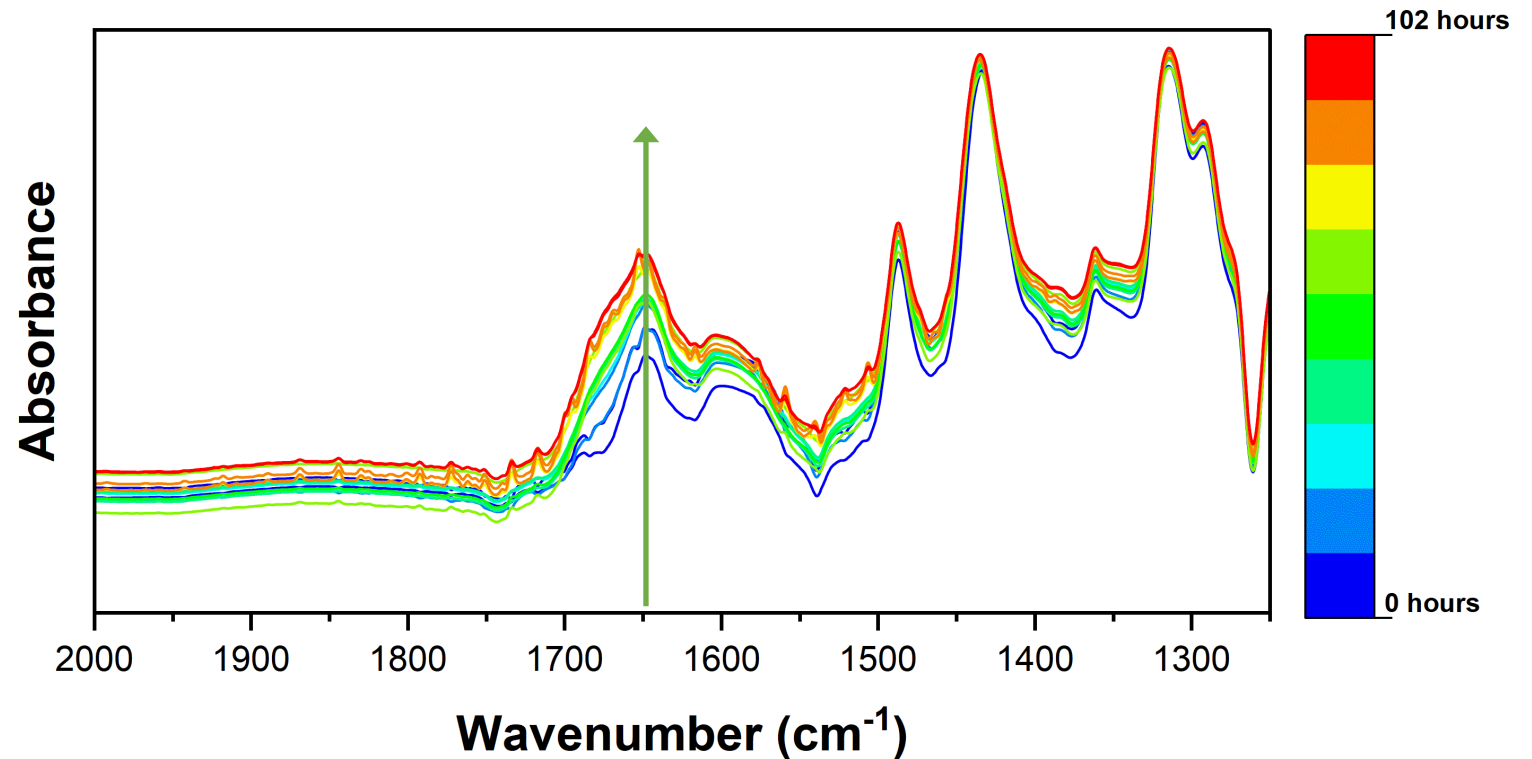


In-Situ Spectroscopic Results for Aging

In-Situ Fourier Transform Infrared (FT-IR) Spectroscopy of Sorbent Material Exposed to Flowing Gas Mixtures

- In Situ Experiments carried out for ~8 days
 - 20°C, dry air
 - 70°C, dry air
 - 70°C, 50% RH air
- Significant intensity increase of 1650 cm⁻¹ peak associated with C=O and C=N bonds.

