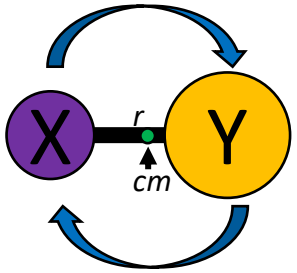
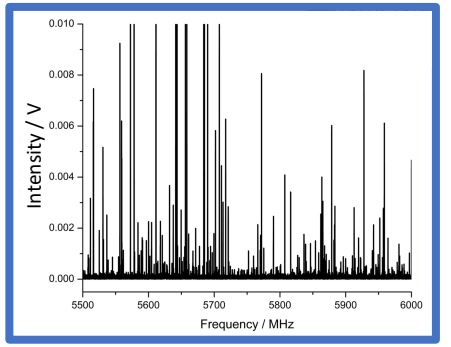




Spectroscopic models of CO_2 microsolvation: Bringing data analytics techniques to undergraduate physical chemistry research

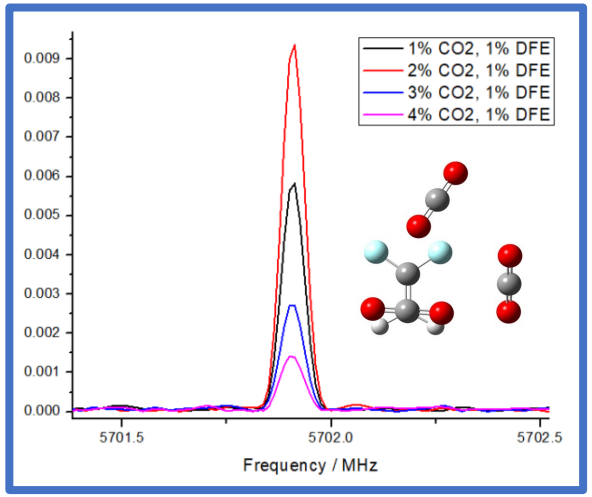
Rebecca A. Peebles, Sean A. Peebles, Prashansa B. Kannangara,[m]

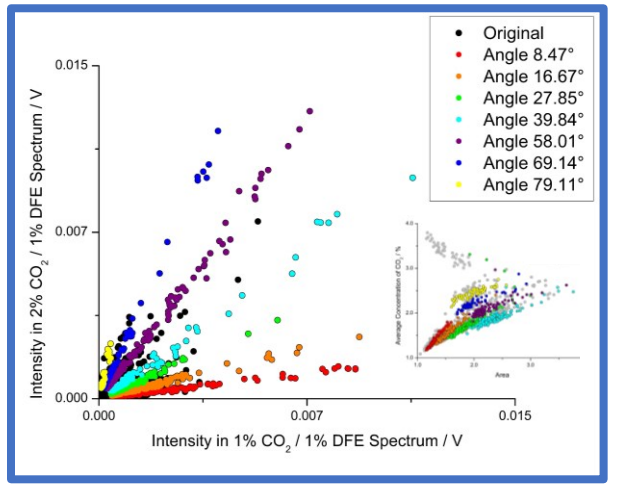
Hannah L. Fino,*,[m] Melissa A. Martinez,* Tulana Ariyaratne[m]

Department of Chemistry, Eastern Illinois University, Charleston, IL

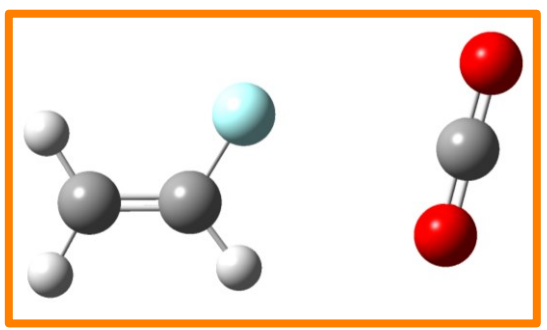
Channing T. West, Brooks H. Pate

Department of Chemistry, The University of Virginia, Charlottesville, VA

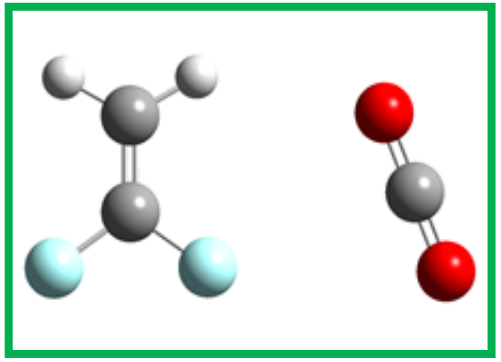




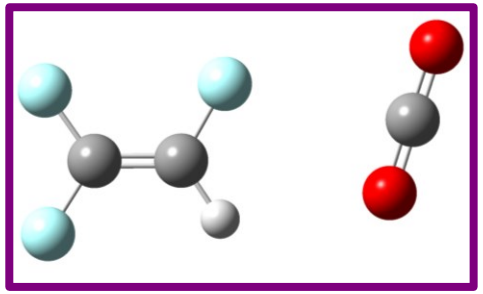
Increasing Fluorination



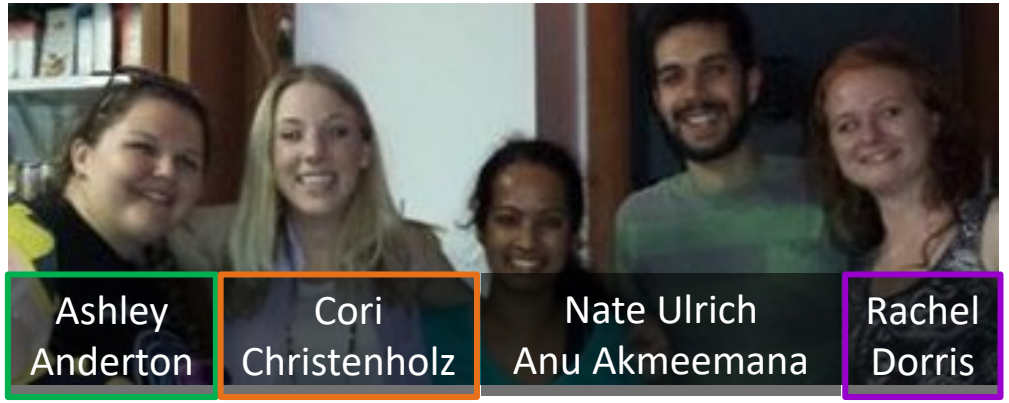
Fluoroethylene (FE)-CO_2



Difluoroethylene (DFE)-CO_2



Trifluoroethylene (TFE)-CO_2

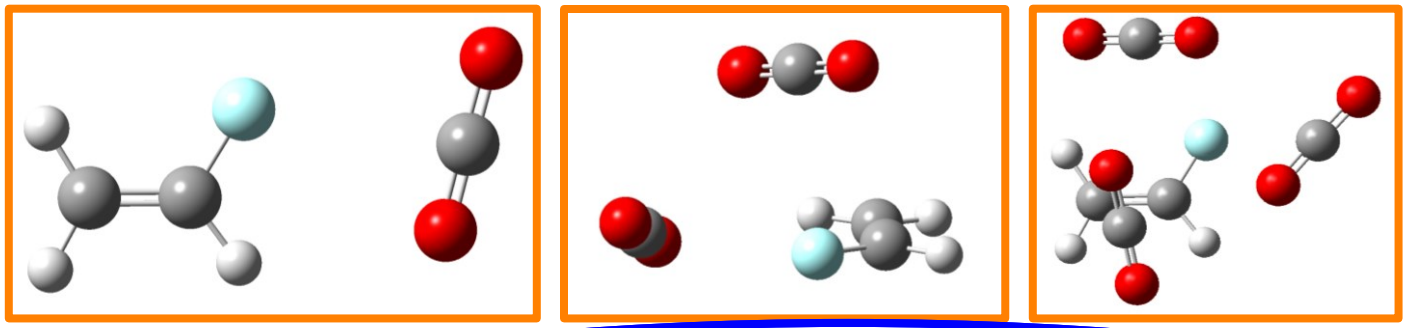


FE: P.B. Kannangara,[m] C.T. West, B.H. Pate, S.A. Peebles, R.A. Peebles, Chem. Phys. Lett., 2018, 706, 538.
P.B. Kannangara, [m] MS Thesis, Eastern Illinois University, 2019.
C.L. Christenholz,* R.E. Dorris,* R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2014, 118, 8765.

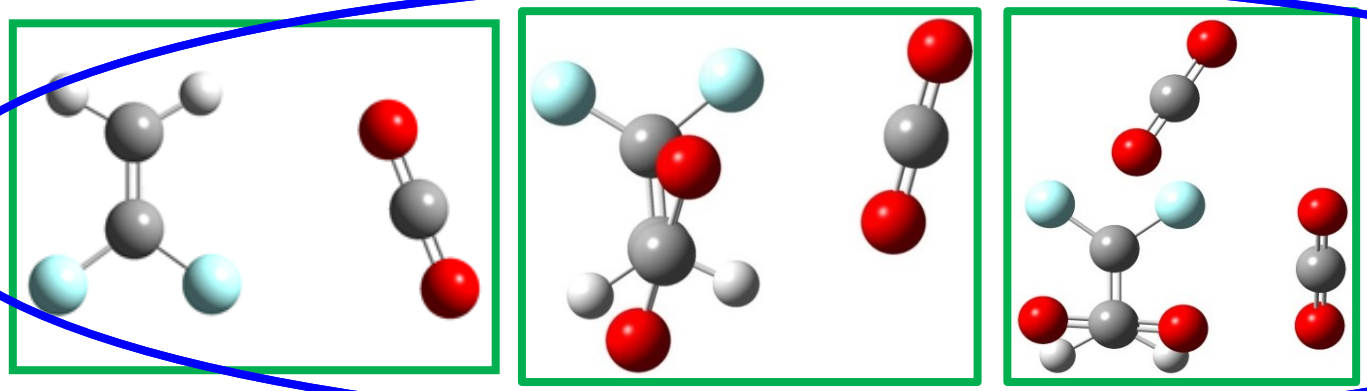
DFE: T. Ariyaratne, [m] MS Thesis, Eastern Illinois University, 2019.
A.M. Anderton,* R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2016, 120, 247.
TFE: R.E. Dorris,* W.C. Trendell, [m] R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2016, 120, 7865.

Increasing CO_2

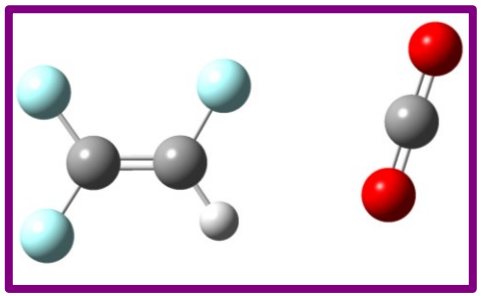
Increasing Fluorination



Fluoroethylene (FE)-CO_2 Clusters



Difluoroethylene (DFE)-CO_2 Clusters



Trifluoroethylene (TFE)-CO_2 Clusters

FE: P.B. Kannangara,[m] C.T. West, B.H. Pate, S.A. Peebles, R.A. Peebles, Chem. Phys. Lett., 2018, 706, 538.
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C.L. Christenholz,* R.E. Dorris,* R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2014, 118, 8765.

DFE: T. Ariyaratne, [m] MS Thesis, Eastern Illinois University, 2019.
A.M. Anderton,* R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2016, 120, 247.
TFE: R.E. Dorris,* W.C. Trendell, [m] R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2016, 120, 7865.

Why look at larger clusters?

- Practical:
  - Can we learn something about the properties of supercritical CO_2?

- Fundamental:
  - Many-body effects
  - Isomers
  - Data for improvement of theoretical models

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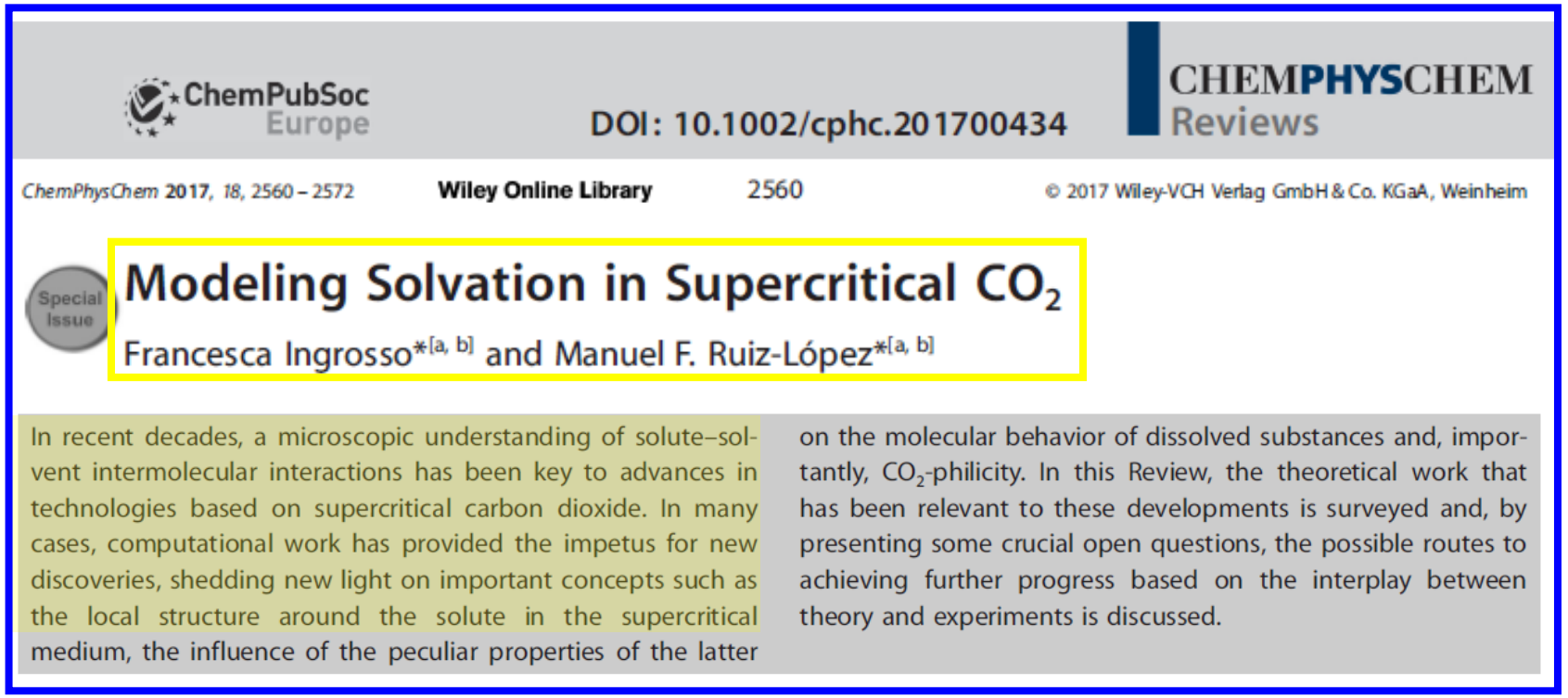

