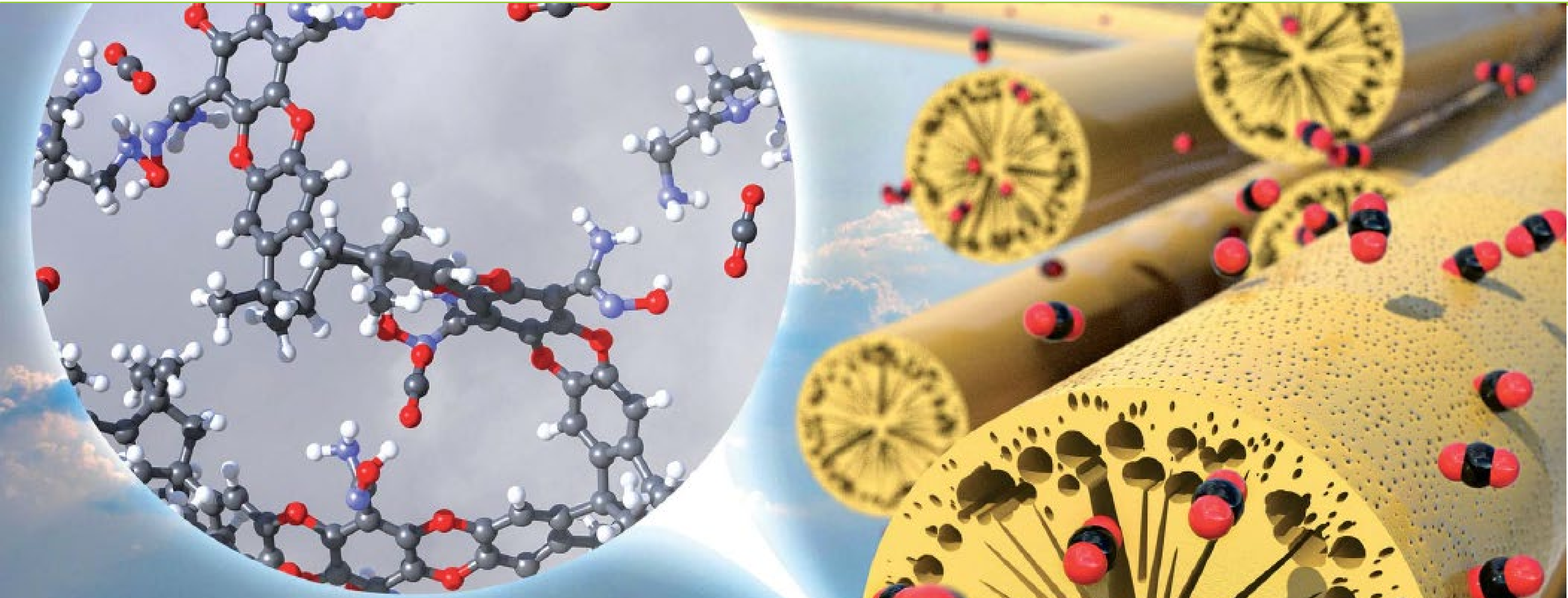
Amine Degradation Experiments on a Polymer Supported Molecular Amine DAC Sorbent

2024 FECM / NETL Carbon Management Research Project Review Meeting

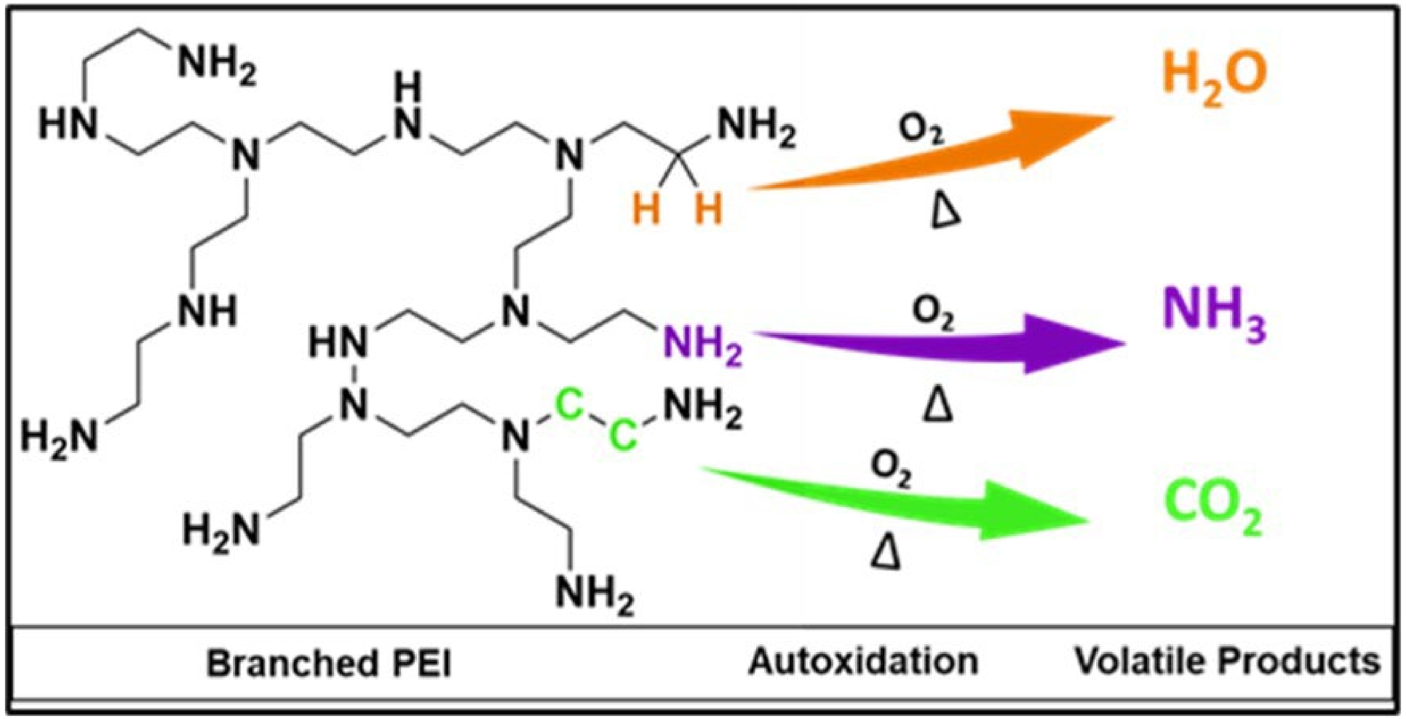
Jan Steckel, NETL



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)