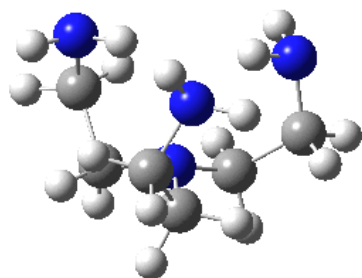
FT-IR in-situ 70°C, 50% RH air (400 ppm CO₂, 20% O₂, balance N₂).



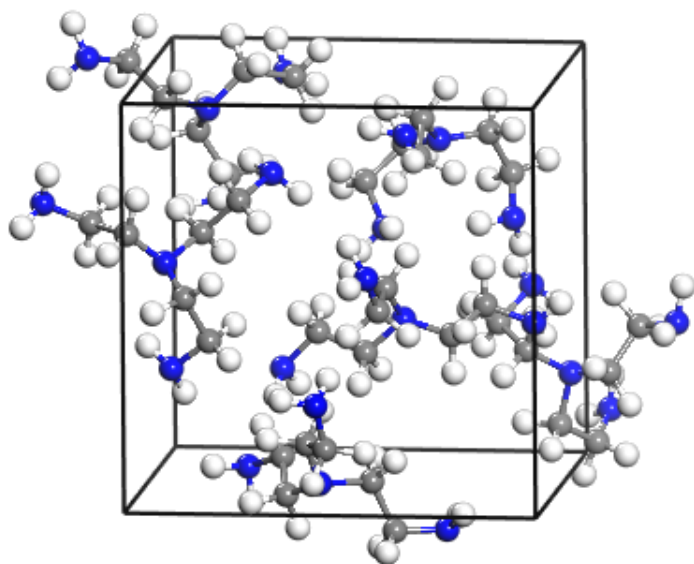
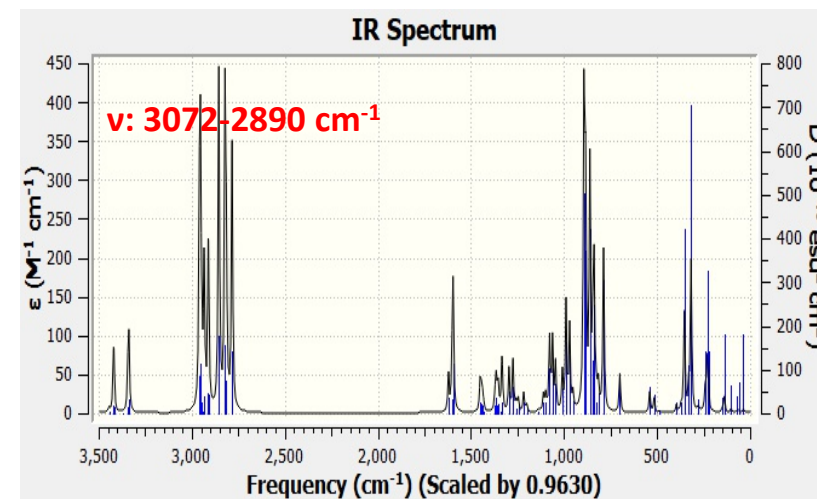
Computational Prediction of FT-IR Spectra

Gas Phase vs Condensed Phase

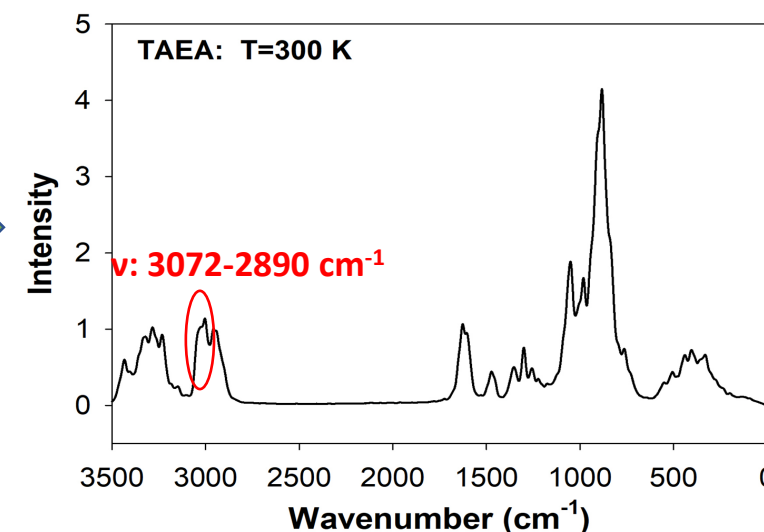
C-H stretch
3072....2890



Molecule in the Gas Phase
2nd Deriv. (E / coordinates)
Sharp Distinct Peaks
Clear Interpretation