ChemPubSoc Europe
DOI: 10.1002/cphc.201700434
CHEMPHYSCHEM Reviews
ChemPhysChem **2017**, *18*, 2560 – 2572 **Wiley Online Library** 2560

Special Issue

Modeling Solvation in Supercritical CO_2

Francesca Ingrosso*[a, b] and Manuel F. Ruiz-López*[a, b]

In recent decades, a microscopic understanding of solute–solvent intermolecular interactions has been key to advances in technologies based on supercritical carbon dioxide. In many cases, computational work has provided the impetus for new discoveries, shedding new light on important concepts such as the local structure around the solute in the supercritical medium, the influence of the peculiar properties of the latter on the molecular behavior of dissolved substances and, importantly, CO_2-philicity. In this Review, the theoretical work that has been relevant to these developments is surveyed and, by presenting some crucial open questions, the possible routes to achieving further progress based on the interplay between theory and experiments is discussed.

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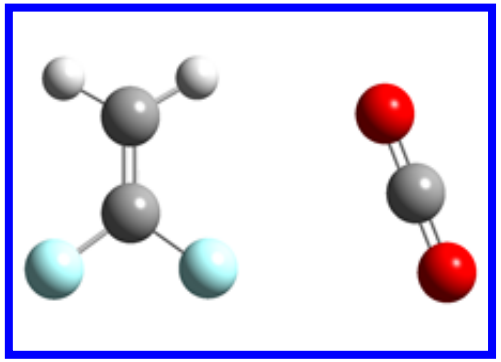
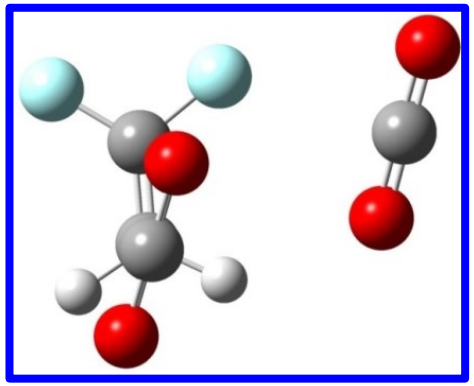
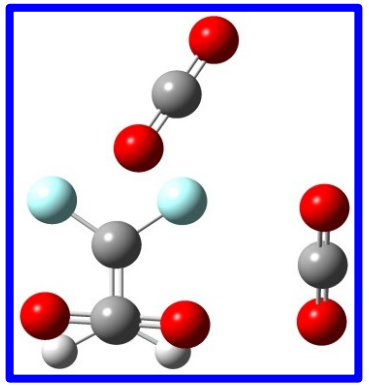
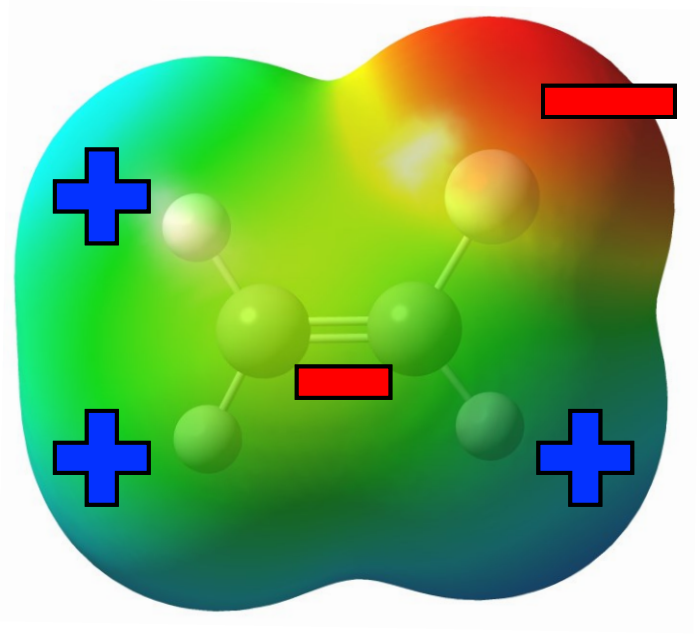
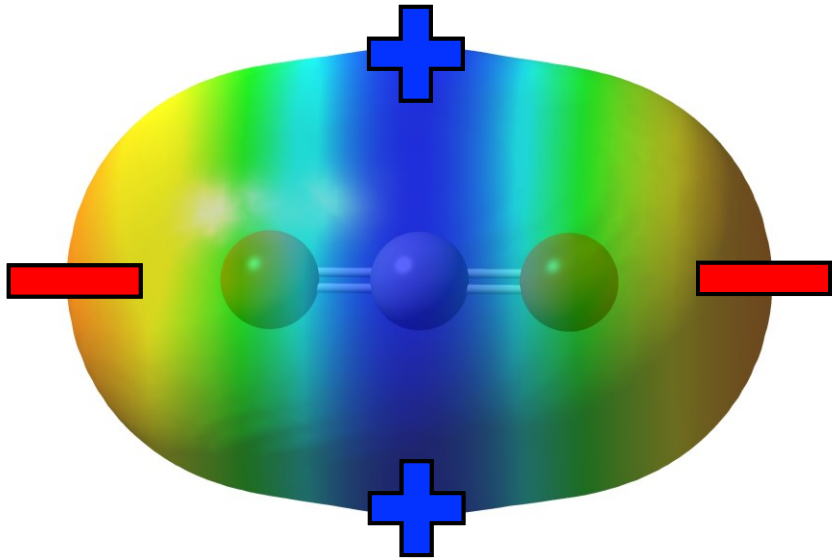
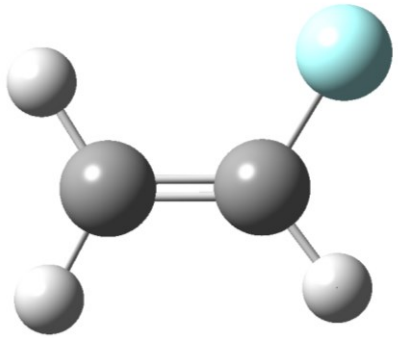
- Fundamental:
  - Many-body effects
  - Isomers
  - Data for improvement of theoretical models

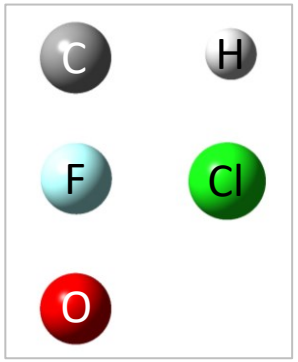
How and why do molecules “stick”?







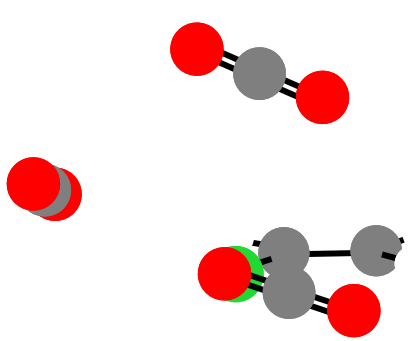
Fluoroethylene (FE)



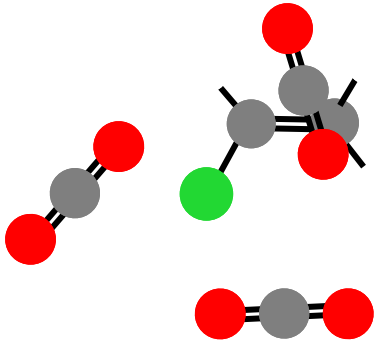
Carbon Dioxide (CO_2)

Larger Solvation Shells?

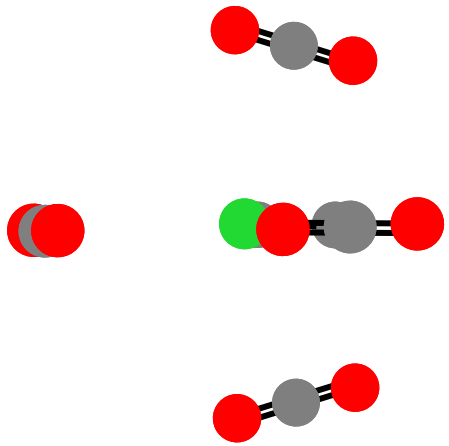
- Two FE-CO_2-CO_2 trimers observed
  - Nearly isoenergetic
- Tetramer?
- Pentamer? Hexamer?
  - How far can we go?!



$FE(CO_2)_3$



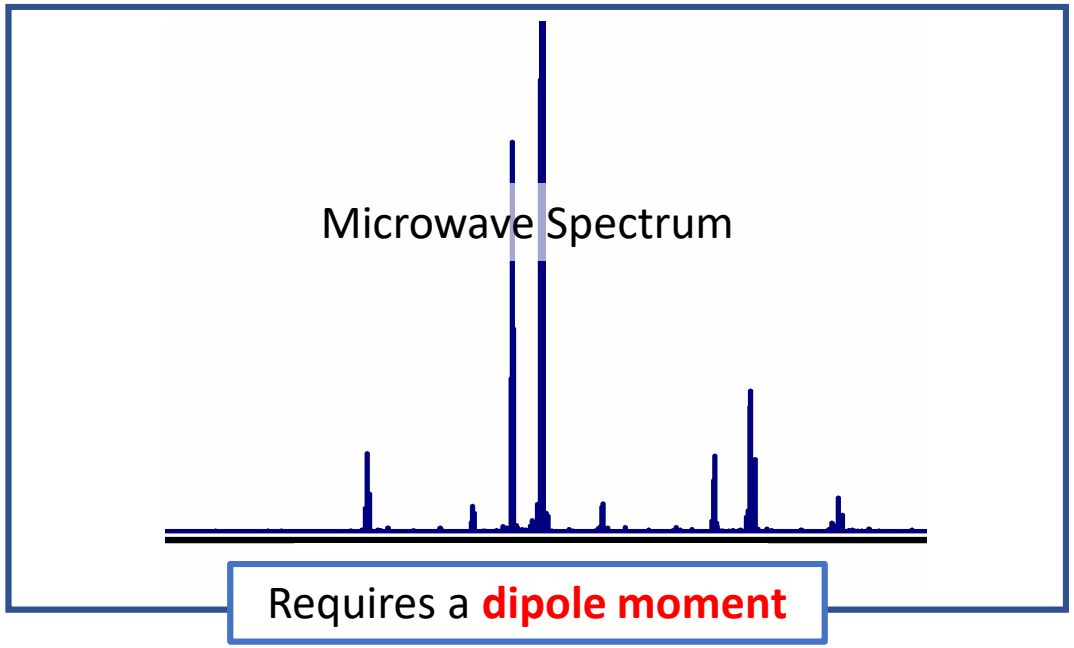
$FE(CO_2)_3$

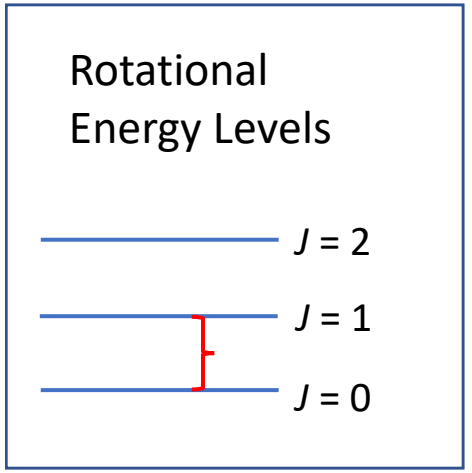


$FE(CO_2)_4$

Computational work:
- Gaussian 09 or G09W
  - MP2/6-311++G(2d,2p) or ωB97X-D/6-31+G(d,p)
- ABCluster
  - xtb for optimization

ABCluster: J. Zhang, M. Dolg, ABCluster: The Artificial Bee Colony Algorithm for Cluster Global Optimization. Phys. Chem. Chem. Phys., 2015, 17, 24173.
Zhang, J.; Dolg, M. Global Optimization of Rigid Molecular Clusters by the Artificial Bee Colony Algorithm. Phys. Chem. Chem. Phys., 2016, 18, 3003.
Xtb: C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher, S. Grimme, WIREs Comput. Mol. Sci., 2020, 11, e01493; https://www.chemie.uni-bonn.de/pctc/mulliken-center/software/xtb/xtb