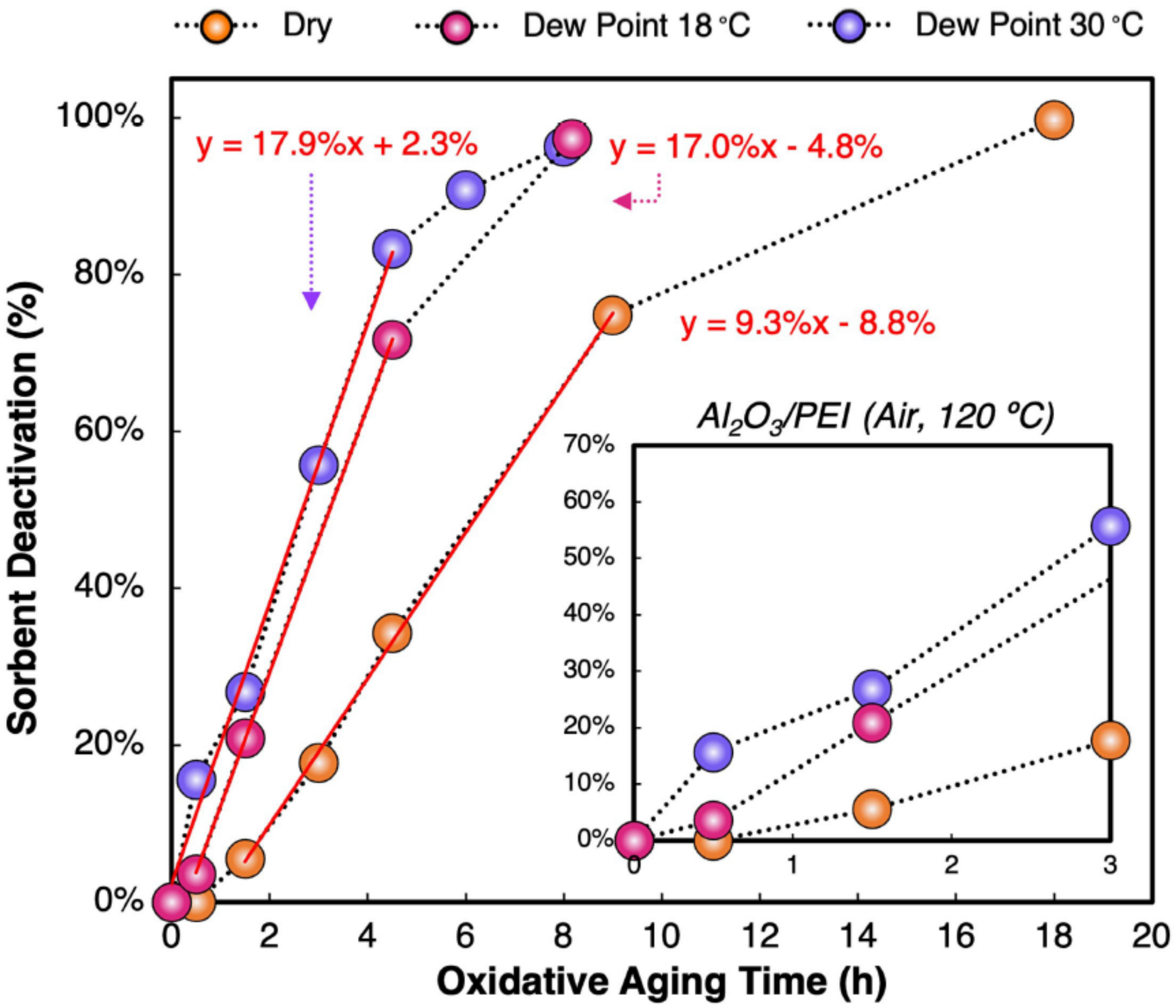


Racicot et al. Volatile Products of the Autoxidation of Poly(Ethylenimine) in CO_2 Sorbents. J. Phys. Chem. C 2022, 126 (20), 8807–8816. https://doi.org/10.1021/acs.jpcc.1c09949.
Wiegner et al. Optimal Design and Operation of Solid Sorbent Direct Air Capture Processes at Varying Ambient Conditions. *Ind. Eng. Chem. Res.* **2022**, *61* (34), 12649–12667. https://doi.org/10.1021/acs.iecr.2c00681.

Published Works Focus on PEI

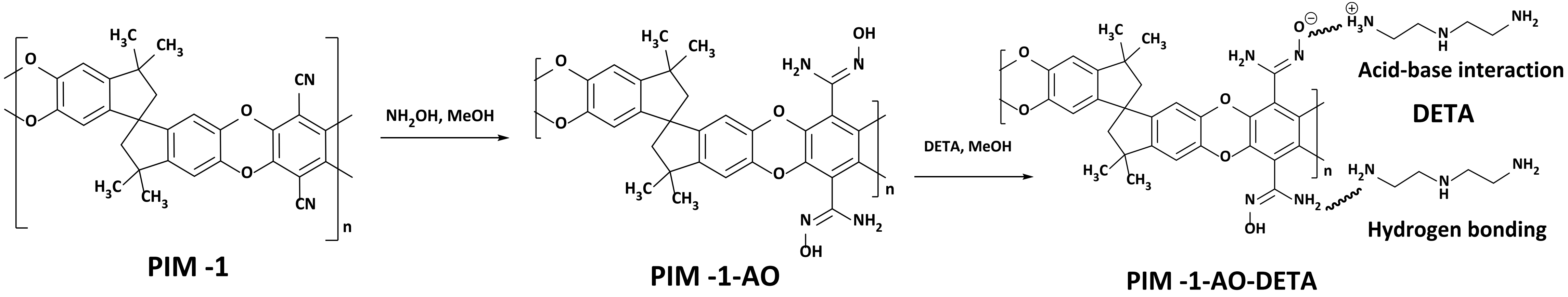
Mechanism of Oxidative Degradation

- ***Polyethylenimine (PEI)*** is a commonly used amine for DAC sorbents
- Deactivation of the sorbent tracked via relative loss in CO_2 adsorption
- Accelerated oxidative deactivation was evaluated with dry and humid aerobic (21% O_2) 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.***



Carneiro, J. S. A.; Innocenti, G.; Moon, H. J.; Guta, Y.; Proaño, L.; Sievers, C.; Sakwa-Novak, M. A.; Ping, E. W.; Jones, C. W. Insights into the Oxidative Degradation Mechanism of Solid Amine Sorbents for CO_2 Capture from Air: Roles of Atmospheric Water. *Angewandte Chemie* **2023**, *135* (24), e202302887. https://doi.org/10.1002/ange.202302887.

PIM-1-AO as an Anchor for Amines



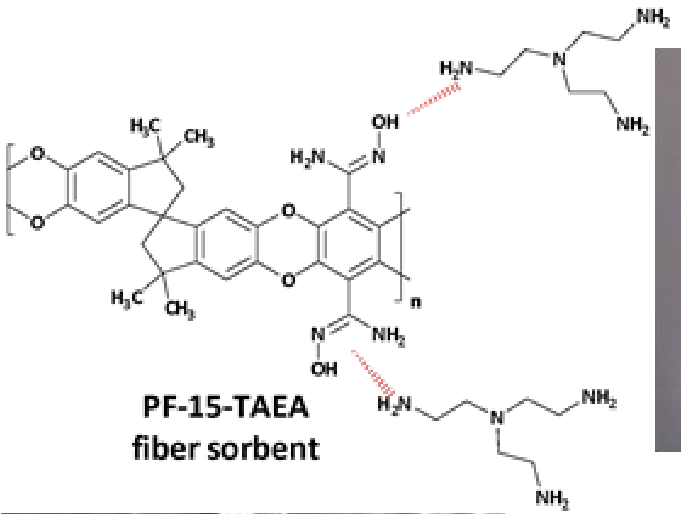
Amines considered:

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

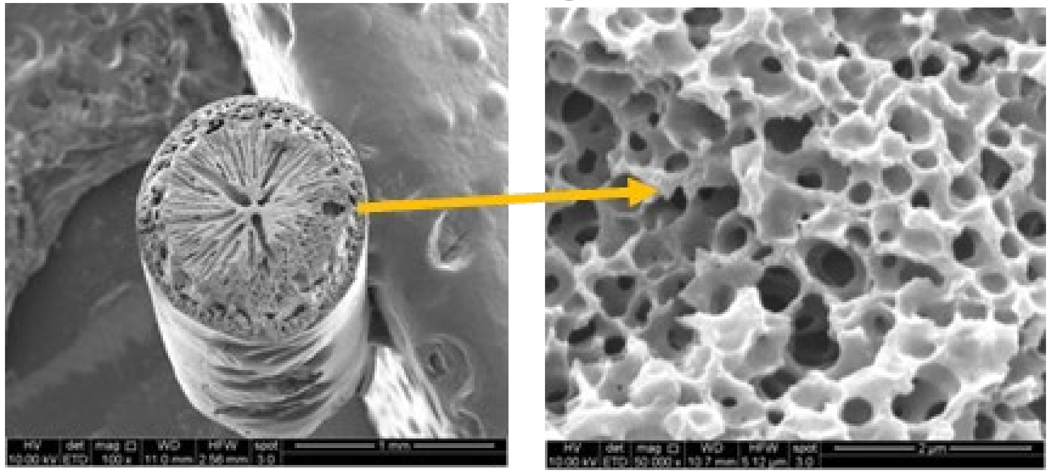
Miles, A.; Wilfong, W. C.; Hopkinson D.; Sekizkardes, A. K. *Energy Technology*, **2020**, 8, 2000419