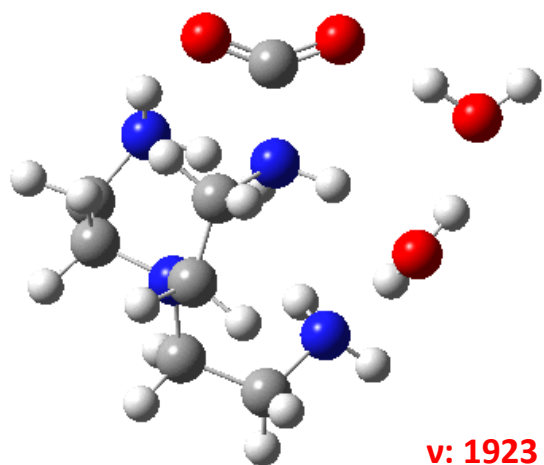


Condensed Phase Model
FT of Dipole Autocorrelation Fxn
Broad Peaks
Includes Complexity, Anharmonicity

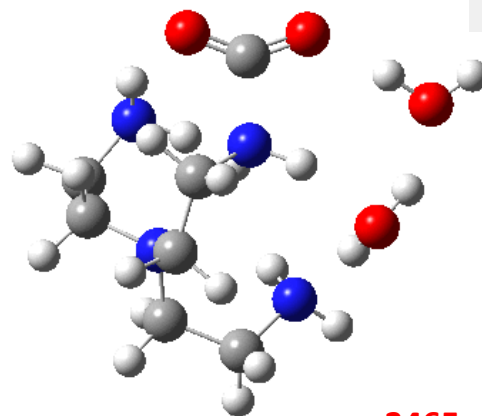


Computational Prediction of FT-IR Spectra

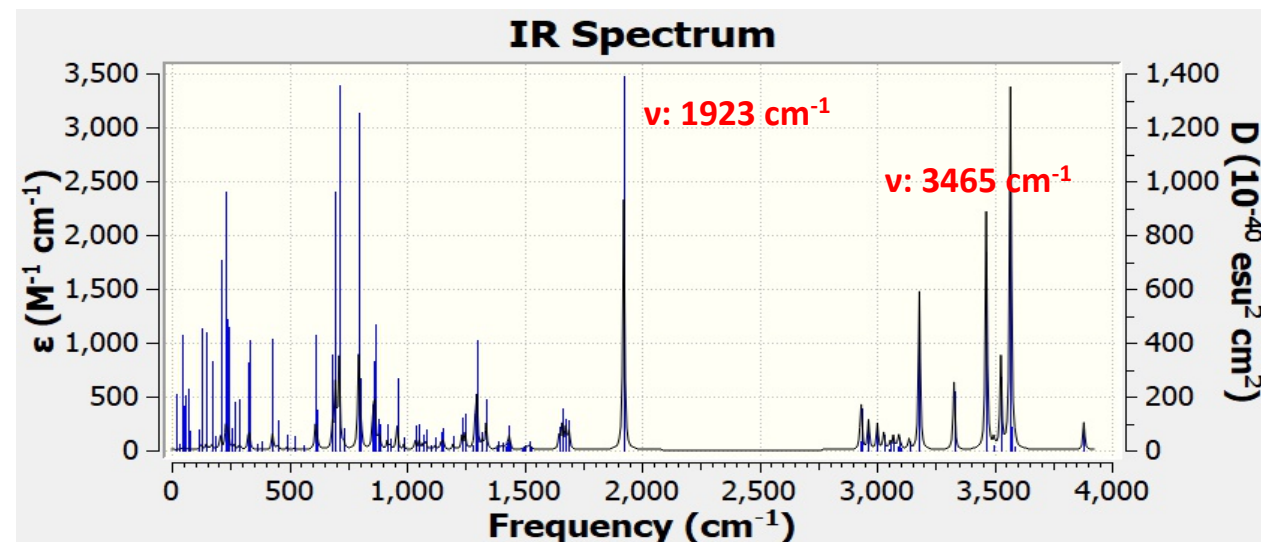
Gas Phase Predictions Useful for Understanding Spectral Evidence of Amine + CO₂ Reaction, Stabilization Provided by Water