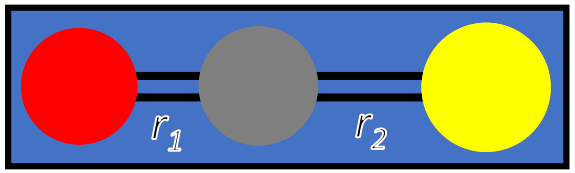




A, B, C
Rotational Constants

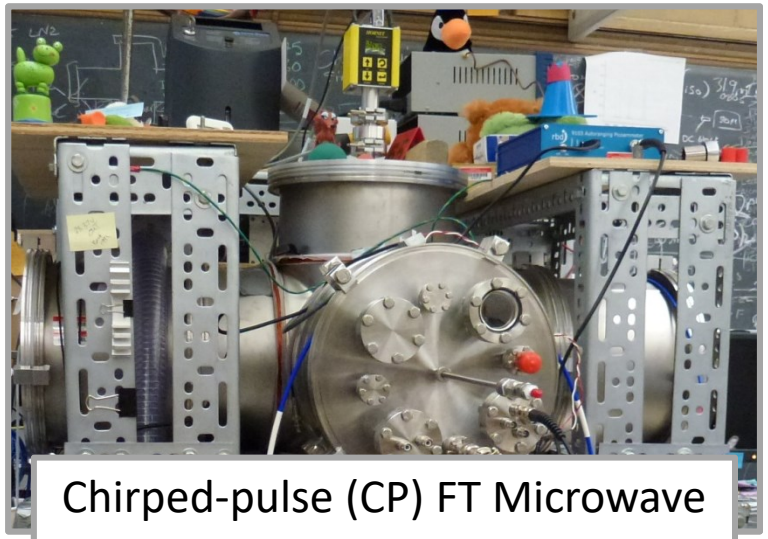
$$B = \frac{h}{8\pi^2 I_b}$$
Moments of Inertia

$I = \Sigma mr^2$
Distances



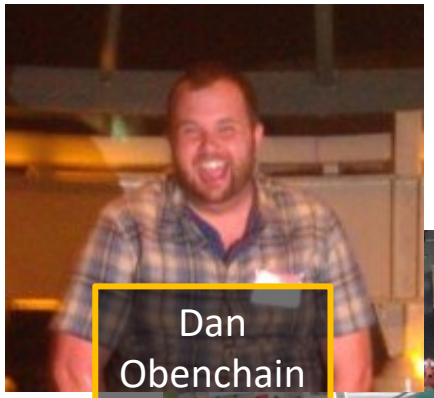
Instrumentation

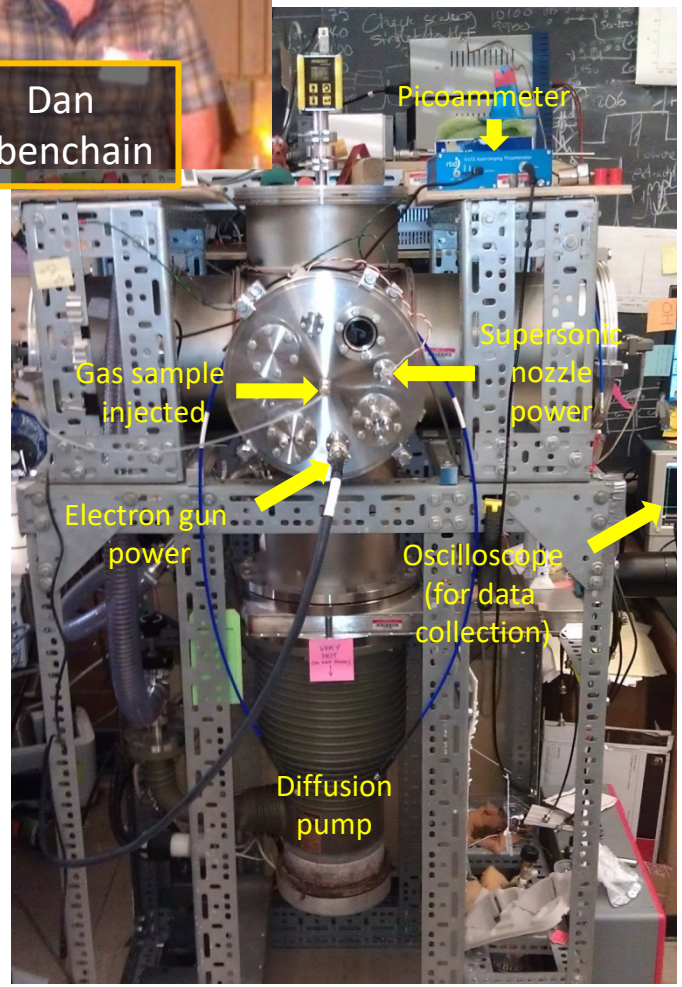
Fourier-Transform Microwave (FTMW) Spectrometer

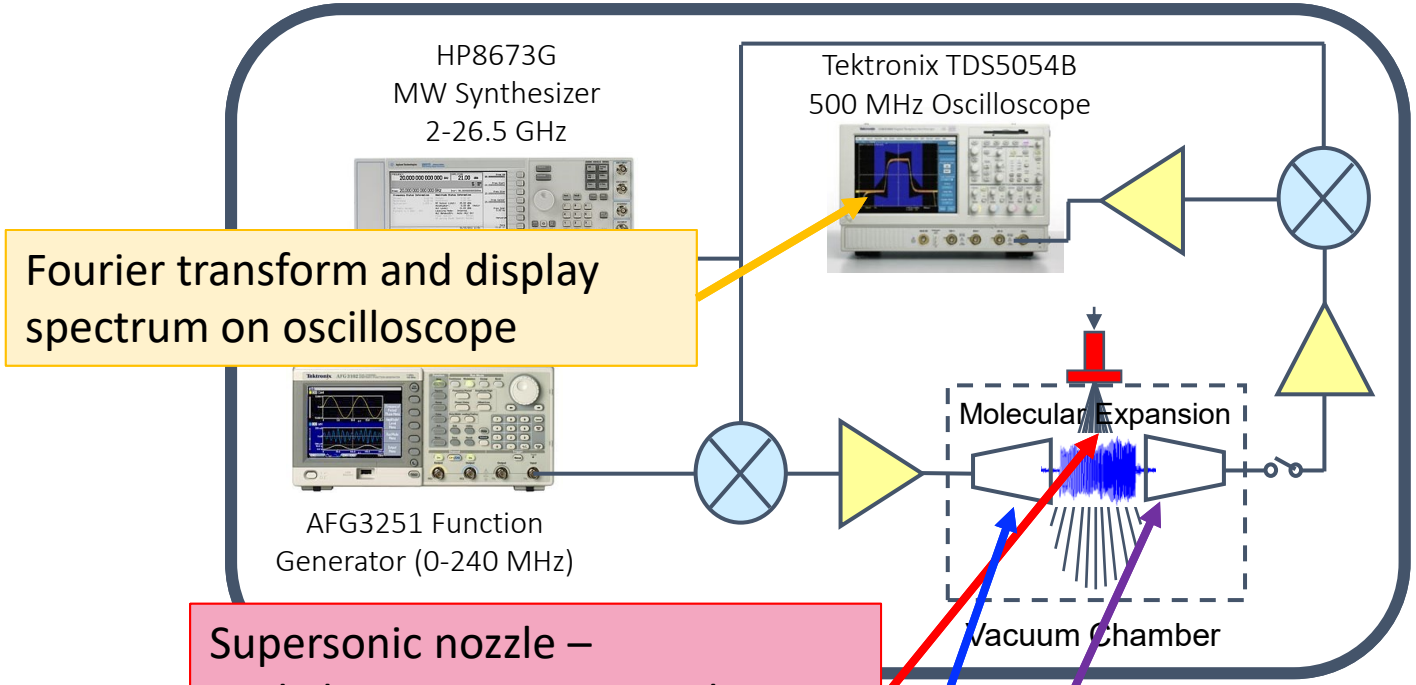


Chirped-pulse (CP) FT Microwave Spectrometer

Prof. Brooks Pate
UVa CP-FTMW Spectrometer







Supersonic nozzle –
- Adiabatic expansion cools gas to ~5 Kelvin

Irradiate gas with wide frequency range of microwaves

“Listen” as absorbing molecules emit a few specific microwave frequencies

Chirped-Pulse

icrowave (CP-

r

- 480 MHz bandwidth

les and assemble into full

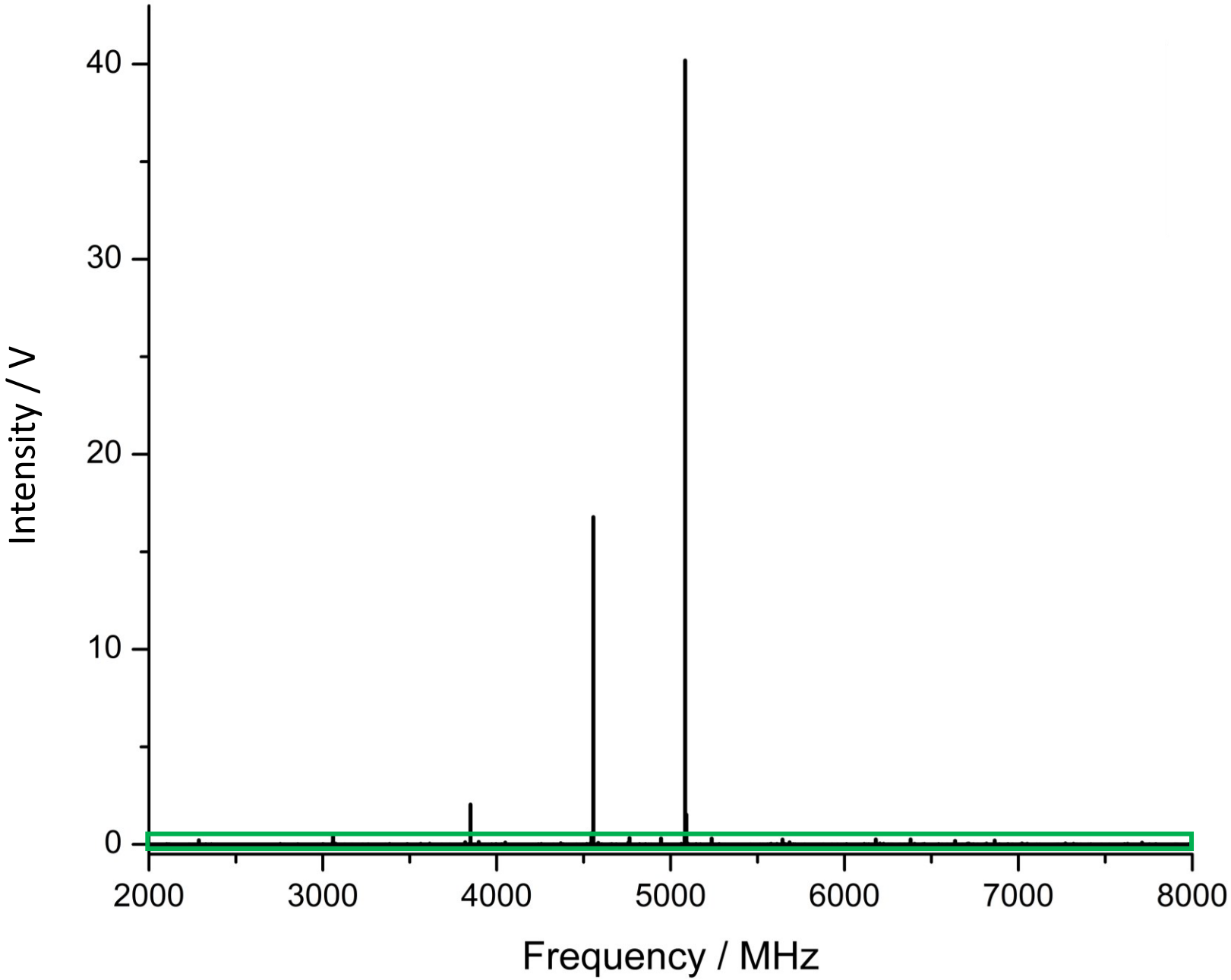
VIEW

- Typically scan a full (10k average) spectrum in 1 day

EIU CP-FTMW: D.A. Obenchain,* A.A. Elliott,[m] A.L Steber,* R.A. Peebles, S.A. Peebles, C.J. Wurrey, G.A. Guirgis, J. Mol. Spectrosc., 2010, 261, 35.