Polymer of Intrinsic Microporosity Amidoxime Tris(2-aminoethyl)amine

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



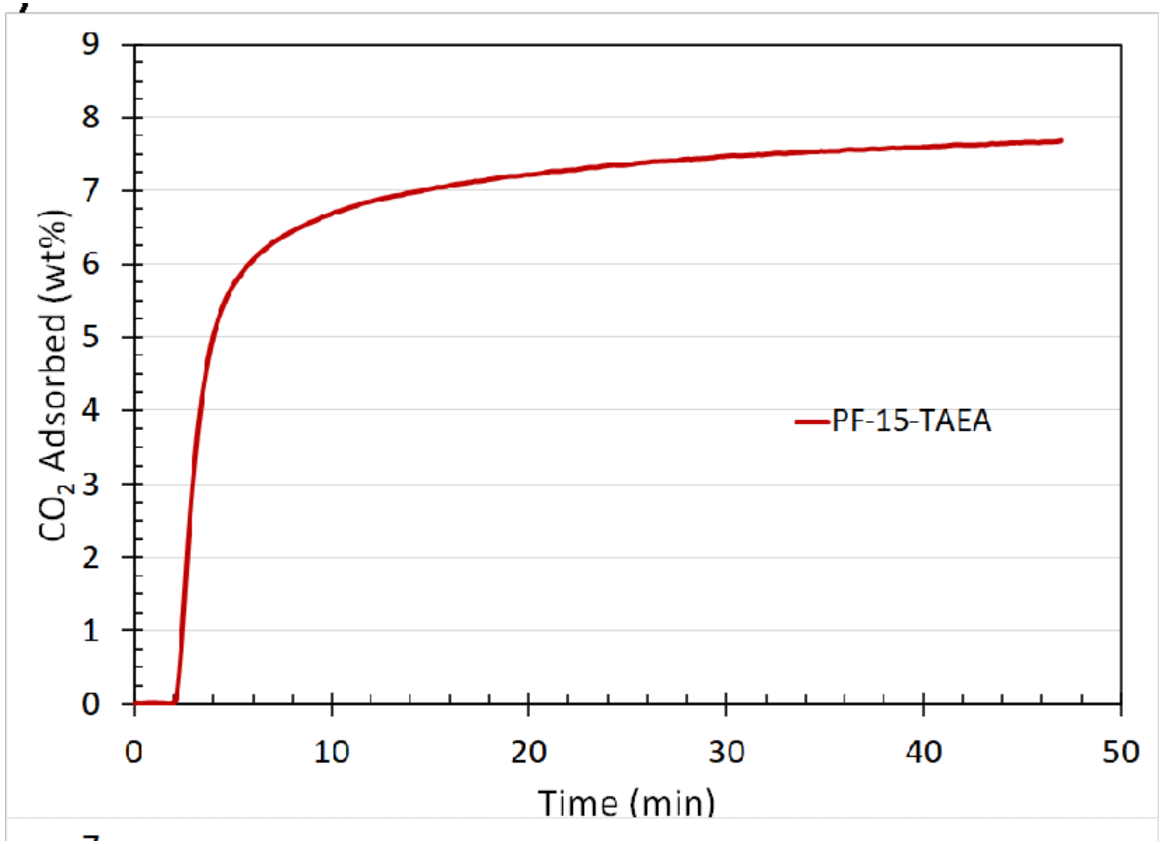
PF-15-TAEA fiber sorbent



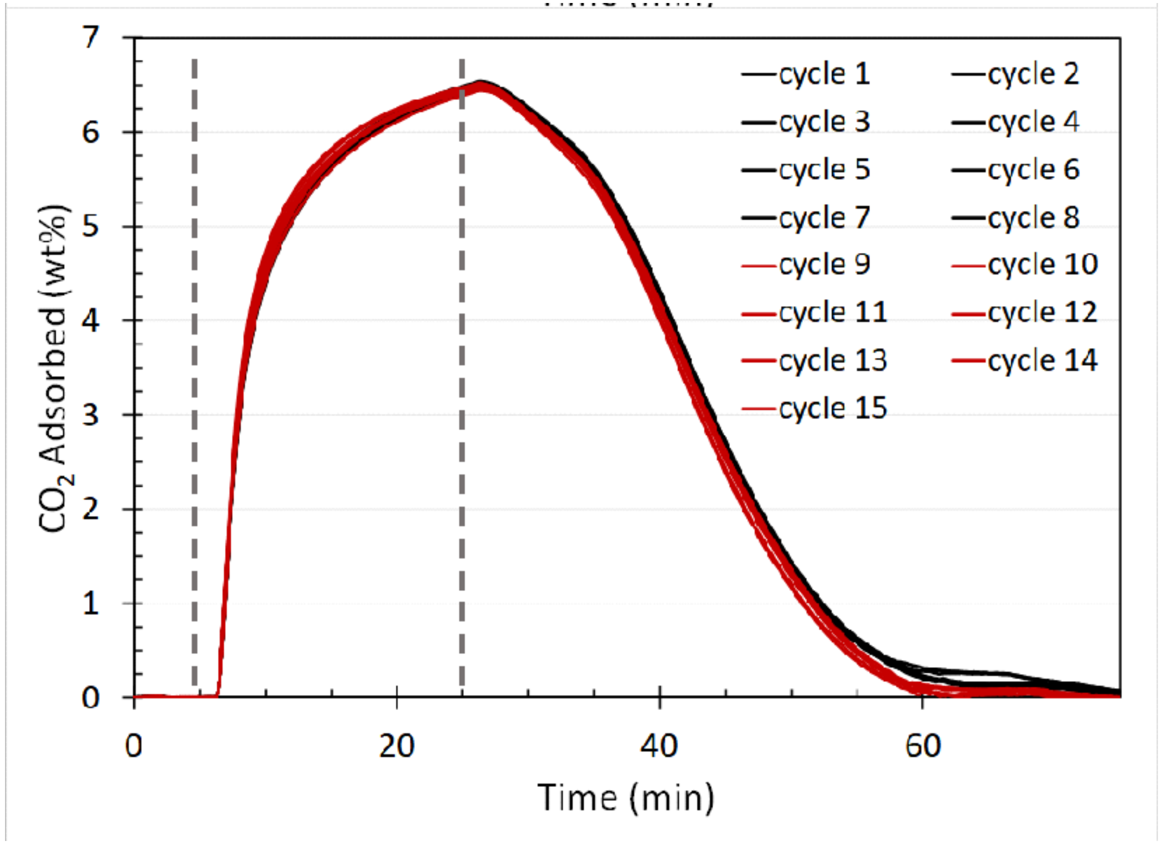
- Based on an amidoxime-functionalized version of PIM-1 polymer (***high surface area***)
- PIM-1-AO is soluble in several common solvents
- Fibers or other form factors are produced from the material directly; no additives needed
- ***The sorbent lifetime of this material has not been investigated***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

Sekizkardes, A. K.; Kusuma, V. A.; Culp, J. T.; Muldoon, P.; Hoffman, J.; Steckel, J. A.; Hopkinson, D. Single Polymer Sorbent Fibers for High Performance and Rapid Direct Air Capture. *J. Mater. Chem. A* **2023**, 10.1039.D2TA09270K. https://doi.org/10.1039/D2TA09270K.

CO_2 Uptake in Flowing Gas



CO_2 uptake in PF-15-TAEA measured in flowing gas at a total pressure of 100 mbar, 25°C. The switch from pure N_2 to 10%CO_2/90%N_2 occurs at 2 min.



Adsorption / desorption cycles in flowing gas at a total pressure of 1bar. Conditions: (1) pure N_2, 25°C; (2) 10%CO_2/90%N_2; (3) temperature ramp in pure N_2 at 3°C/min to 70-75°C (black) or 75-80°C (red).