v: 1923 cm⁻¹

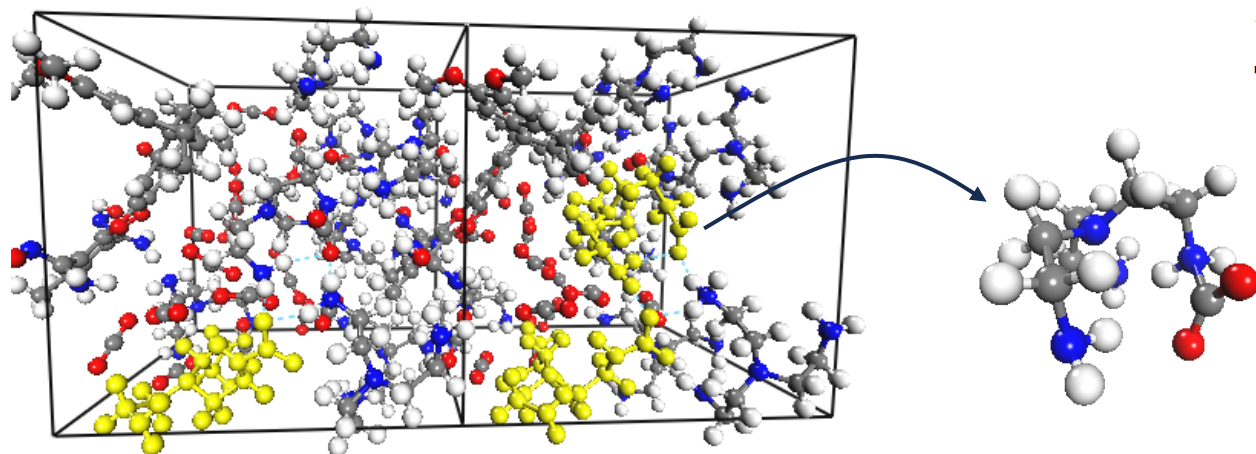
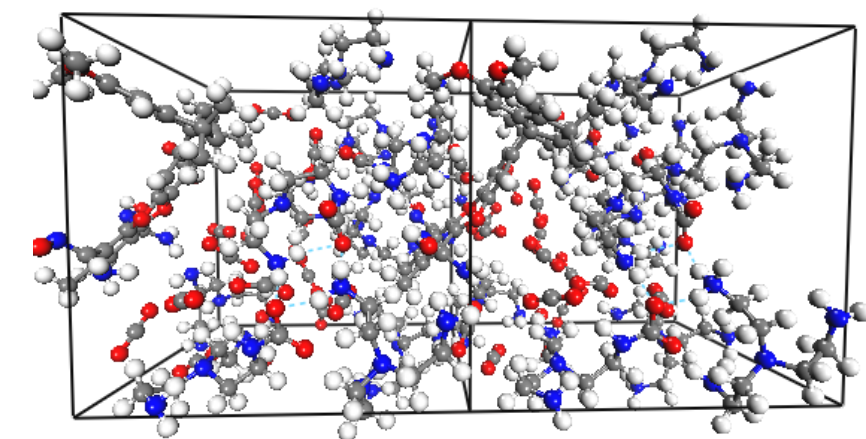