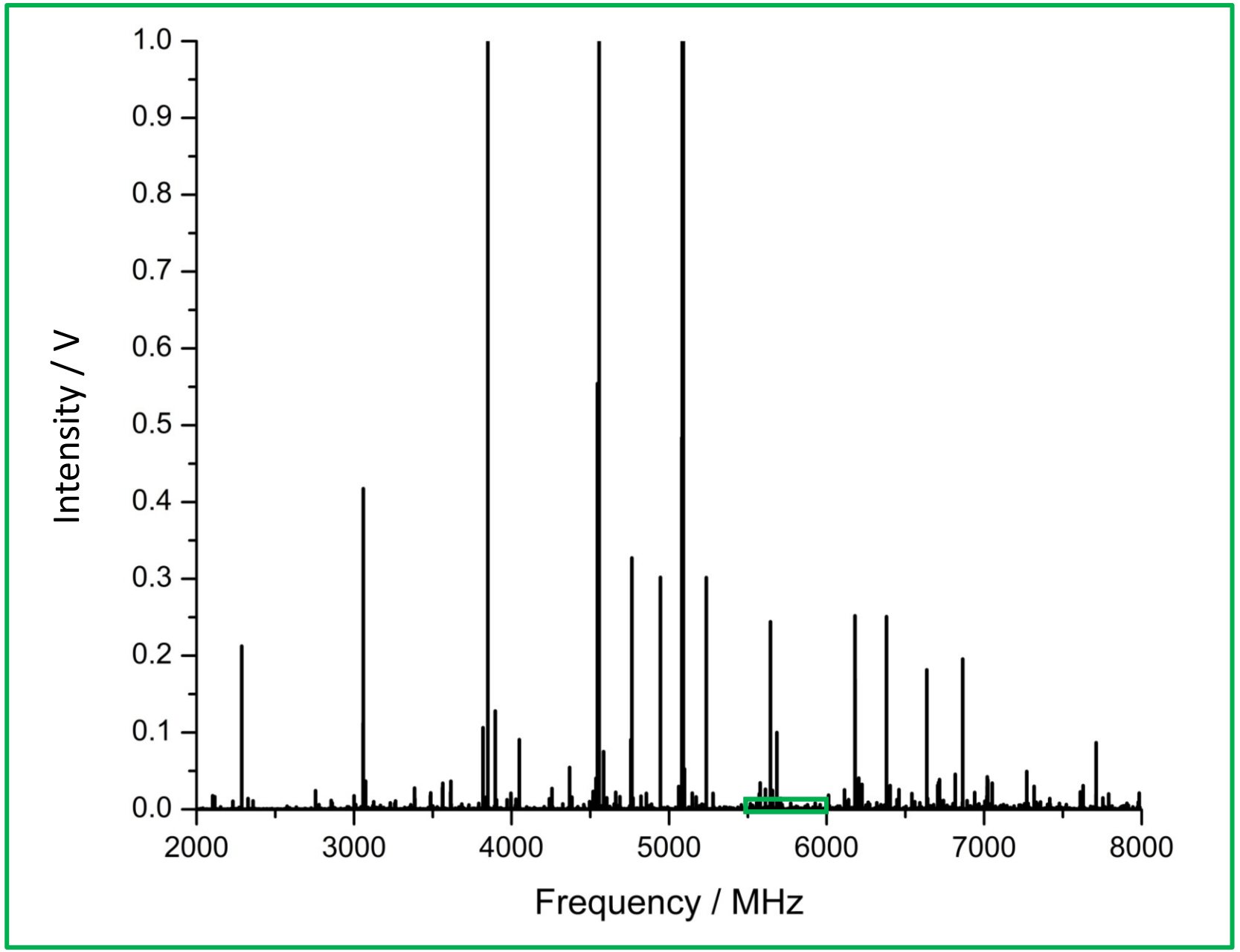
UVa CP-FTMW: G.G. Brown, B.C. Dian, K.O. Douglass, S.M. Geyer, S.T. Shipman, B.H. Pate, Rev. Sci. Instrum., 2008, 79, 53103.

1% Difluoroetheylene (DFE) + 1% CO_2 in ~2 atm Neon – 400,000 FID Average



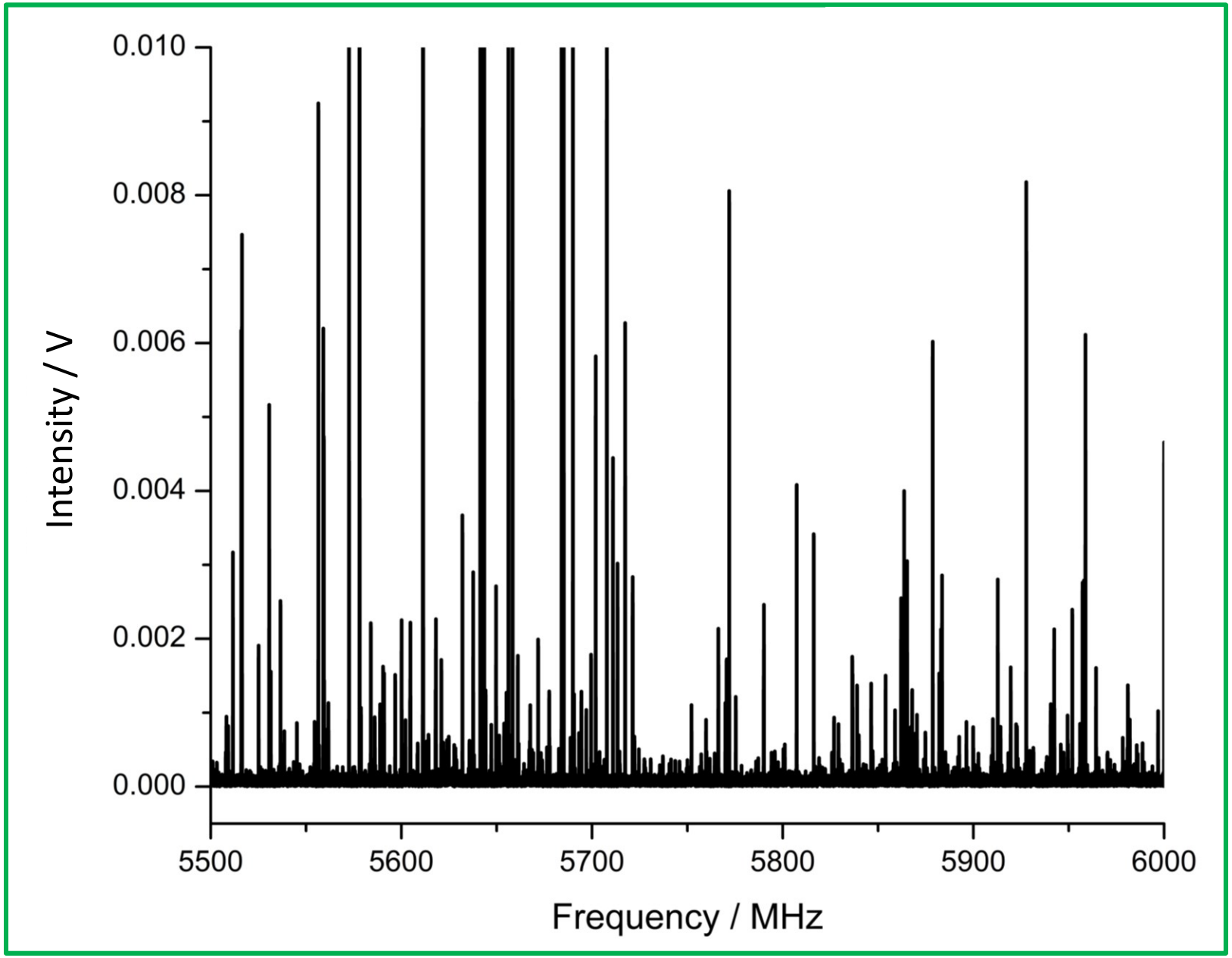
1% Difluoroetheylene (DFE) + 1% CO_2 in ~2 atm Neon – 400,000 FID Average

Dimer level:
Vertical scale times ~40



1% Difluoroetheylene (DFE) + 1% CO_2 in ~2 atm Neon – 400,000 FID Average

Trimer/Tetramer level: Vertical scale times 100 relative to dimer

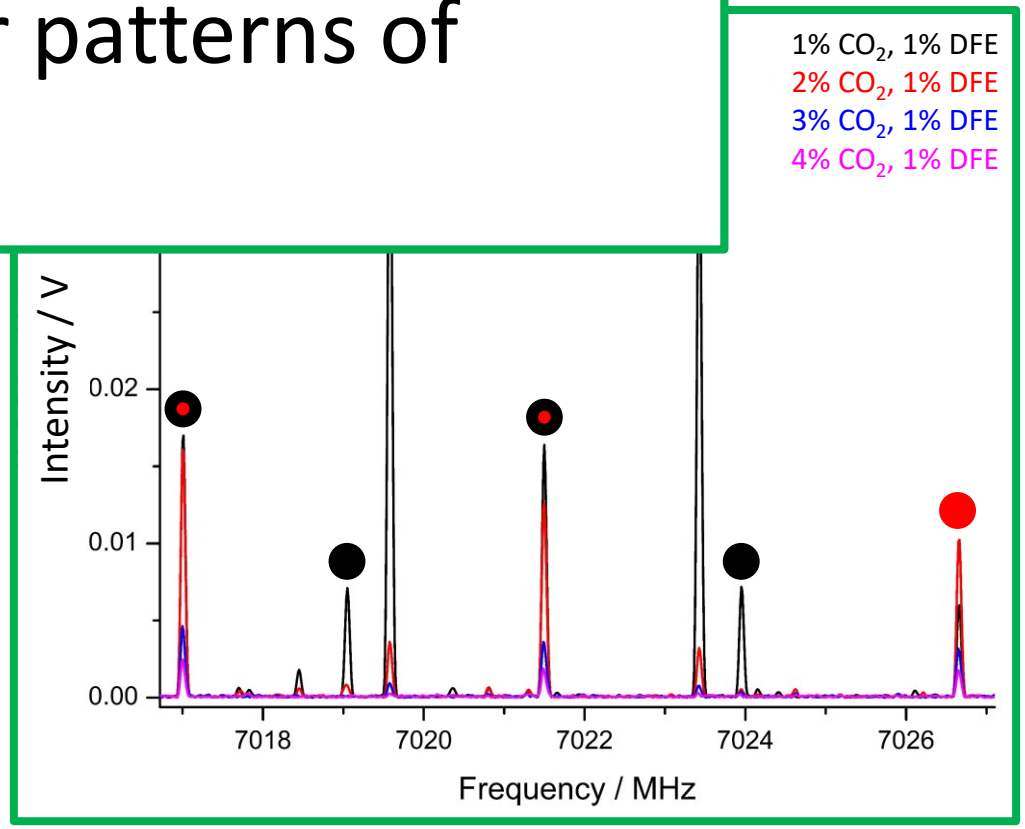


Goals and Experimental Approach

- Distinguish individual spectra from data sets containing complex mixtures
- Automated or semi-automated process
- Prefe

Hypothesis: Transitions of the same species will have similar patterns of intensity variation

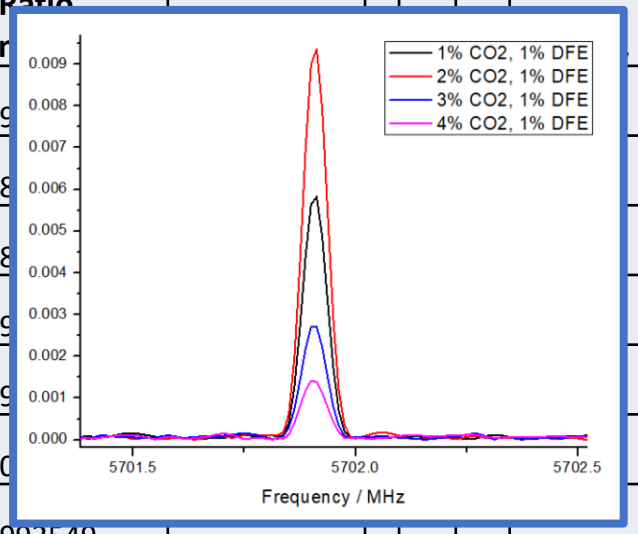
- Record
  system
  - Concentration
  - Pressure
  - Temperature
- Characterize transitions based on pattern of intensity variation

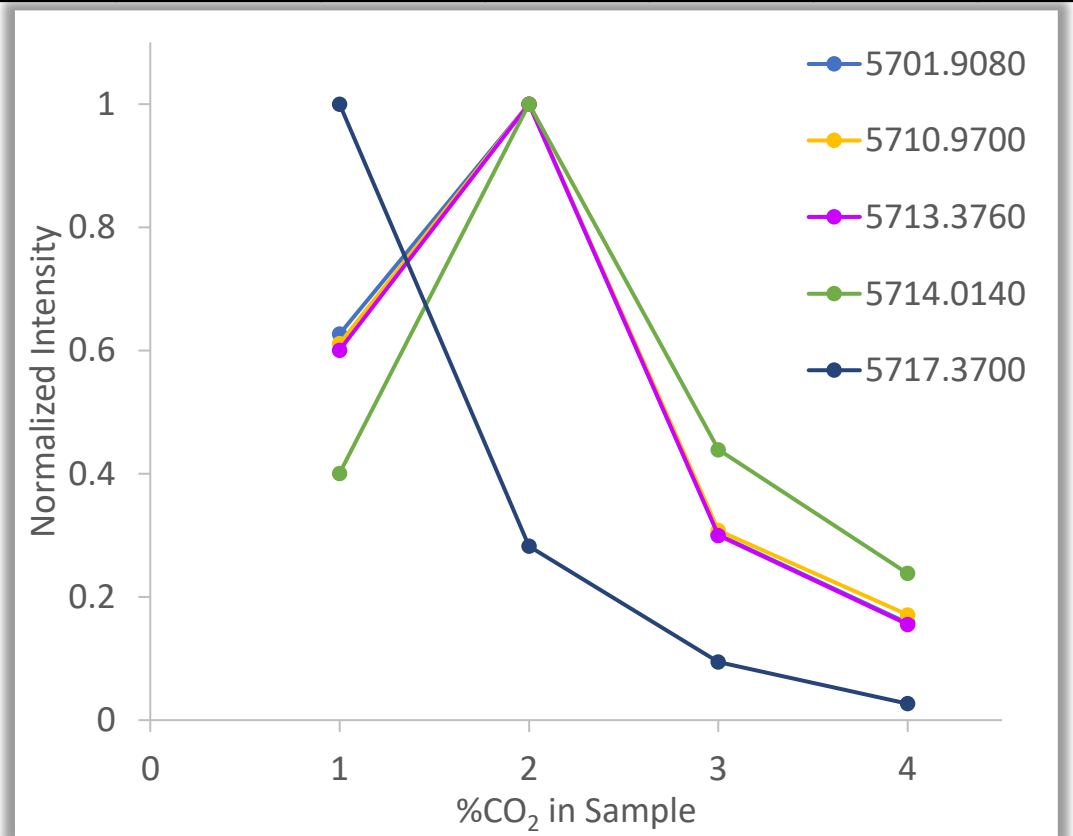


For implementation in course-based research experience at UVa, see, for example, ISMS 2019 Talk TL07, Rotational Spectroscopy of Flavor Compounds in Peach Brandy for Process Monitoring in Craft Distilleries, C.T. West, et al, http://hdl.handle.net/2142/104456.