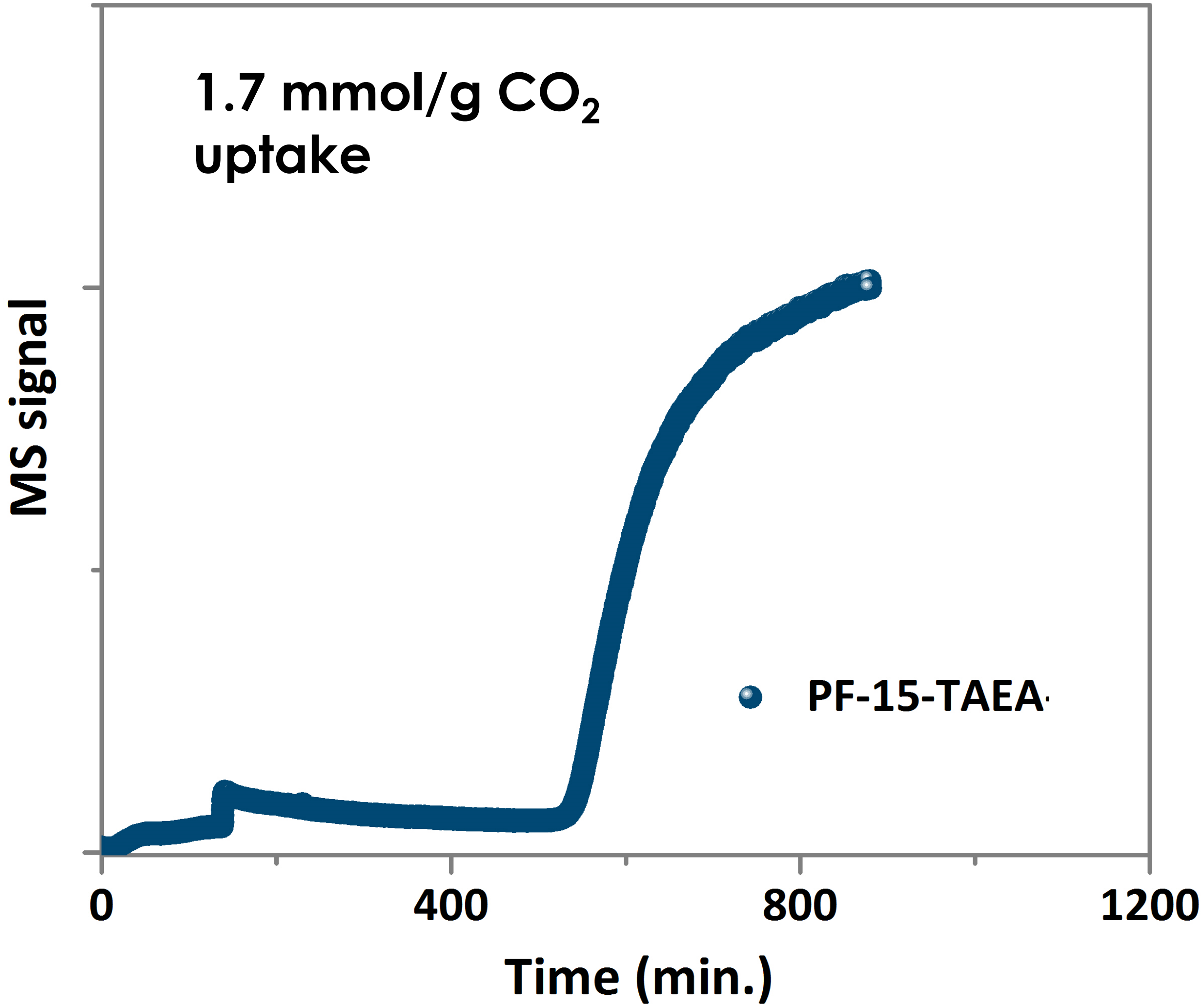
Sekizkardes, A. K.; Kusuma, V. A.; Culp, J. T.; Muldoon, P.; Hoffman, J.; Steckel, J. A.; Hopkinson, D. Single Polymer Sorbent Fibers for High Performance and Rapid Direct Air Capture. *J. Mater. Chem. A* **2023**, 10.1039.D2TA09270K. https://doi.org/10.1039/D2TA09270K.

Breakthrough Analysis: Porous Wet-Spun Fibers

DAC Conditions

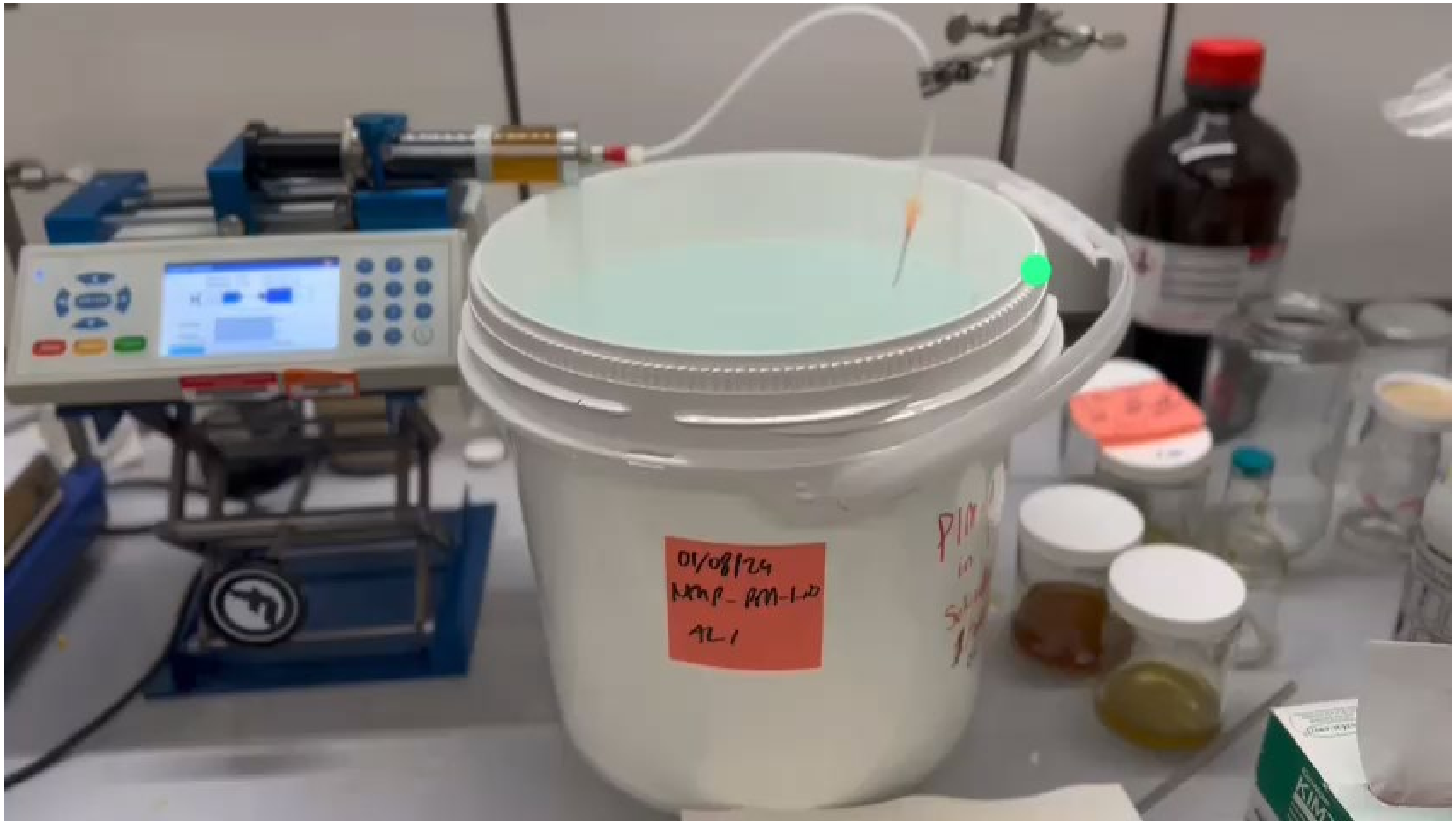
400 ppm CO_2 concentration, 10% O_2, 10% He, balance N_2, and 50 % RH at 25 °C
Regenerated at 75 °C

1.5 mmol/g
400 ppm CO_2 concentration, 10% O_2, 10% He, balance N_2, 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