v: 3465 cm⁻¹

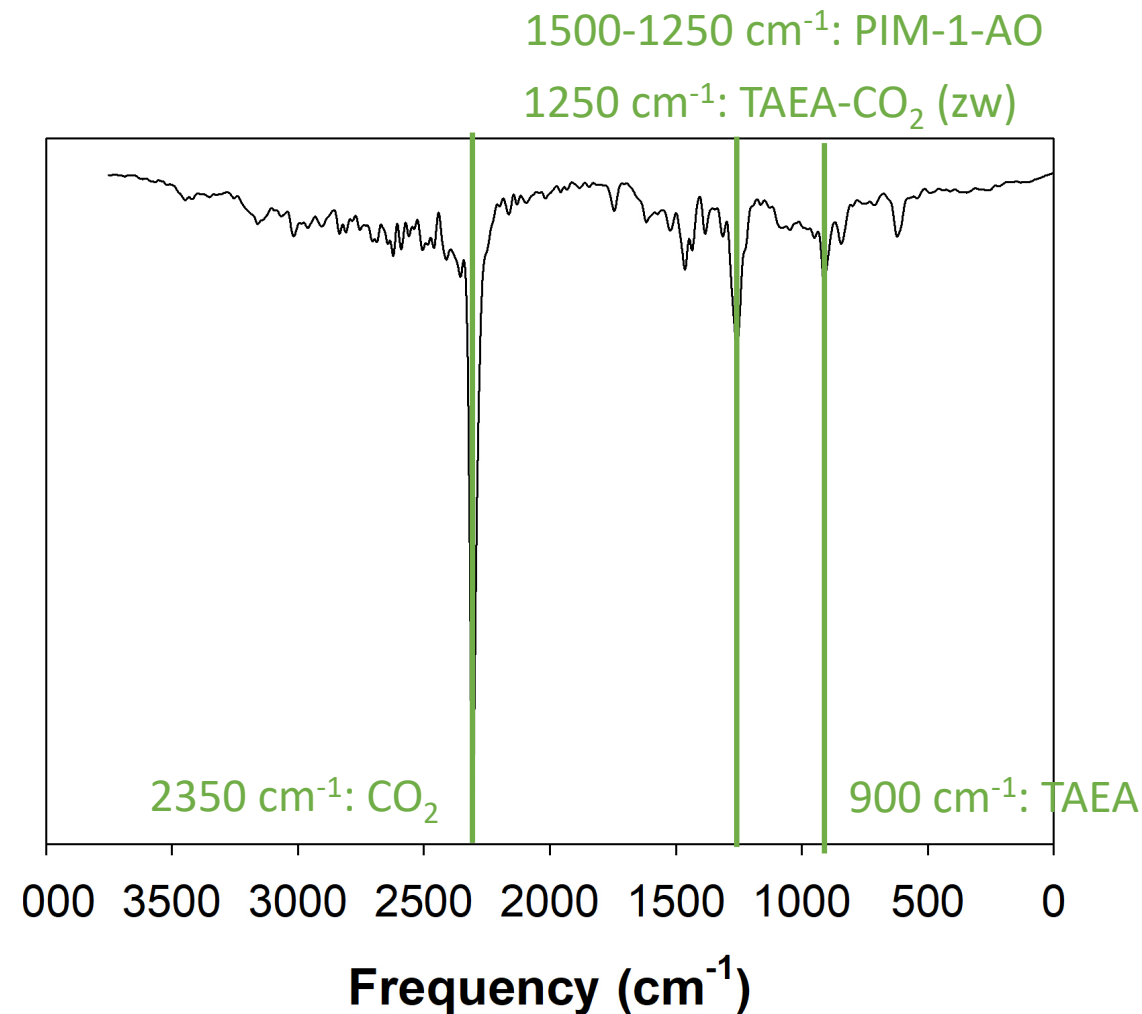


Computational Prediction of FT-IR Spectra

Condensed Phase Simulations: Pristine PIM1-AO + 10 TAEA + 10 CO₂



Intensity (a.u.)



Conclusions

- Oxidative degradation observed after heat $\sim 70^{\circ}\text{C}$ in the presence of O_2 as evidenced by:
 - Capacity loss
 - NMR
 - FT-IR
- Amines on TAEA degraded while amidoxime amines not degraded.
- Gas phase and condensed phase computed spectra for pristine material aid in peak assignments.

Future Plans

- Computational spectra for postulated reaction products.
- Measure the capacity loss for PIM-1-AO TAEA at 45°C .
- Planned experiments with a transfer reaction time of flight mass spectrometry (PTR-TOF-MS) in the DAC Center to identify reaction products.

Acknowledgements

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