Freq / MHz	Normalized I (whole spec)	I 1%	I 2%	I 3%	I 4%	I Ratio (2%/1%)	Area	<Conc>	Width	Ratio (<Cor	b, c)
5701.9080	0.2056699	0.0056380	0.0089929	0.0027093	0.0014197	1.5950465	2.086081	1.995237	0.864660	0.9	
5703.9600	0.0120317	0.0004683	0.0005159	0.0001074	0.0001068	1.1017008	2.322799	1.877021	0.906425	0.8	
5707.7580	0.3117358	0.013873		0015370		0.8450851	2.185809	1.749068	0.838130	0.8	
5710.9700	0.1604804	0.004342		0012158		1.6355032	2.090518	2.018576	0.875760	0.9	
5713.3760	0.1093947	0.0030180			0.0007815	1.6644566	2.056452	2.005077	0.860621	0.9	
5714.0140	0.0220617	0.0004058	0.0010130	0.0004449	0.0002414	2.4959139	2.078173	2.247910	0.895213	1.0	
5717.3700	0.1395936	0.0062314	0.0017600	0.0005886	0.0001682	0.2824346	1.403882	1.393421	0.698966	0.992549	

1379 Transitions

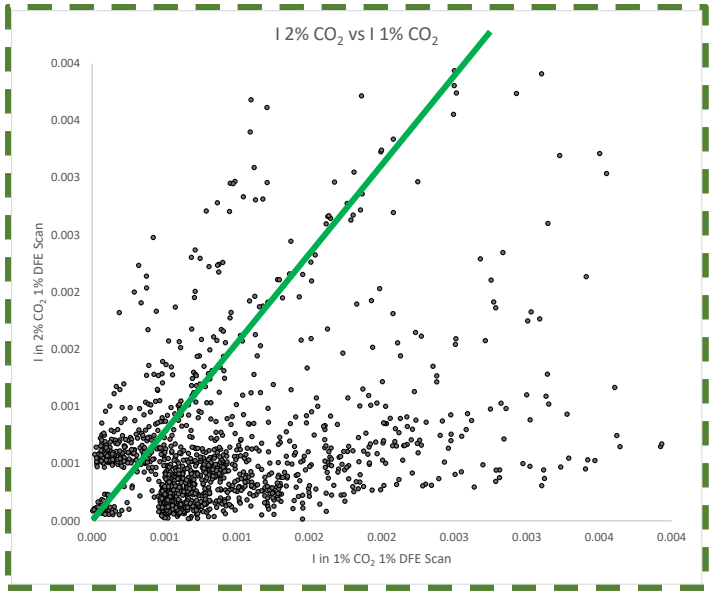


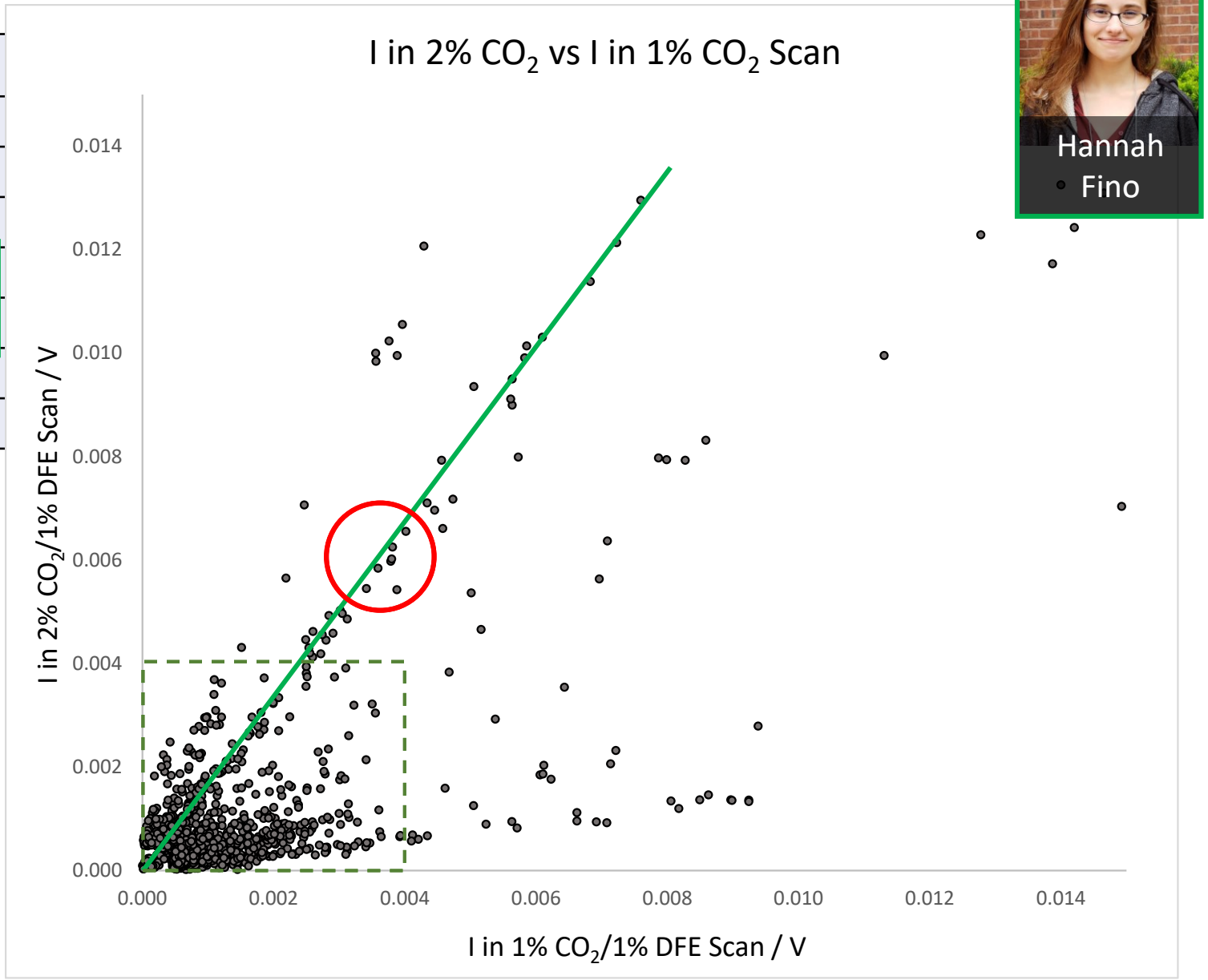


Freq / MHz	I 1% Normalized	I 2% Normalized	I 3% Normalized	I 4% Normalized
5701.9080	0.626941	1.000000	0.301274	0.157866
5703.9600	0.907687	1.000000	0.208193	0.206919
5707.7580	1.000000	0.845085	0.229937	0.110786
5710.9700	0.611433	1.000000	0.307906	0.171179
5713.3760	0.600797	1.000000	0.300072	0.155583
5714.0140	0.400655	1.000000	0.439182	0.238336
5717.3700	1.000000	0.282435	0.094459	0.026988

Intensity vs. Intensity Methods

Freq / MHz	Normalized I (whole spec)	I 1%	I 2%	I Ratio (2%/1%)	4%	
5701.9080	0.2056699	0.0056380	0.0089929	1.5950465	14197	
5703.9600	0.0120317	0.0004683	0.0005159	1.1017008	01068	
5707.7580	0.3117358	0.0138733	0.0117241	0.8450851	15370	
5710.9700	0.1604804	0.0043427	0.0071024	1.6355032	12158	
5713.3760	0.1093947	0.0030180	0.0050232	1.6644566	07815	
5714.0140	0.0220617	0.0004058	0.0010130	2.4959139	02414	
5717.3700	0.1395936	0.0062314	0.0017600	0.2824346	01682	





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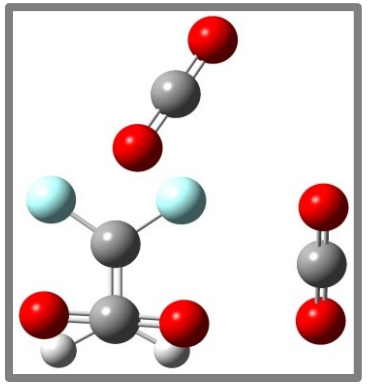
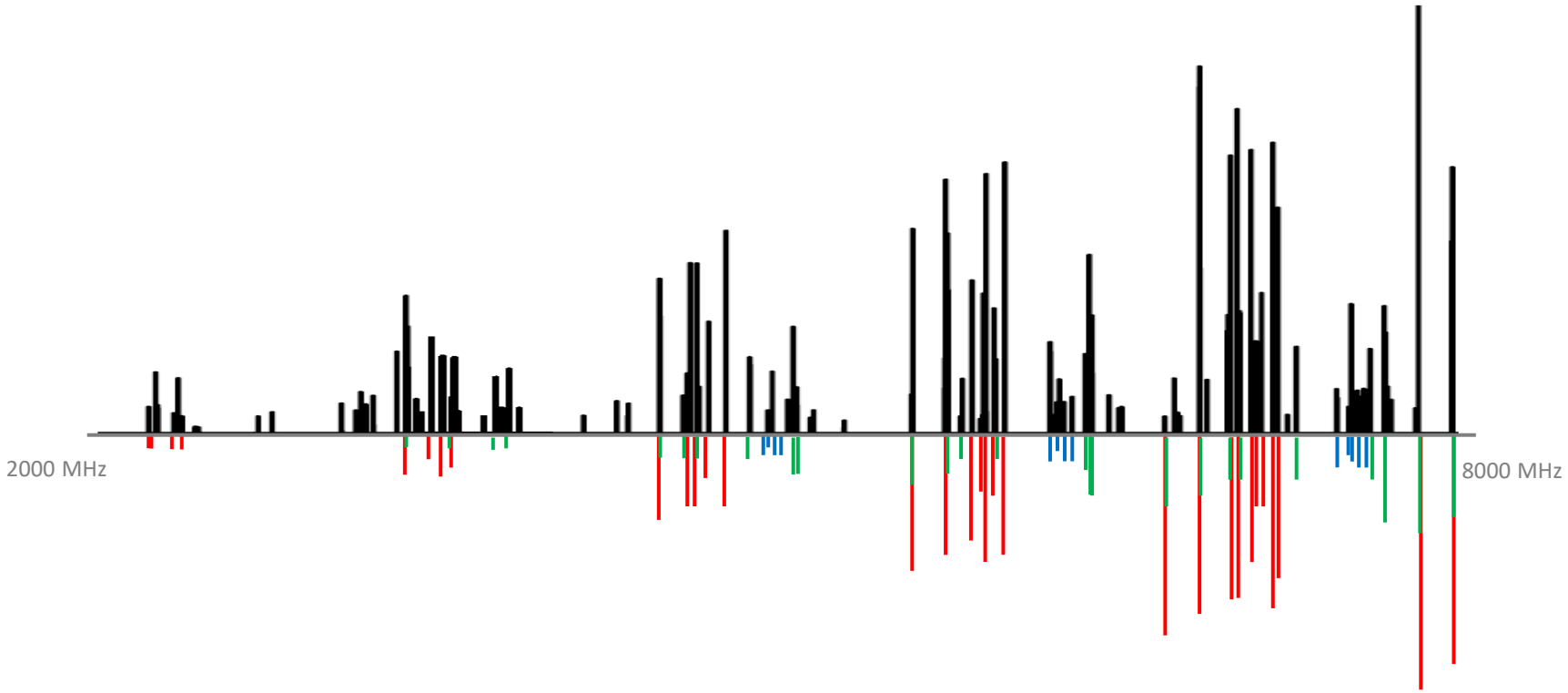
See Poster: Developing automated tools to facilitate assignment of microwave spectra of complex mixtures: Three intensity-correlation methods applied to mixed 1,1-difluoroethylene-CO_2 clusters, Hannah Fino. et al.