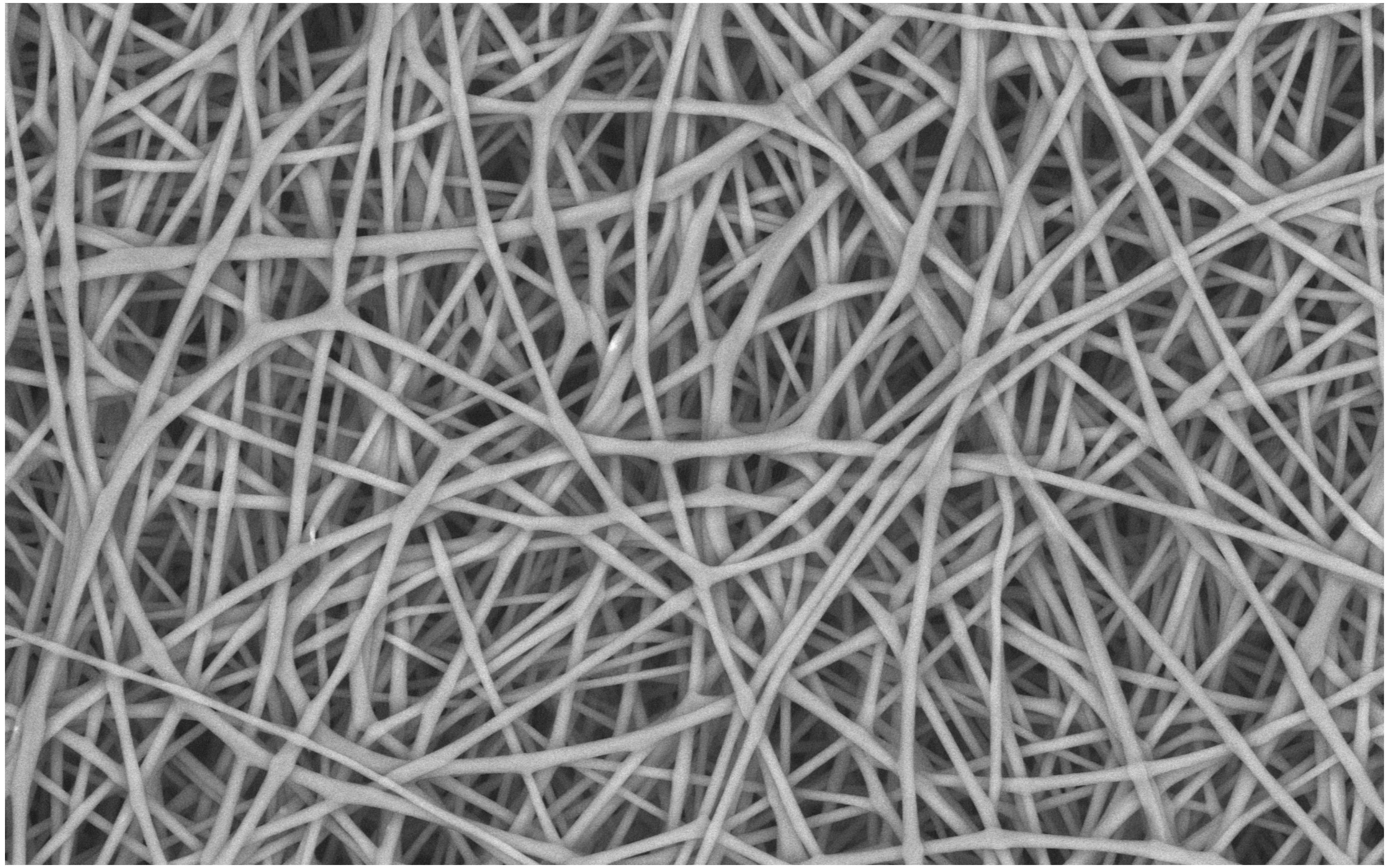


diameter of fibers: 1 mm

Hopkinson D., Sekizkardes, A. K, Hoffman J., Yi S., Kusuma V. US Patent App. 17/891,153

Structured porous adsorbent forms

Electrospun Flat Sheets (30 x 5 cm)



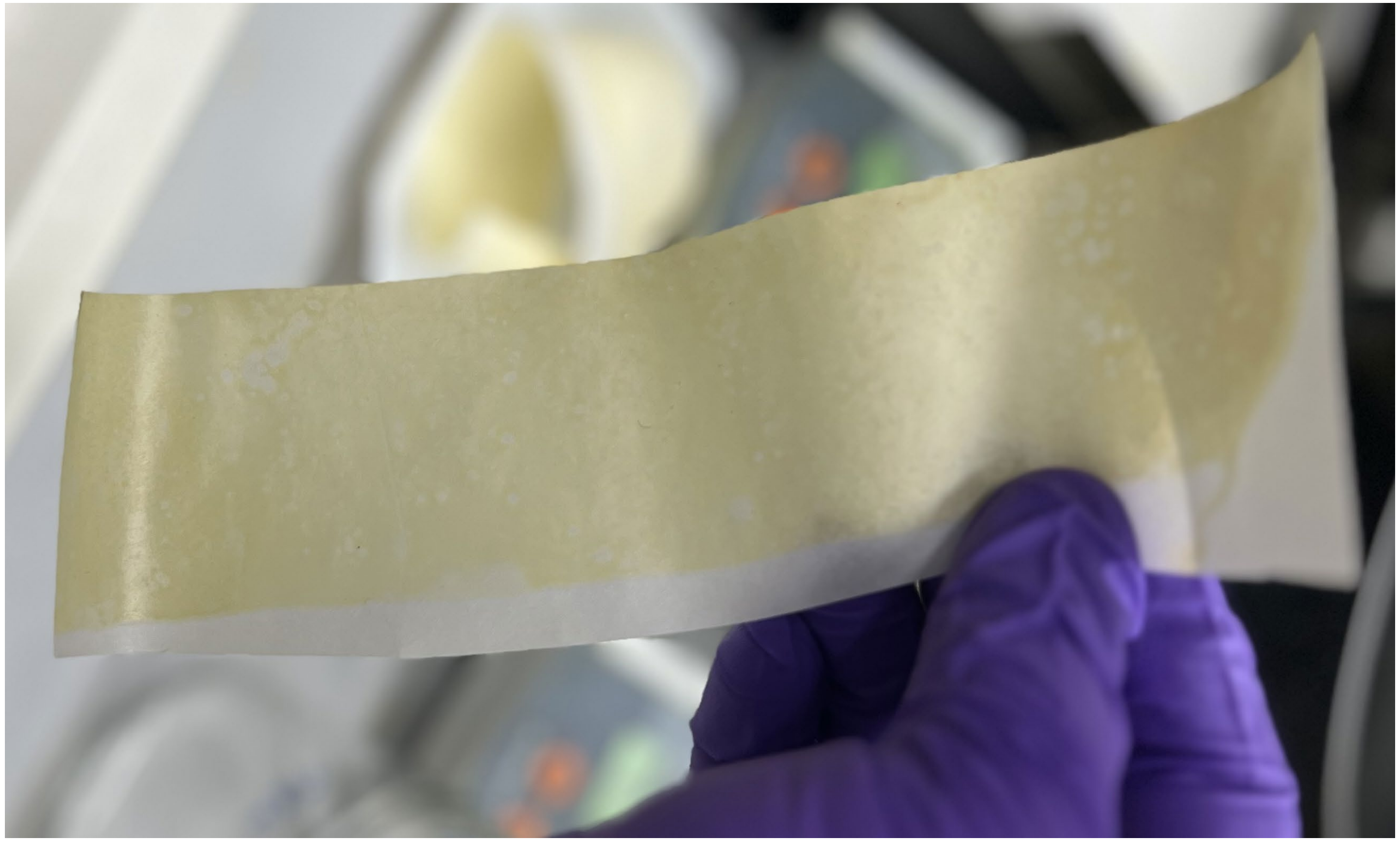
diameter of fibers: 2 micron

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 CO_2/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

NATIONAL ENERGY TECHNOLOGY LABORATORY

Breakthrough Analysis (BTA) Provides a Measure of CO_2 Uptake

- Pristine (un-aged) sample:
  - CO_2 capacity: **1.40** mmol/g

- Aged under N_2 420 ppm CO_2 Dry 75°C
  - After 4 days: CO_2 capacity: **1.36** mmol/g
  - After 7 days: CO_2 capacity: **1.37** mmol/g

- Aged under N_2 420 ppm CO_2 20% O_2 Dry 75°C
  - After 3.5 days: CO_2 capacity: **0.70** mmol/g
  - After 7 days: CO_2 capacity: **0.43** mmol/g