Frequency	Norm. I (whole spec)	I 1%	I 2%	I 3%	I 4%	I Ratio (2%/1%)	Area	<Conc>	Width	Ratio (<Conc>/Area)	I 1% Normalized	I 2% Normalized	I 3% Normalized	I 4% Normalized
7122.4080	0.2309081	0.0061003	0.0103023	0.0030408	0.0015183	1.6888231	2.034666	1.998912	0.851948	0.982427	0.592128	1.000000	0.295162	0.147376
7223.9540	0.0666855	0.0018086	0.0030487	0.0010971	0.0005506	1.6856218	2.133699	2.059891	0.884117	0.965408	0.593253	1.000000	0.359850	0.180596
7606.5980	0.0237152	0.0006035	0.0010168	0.0003635	0.0002035	1.6849362	2.151079	2.076355	0.899129	0.965262	0.593494	1.000000	0.357430	0.200155
2462.6360	0.0209086	0			0.0009334	1.6843299	1.361790	3.406792	1.036428	2.501701	0.121063	0.203909	0.036818	1.000000
5958.7620	0.2237501	0			0.0015000	1.6837863	2.075816	2.022145	0.863740	0.974145	0.593900	1.000000	0.323963	0.157953
6802.0380	0.2642183	0			0.0018843	1.6784326	2.068754	2.015686	0.861136	0.974348	0.595794	1.000000	0.317676	0.155284
6967.2360	0.2631957	0			0.0018988	1.6669091	2.080108	2.022659	0.871424	0.972382	0.599913	1.000000	0.313345	0.166850
6720.2200	0.0134024	0			0.0001198	1.6650368	2.055034	2.026090	0.896839	0.985916	0.600587	1.000000	0.254690	0.199757
5713.3760	0.1093947	0.0030180	0.0050232	0.0015073	0.0007815	1.6644566	2.056452	2.005077	0.860621	0.975018	0.600797	1.000000	0.300072	0.155583
7460.7160	0.0996910	0.0027435	0.0045547	0.0013843	0.0006569	1.6601703	2.050501	1.995137	0.850469	0.973000	0.602348	1.000000	0.303930	0.144223
4582.4960	0.0483008	0.0012806	0.0021082	0.0005323	0.0002270	1.6462149	1.967581	1.929012	0.806761	0.980398	0.607454	1.000000	0.252473	0.107654
6926.3300	0.0934032	0.0025551	0.0042003	0.0014291	0.0006644	1.6438697	2.106715	2.022899	0.866047	0.960215	0.608321	1.000000	0.340226	0.158168

133 Transitions

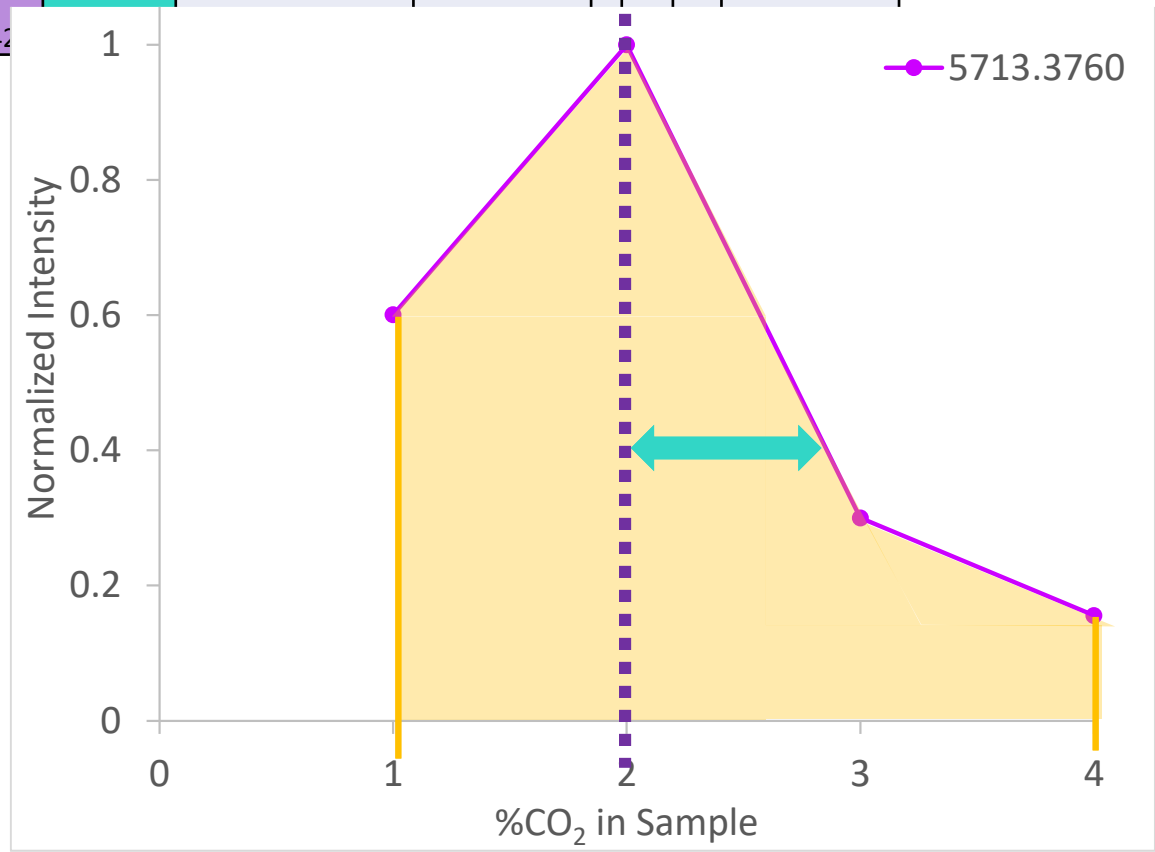




Intensity vs. Concentration Methods

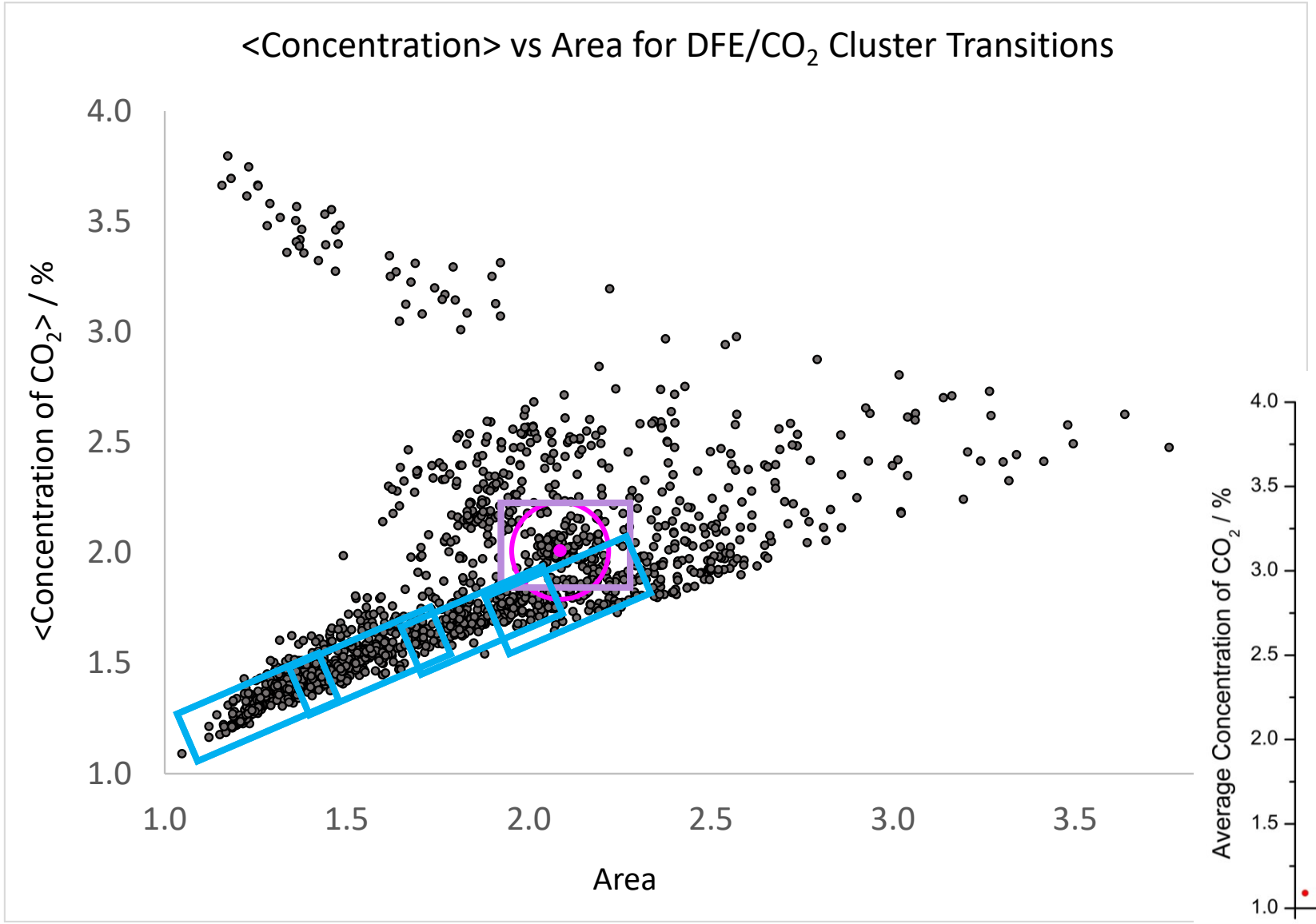
Freq / MHz	Normalized I (whole spec)	I 1%	I 2%	I 3%	I 4%	I Ratio (2%/1%)	Area	<Conc>	Width	Ratio (<Conc>/Area)	$(DFE)_n(CO_2)_m$	J	K_a	K_c	Type (*a, b, c*)
5701.9080	0.2056699	0.0056380	0.0089929	0.0027093	0.0014197	1.5950465	2.086081	1.995237	0.864660	0.956453					
5703.9600	0.0120317	0.0004683	0.0005159	0.0001074	0.0001068	1.1017008	2.322799	1.877021	0.906425	0.808086					
5707.7580	0.3117358	0.0138733	0.0117241	0.0031900	0.0015370	0.8450851	2.185809	1.749068	0.838130	0.800192					
5710.9700	0.1604804	0.0043427	0.0071024	0.0021869	0.0012158	1.6355032	2.090518	2.018576	0.875760	0.965586					
5713.3760	0.1093947	0.0030180	0.0050232	0.0015073	0.0007815	1.6644566	2.056452	2.005077	0.860621	0.975018					
5714.0140	0.0220617	0.0004058	0.0010130	0.0004449	0.0002414	2.4959139	2.078173	2.247910	0.895213	1.081676					
5717.3700	0.1395936	0.0062314	0.0017600	0.0005886	0.0001682	0.2824346	1.403882	1.39342							

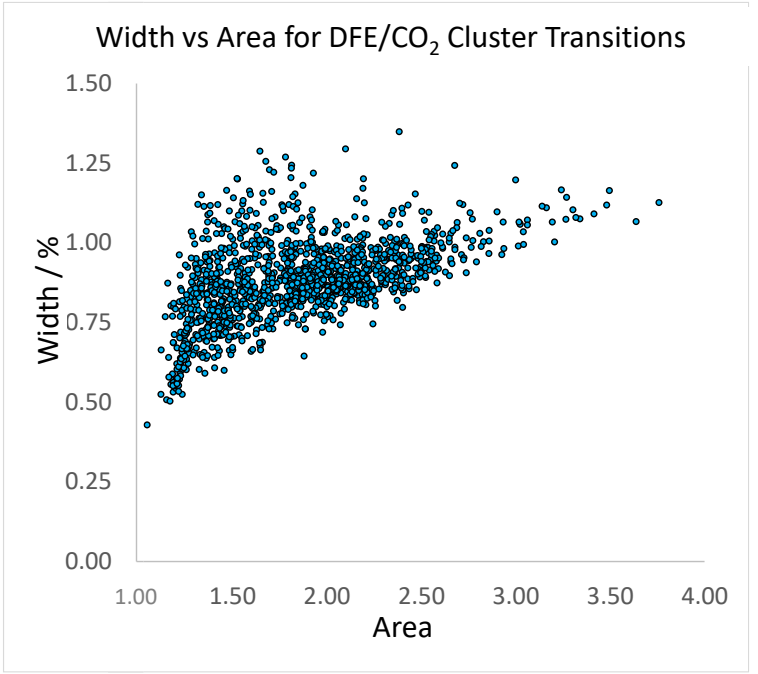
- Parameterize description of I vs $\%CO_2$ curve using moments
  - Area = Sum of normalized intensities
    - Larger means less I variation
  - <Concentration> = $\sum_i \left(\frac{I_i^{norm}}{\text{Area}}\right) \text{conc}_i$
    - Concentration of max I
  - Width = $\sqrt{\sum_i \left(\frac{I_i^{norm}}{\text{Area}}\right) \text{conc}_i^2 - \left(\sum_i \left(\frac{I_i^{norm}}{\text{Area}}\right) \text{conc}_i\right)^2}$

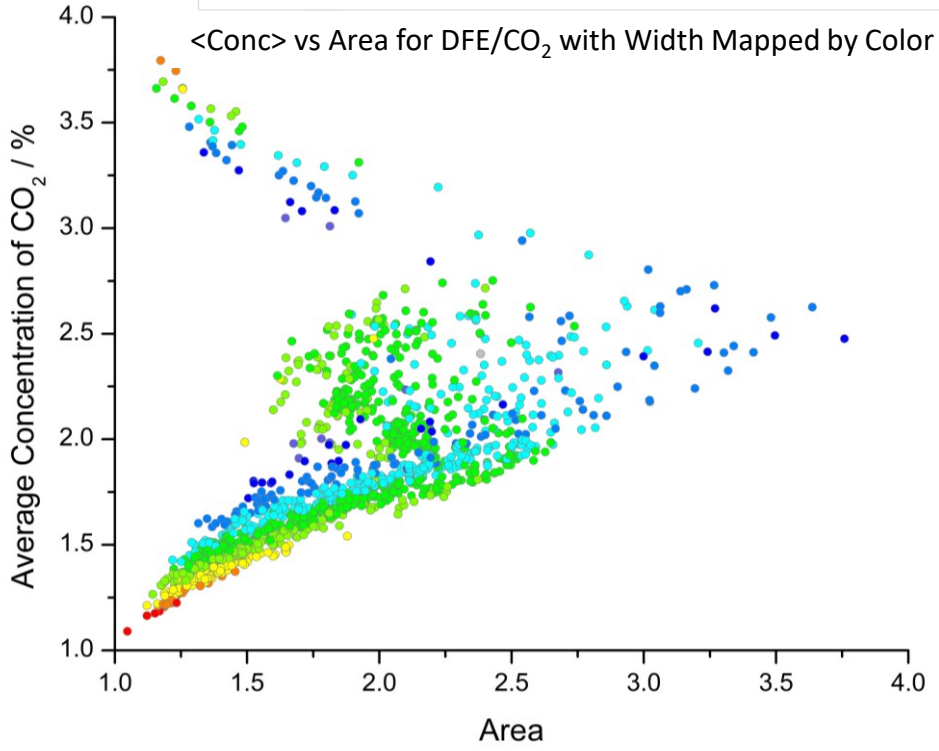


For implementation in course-based research experience at UVa, see, for example, ISMS 2019 Talk TL07, Rotational Spectroscopy of Flavor Compounds in Peach Brandy for Process Monitoring in Craft Distilleries, C.T. West, et al, http://hdl.handle.net/2142/104456.

Intensity vs. Concentration Methods







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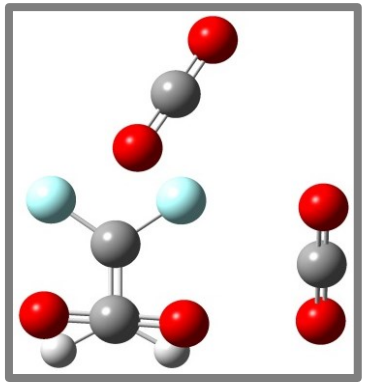
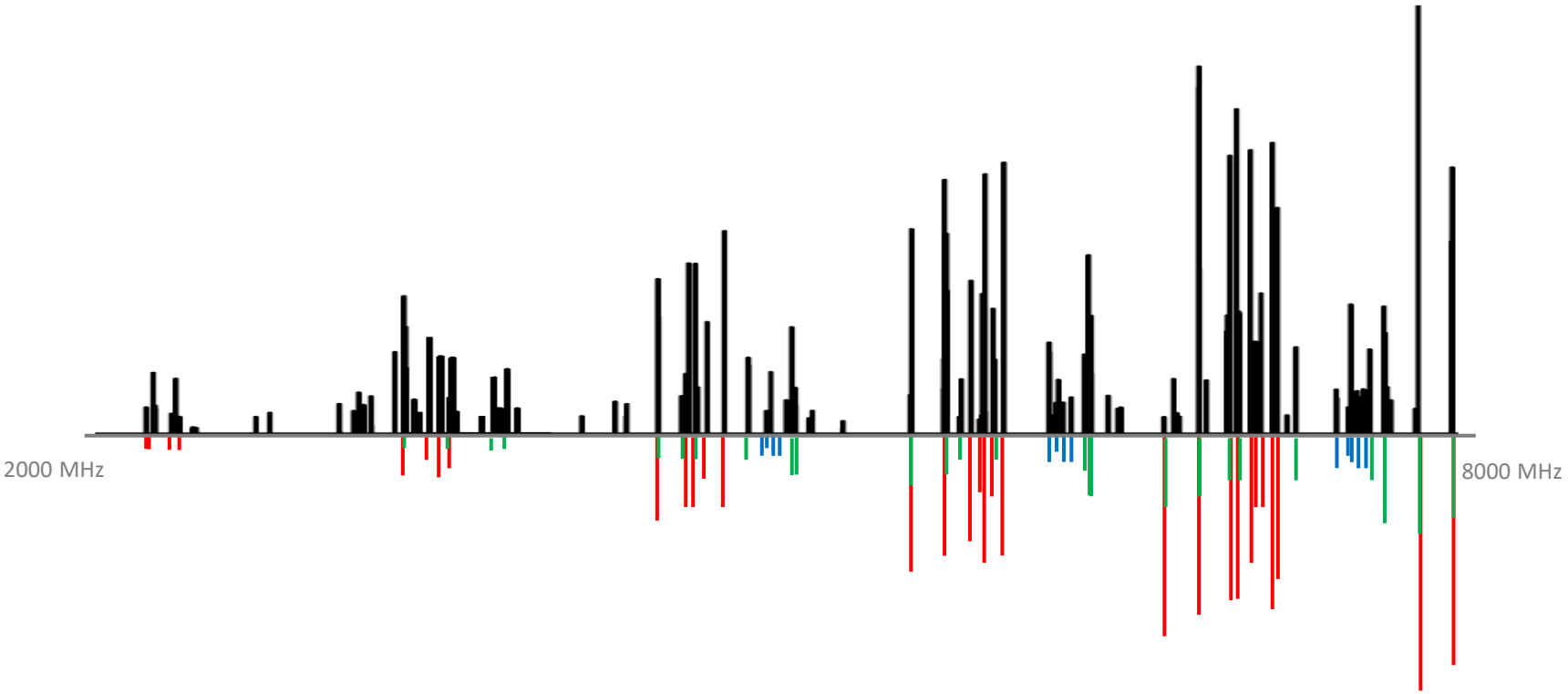
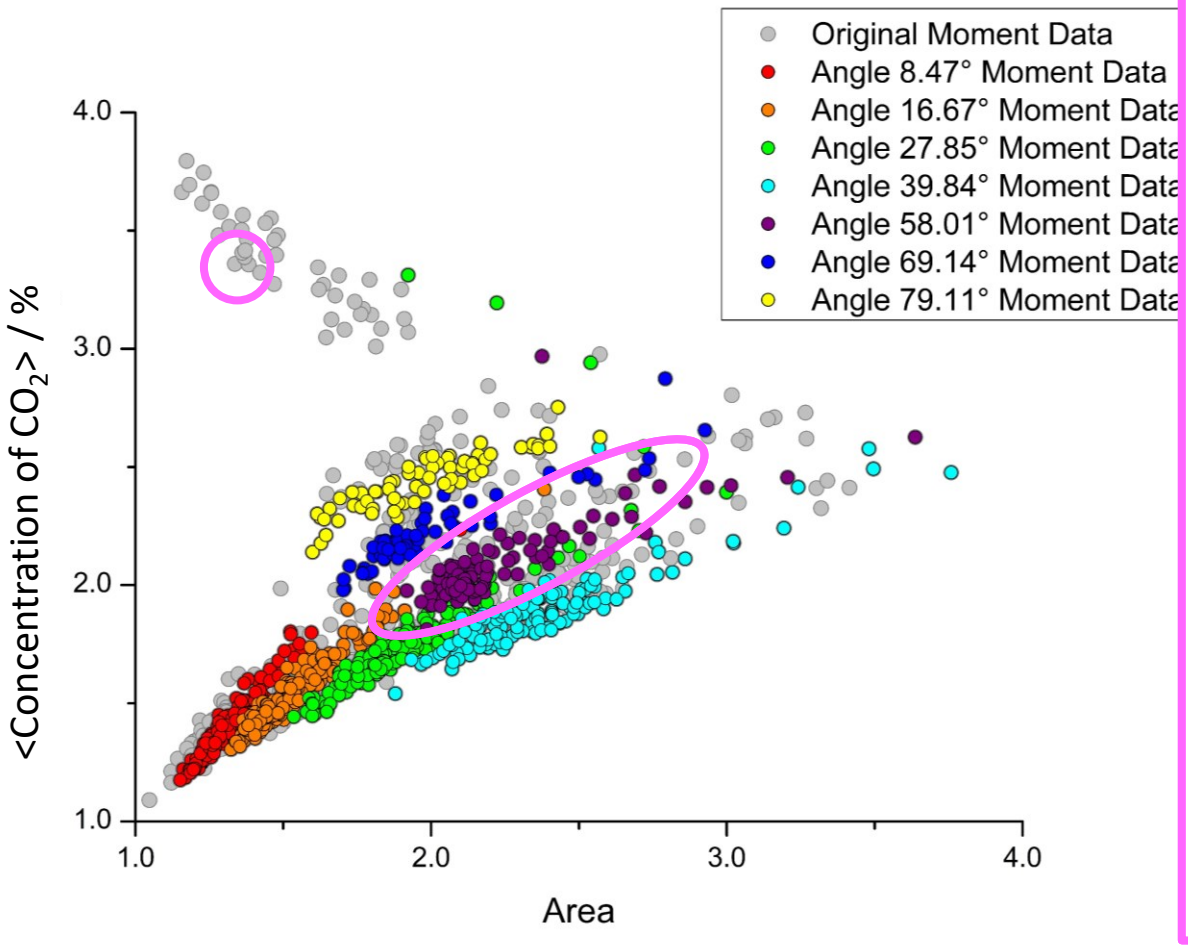
7460.7160	0.0996910	0.0027435	0.0045547	0.0013843	0.0006569	1.6601703	2.050501	1.995137	0.850469	0.973000	0.602348	1.000000	0.303930	0.144223
4582.4960	0.0483008	0.0012806	0.0021082	0.0005323	0.0002270	1.6462149	1.967581	1.929012	0.806761	0.980398	0.607454	1.000000	0.252473	0.107654
6926.3300	0.0934032	0.0025551	0.0042003	0.0014291	0.0006644	1.6438697	2.106715	2.022899	0.866047	0.960215	0.608321	1.000000	0.340226	0.158168