Diminished CO_2 uptake capacity after aging with O_2

Uptake Loss – DAC Center Aging - Humid

Breakthrough Analysis (BTA) Provides a Measure of CO_2 Uptake

- Pristine (un-aged) sample:
  - CO_2 capacity: **1.40** mmol/g

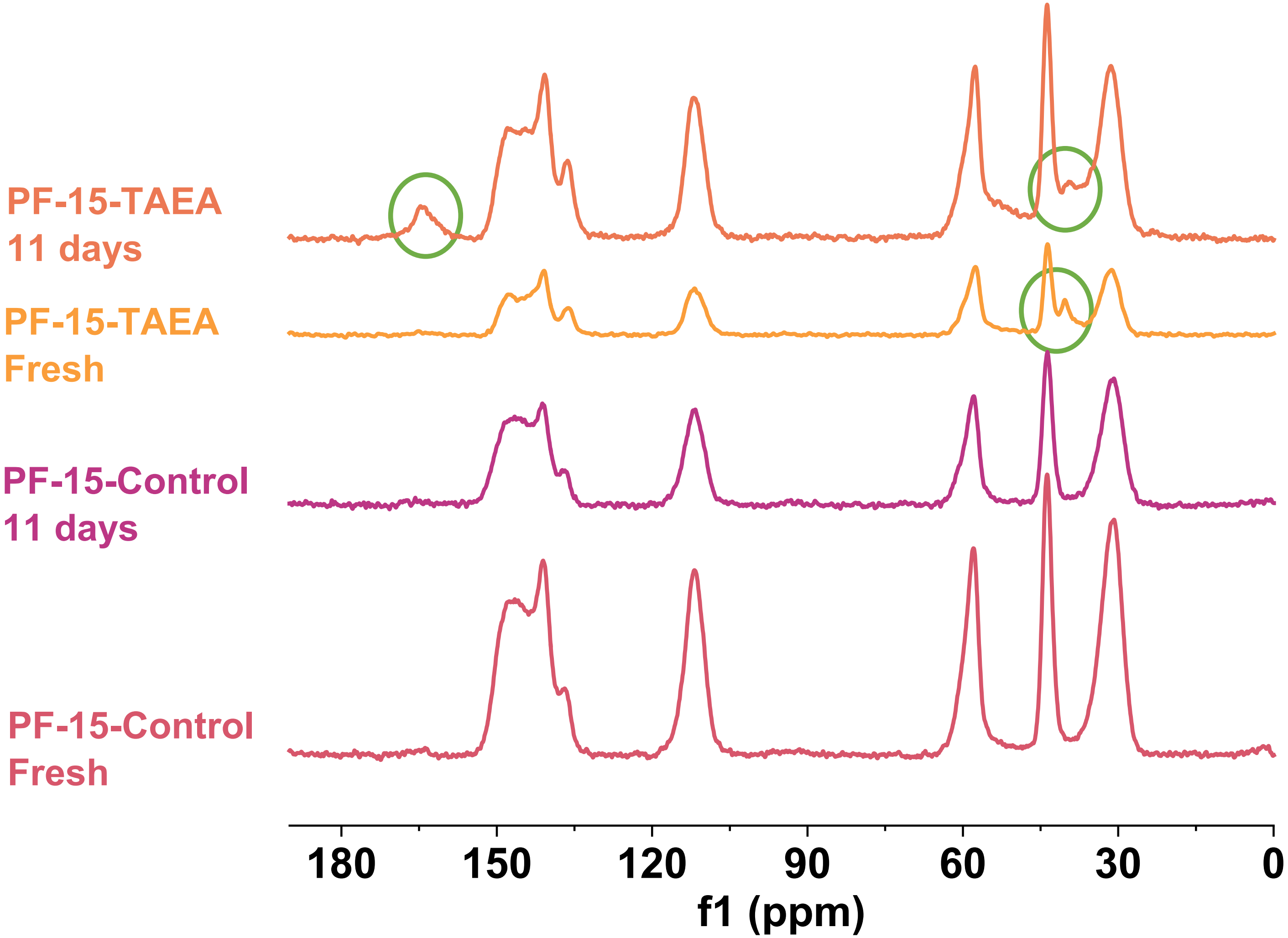
- Aged under house air, (420 ppm CO_2) 40-50% RH, 75°C
  - After 3.5 days: CO_2 capacity: **0.39** mmol/g
  - After 7 days: CO_2 capacity: **0.14** mmol/g

Presence of humidity increases the rate of oxidative degradation

NMR Results for Aging

Solid State NMR Analysis (University of Pittsburgh)

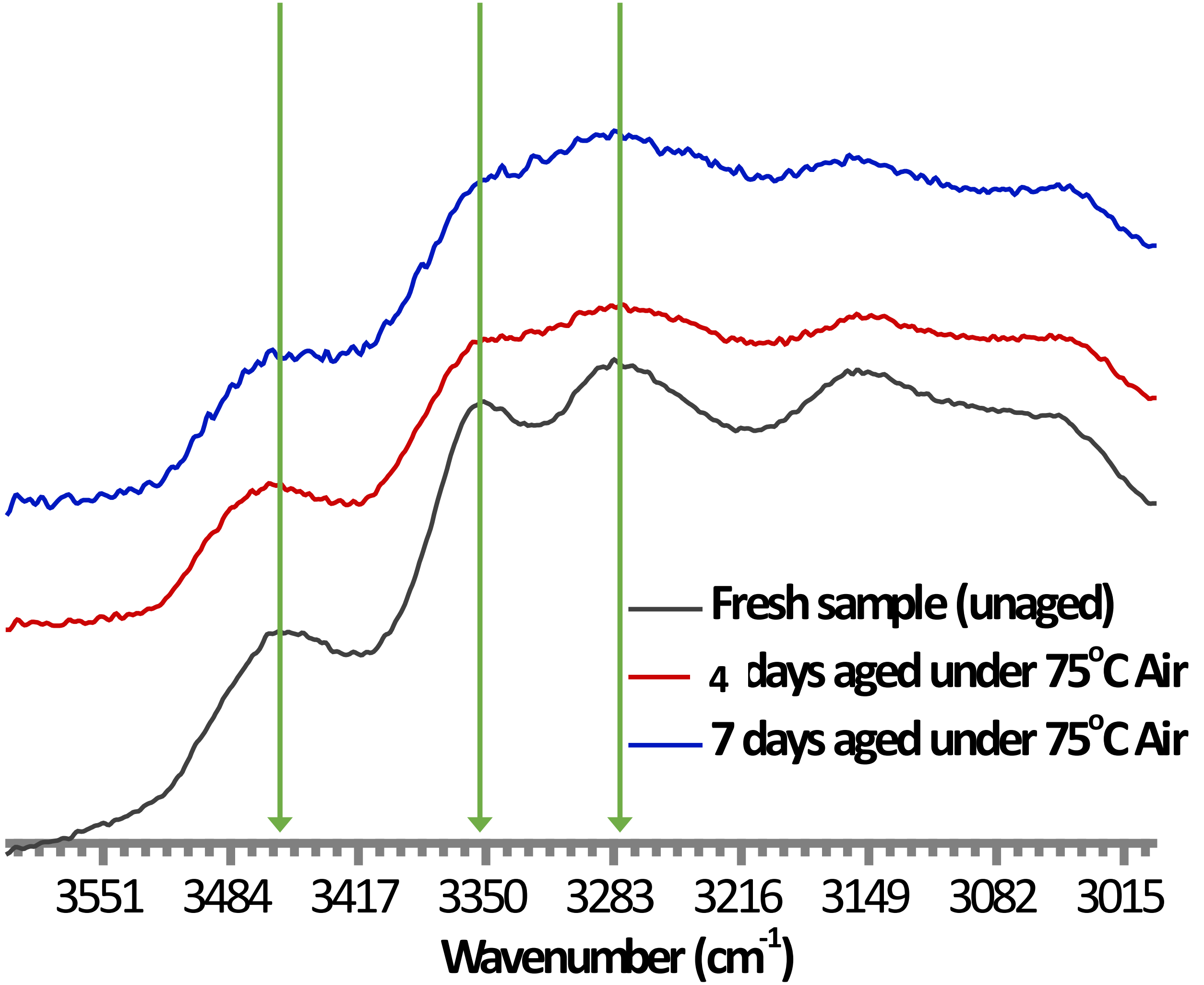
- TAEA Tris(2-aminoethyl)amine
- Aging in oven, 70˚C, RH ambient
- Peak around 160 ppm increasing, associated with degradation
- Peak near 39-40 ppm corresponds to the C near the NH_2 group. Decreasing with aging.
- Natural abundance of ^{13}C is very low, leading to a low signal to noise ratio. We are investigating synthesizing the ^{13}C or ^{15}N versions of the amines.



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 cm^{-1}
  - Disappear with aging
- Aging leads to ***loss of the alkyl amine group*** but not the amidoxime amine group

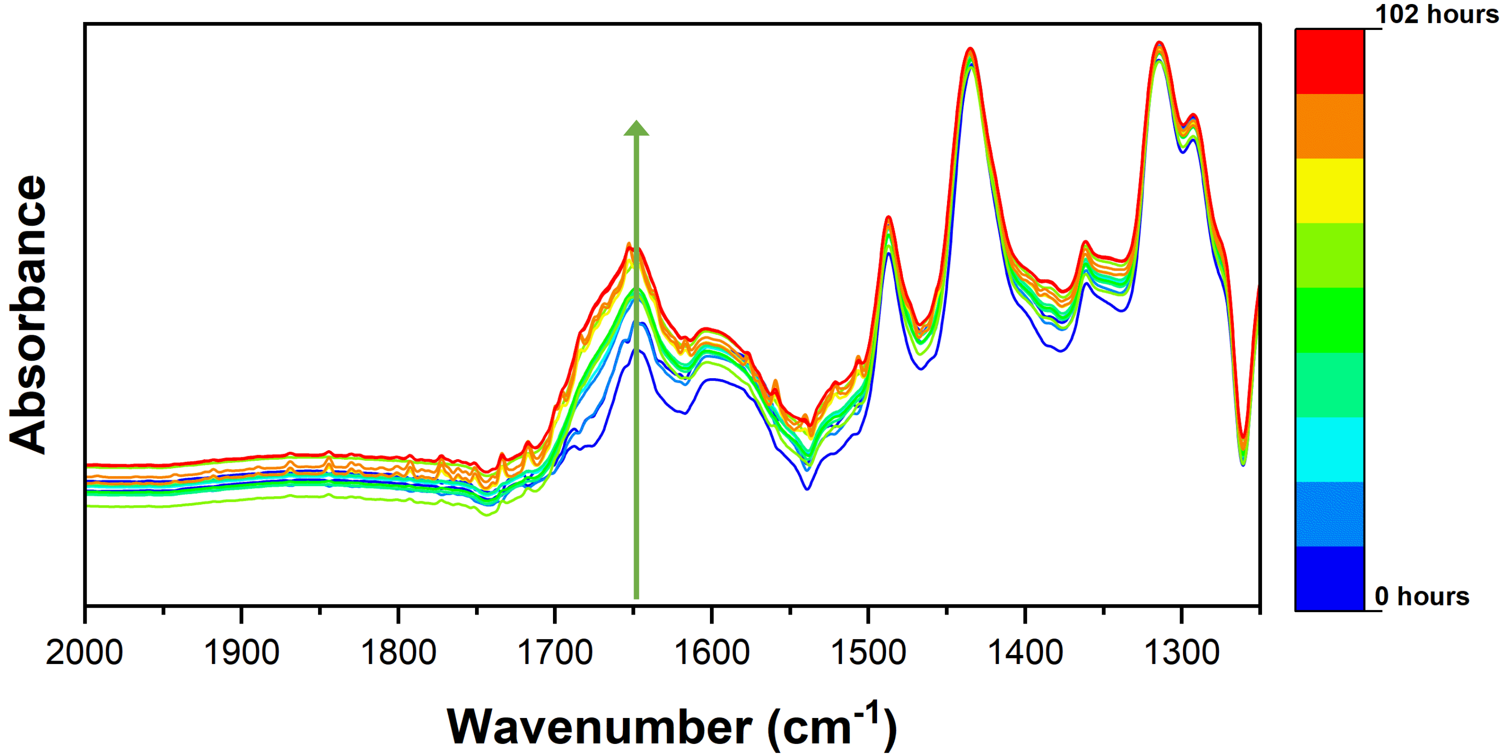


In-Situ Spectroscopic Results for Aging

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.

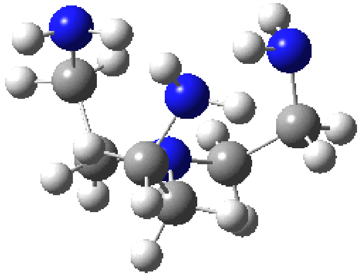
FT-IR in-situ 70˚C, 50% RH air (400 ppm CO_2, 20% O_2, balance N_2).



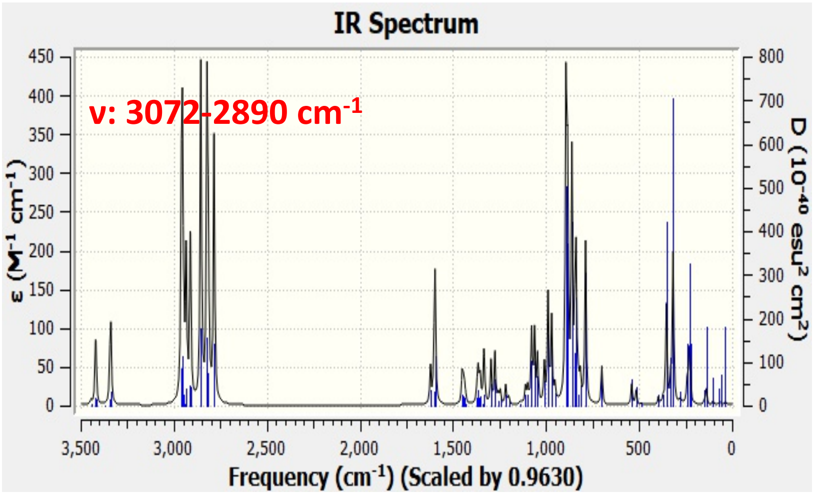
Computational Prediction of FT-IR Spectra

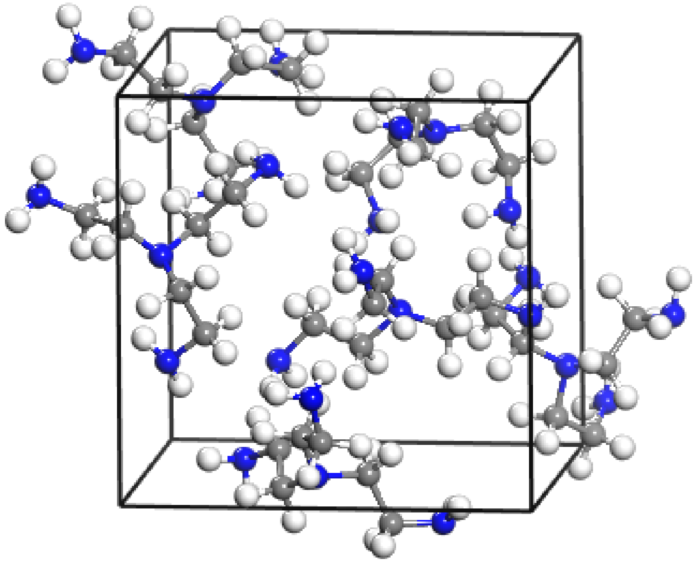
Gas Phase vs Condensed Phase

C-H stretch
3072….2890

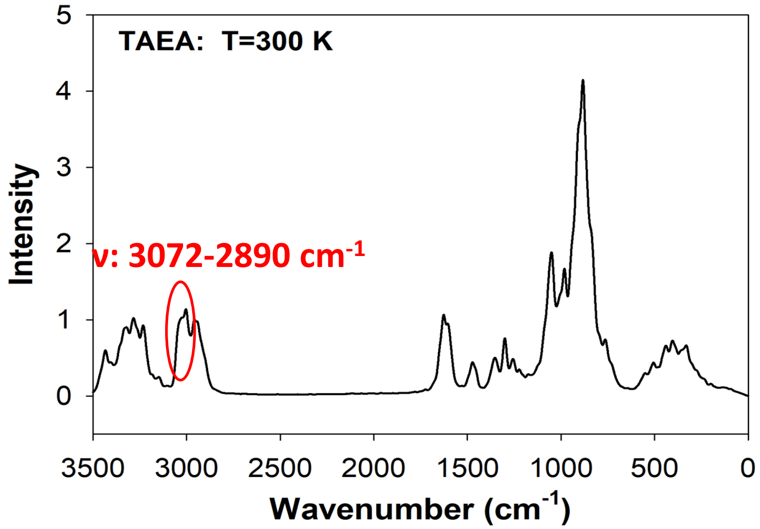


Molecule in the Gas Phase
2nd Deriv. (E / coordinates)
Sharp Distinct Peaks
Clear Interpretation



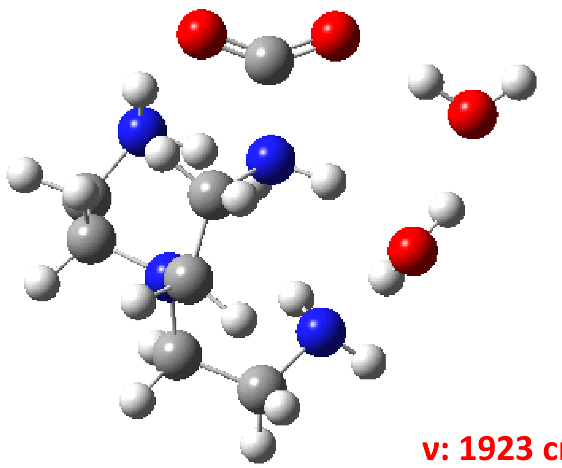


Condensed Phase Model
FT of Dipole Autocorrelation Fxn
Broad Peaks
Includes Complexity, Anharmonicity

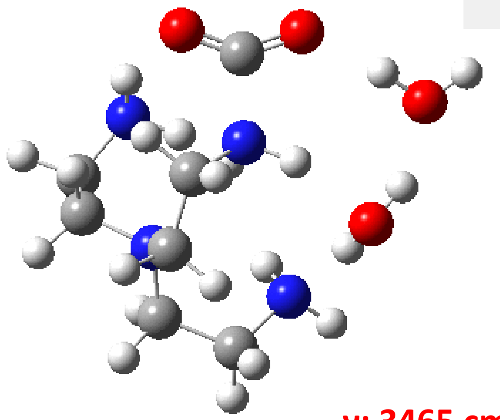


Computational Prediction of FT-IR Spectra

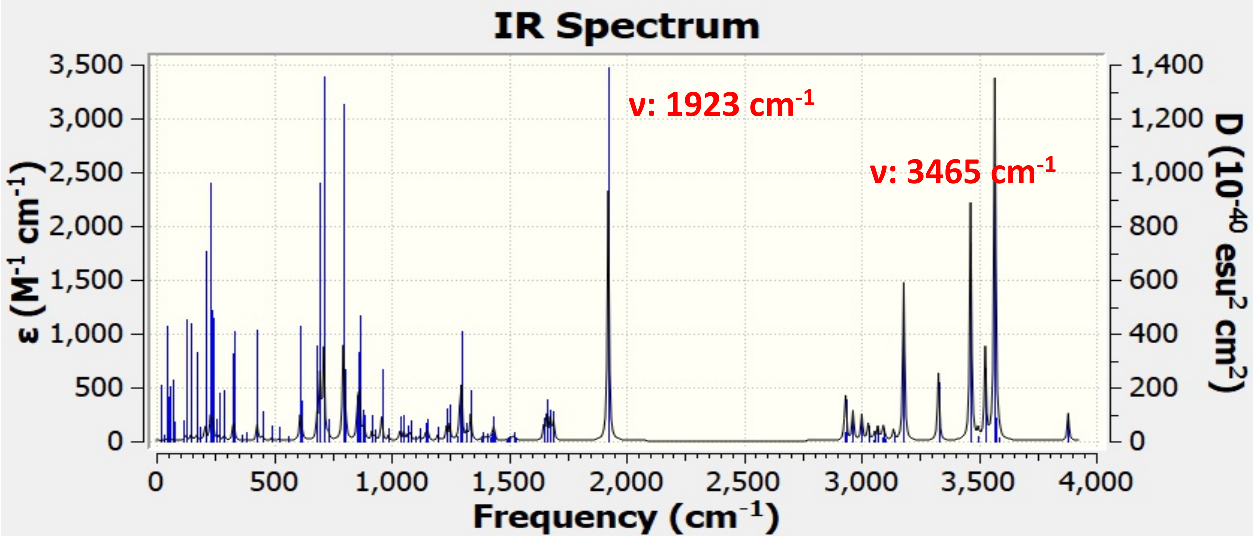
Gas Phase Predictions Useful for Understanding Spectral Evidence of Amine + CO_2 Reaction, Stabilization Provided by Water



v: 1923 cm^{-1}

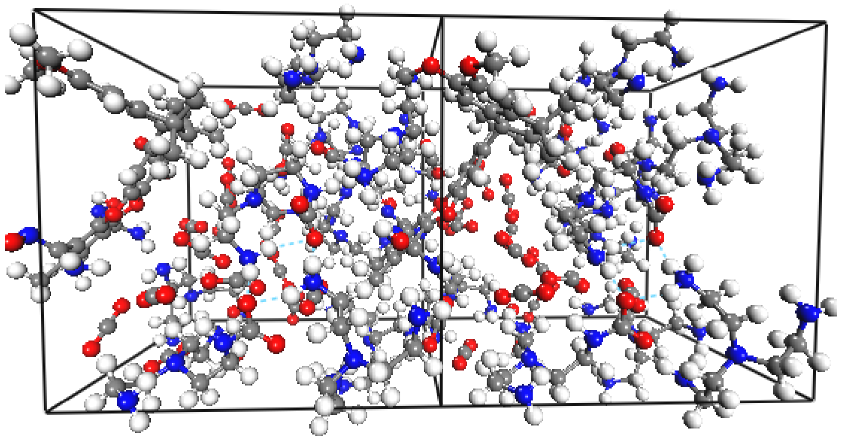


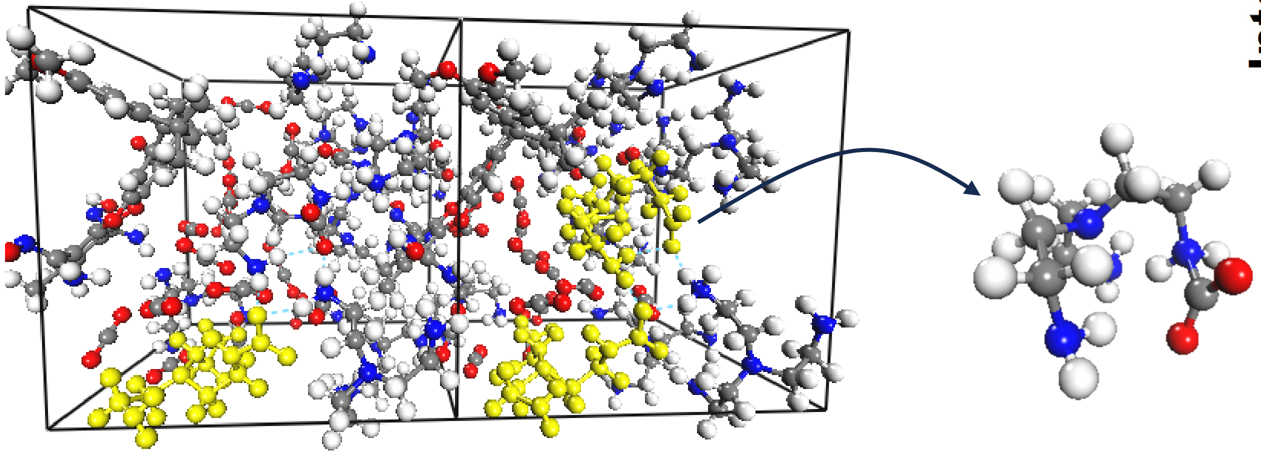
v: 3465 cm^{-1}

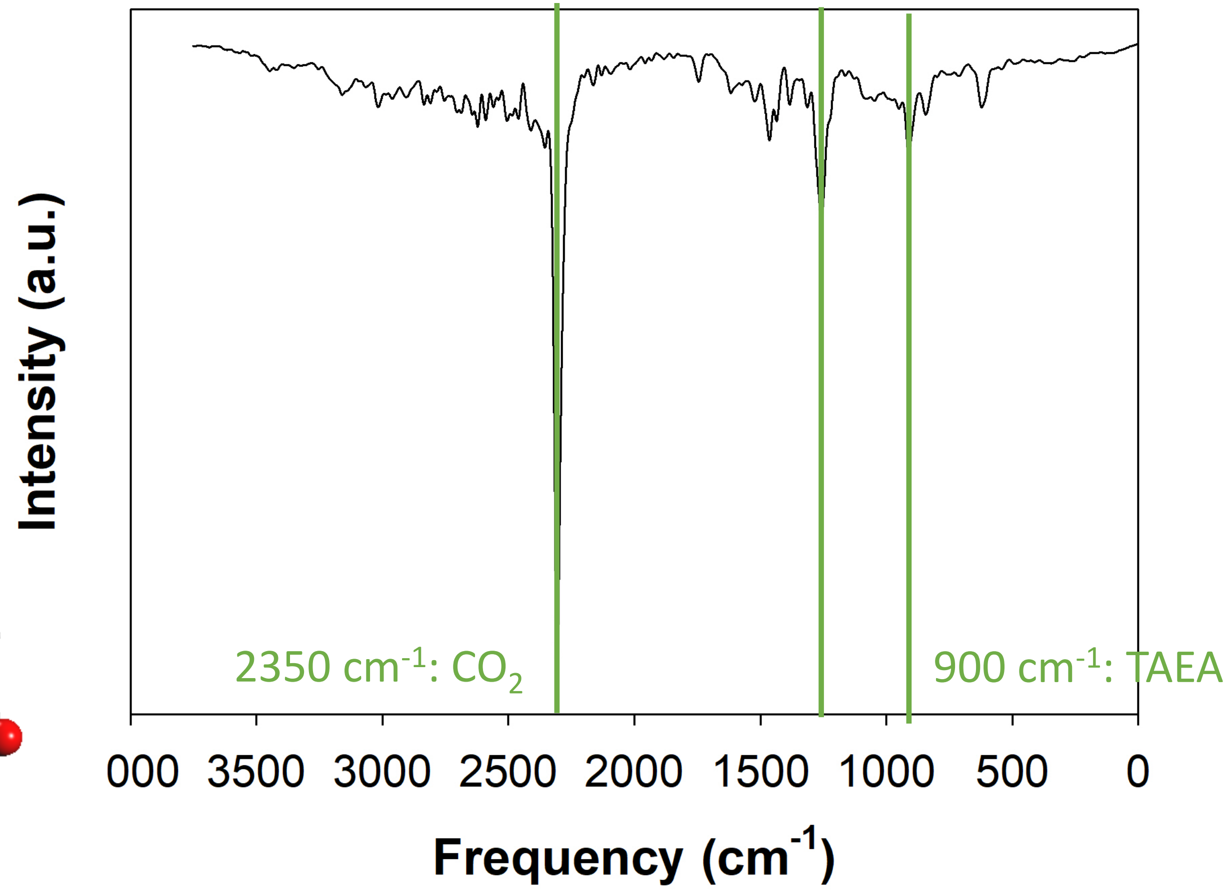


Computational Prediction of FT-IR Spectra

Condensed Phase Simulations: Pristine PIM1-AO + 10 TAEA + 10 CO_2







Conclusions and Future Work

Conclusions

- Oxidative degradation observed after heat ~70˚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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