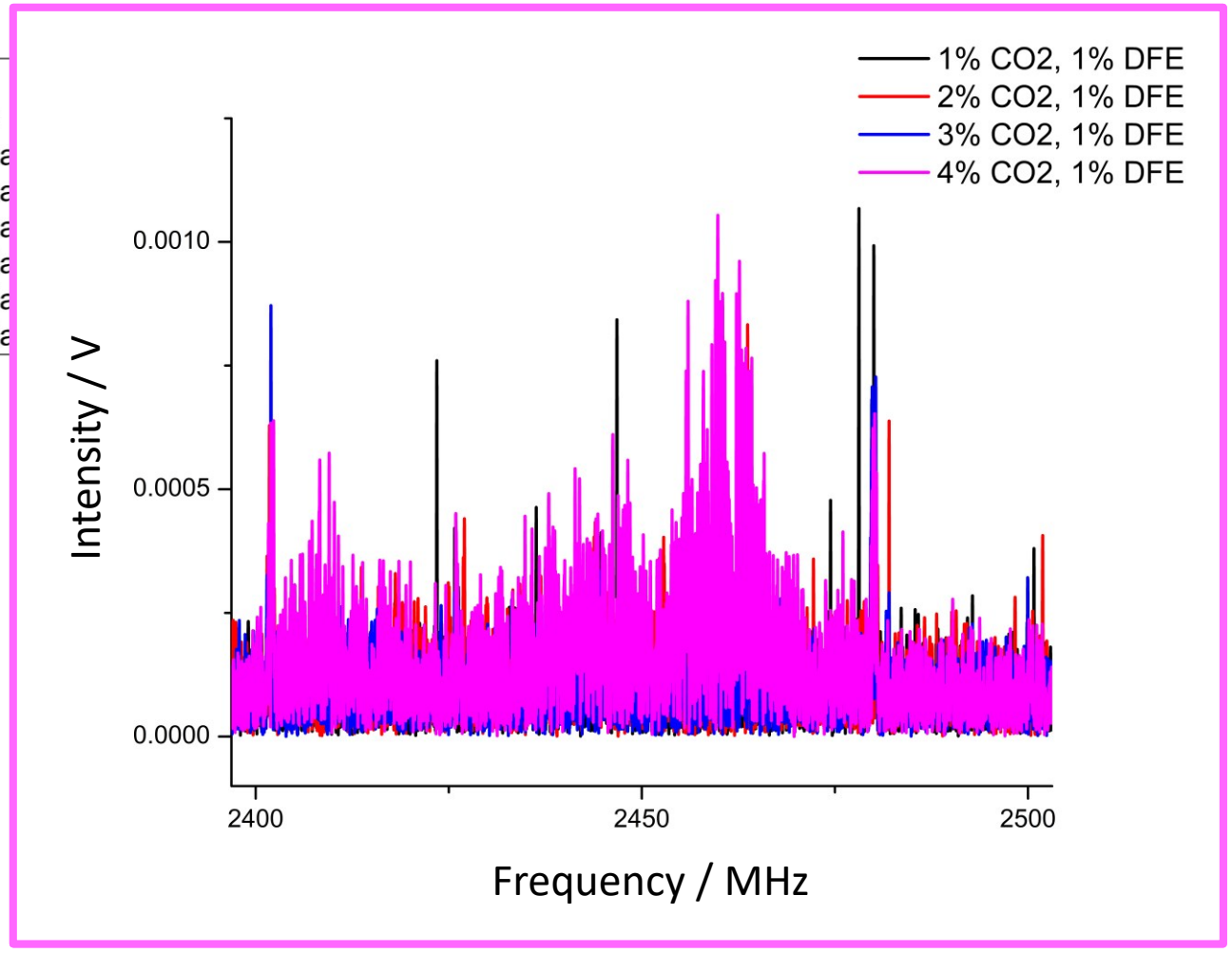
133 Transitions





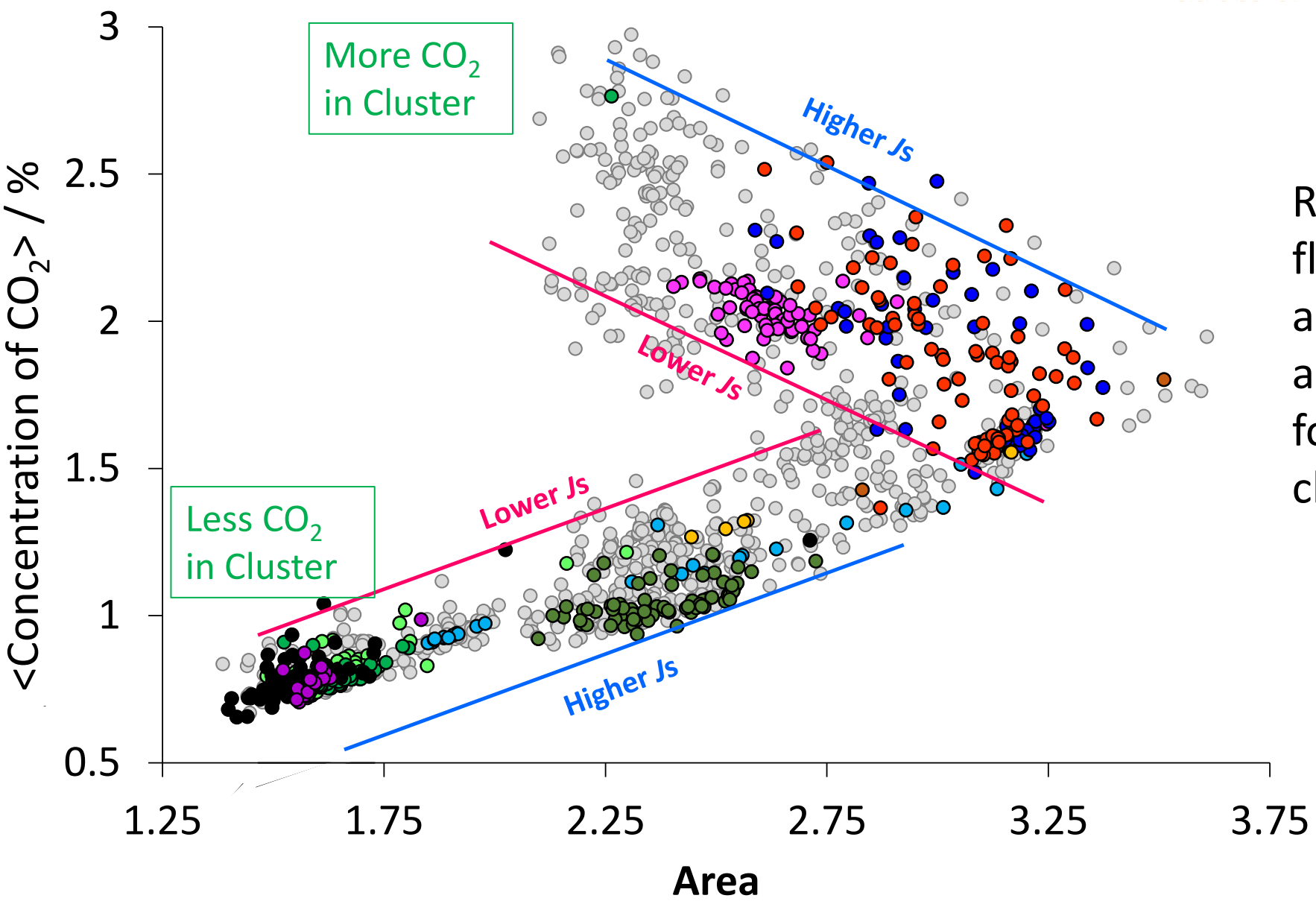
Correlation of Intensity vs Intensity and Intensity vs Concentration Results





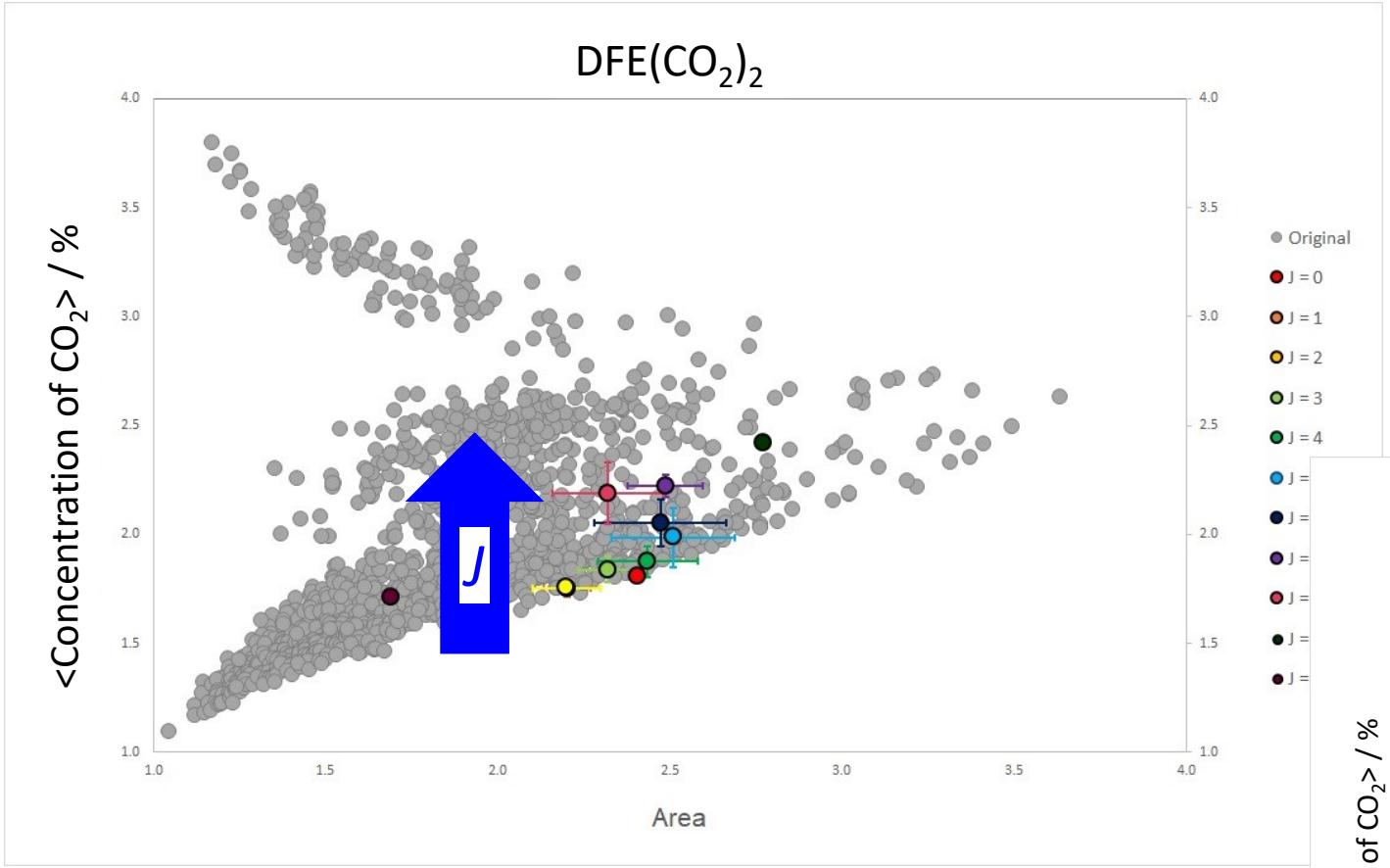
See Poster On Demand: Developing automated tools to facilitate assignment of microwave spectra of complex mixtures: Three intensity-correlation methods applied to mixed 1,1-difluoroethylene-CO_2 clusters, Hannah Fino, et al.

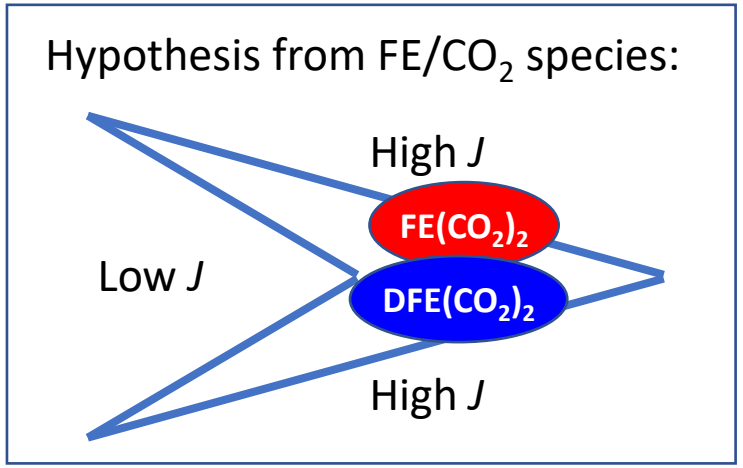
Further Analysis of Intensity vs Concentration Results



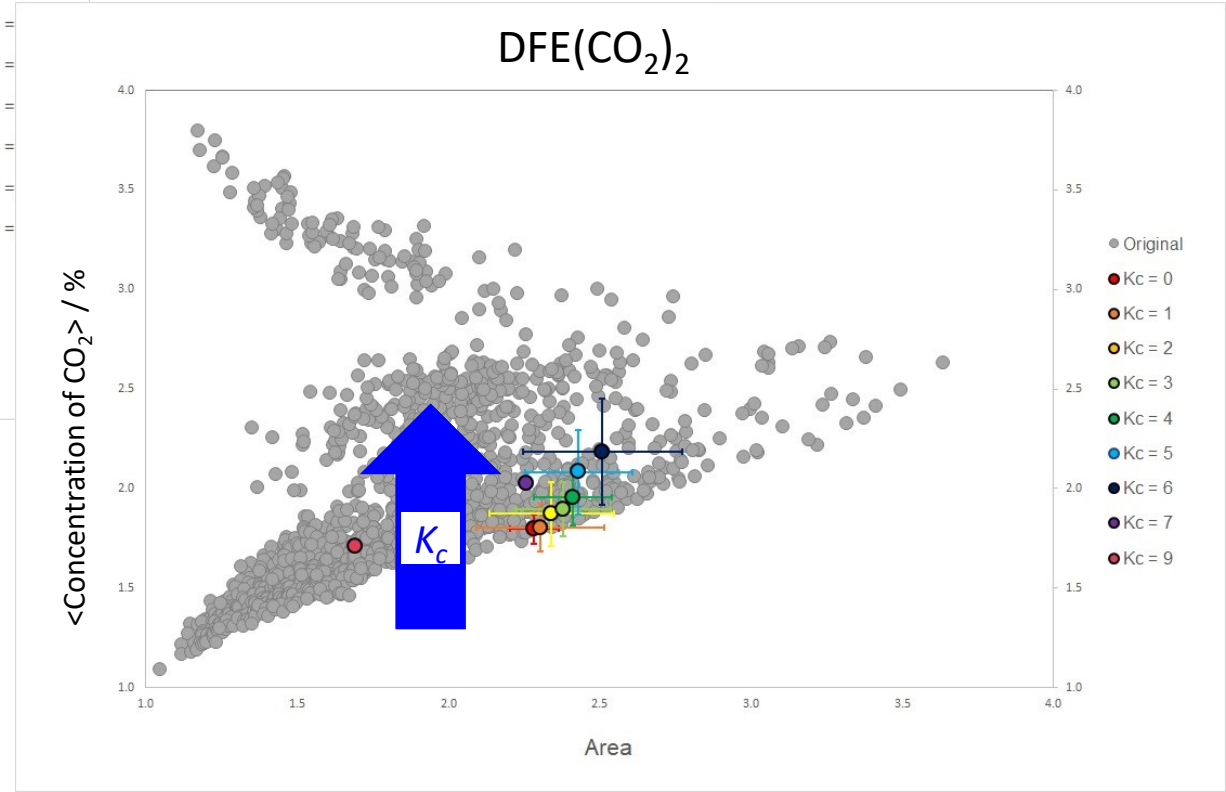
Results from fluoroethylene (FE)/ CO_2 analysis: colored points are assigned transitions for different $(FE)_n(CO_2)_m$ clusters

Further Analysis of Intensity vs Concentration Results





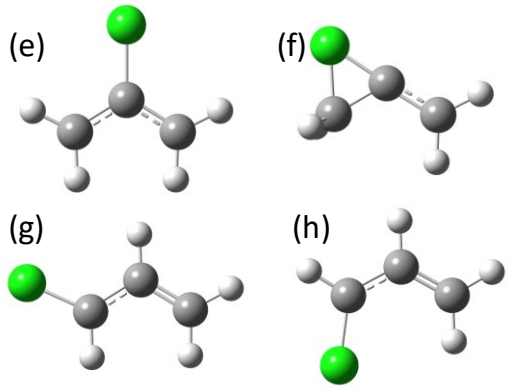
Explanation?
Trimer and tetramer have slightly different position on FE and DFE IVA plots

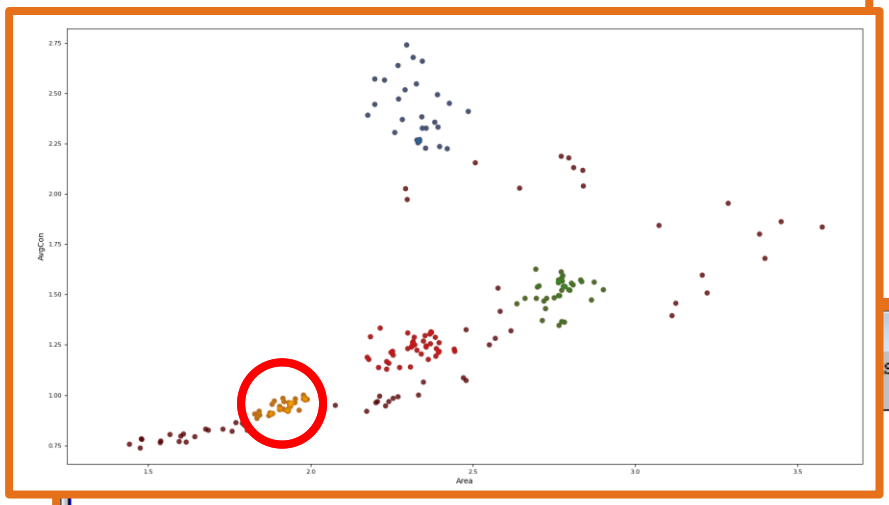


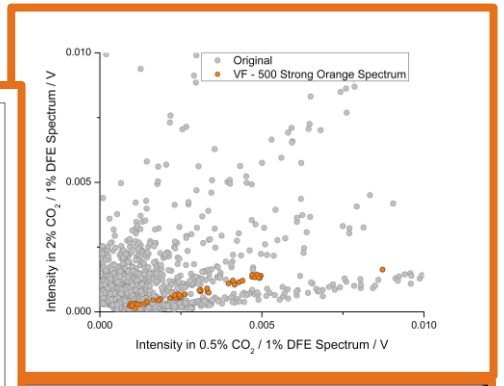
Where does that leave us?

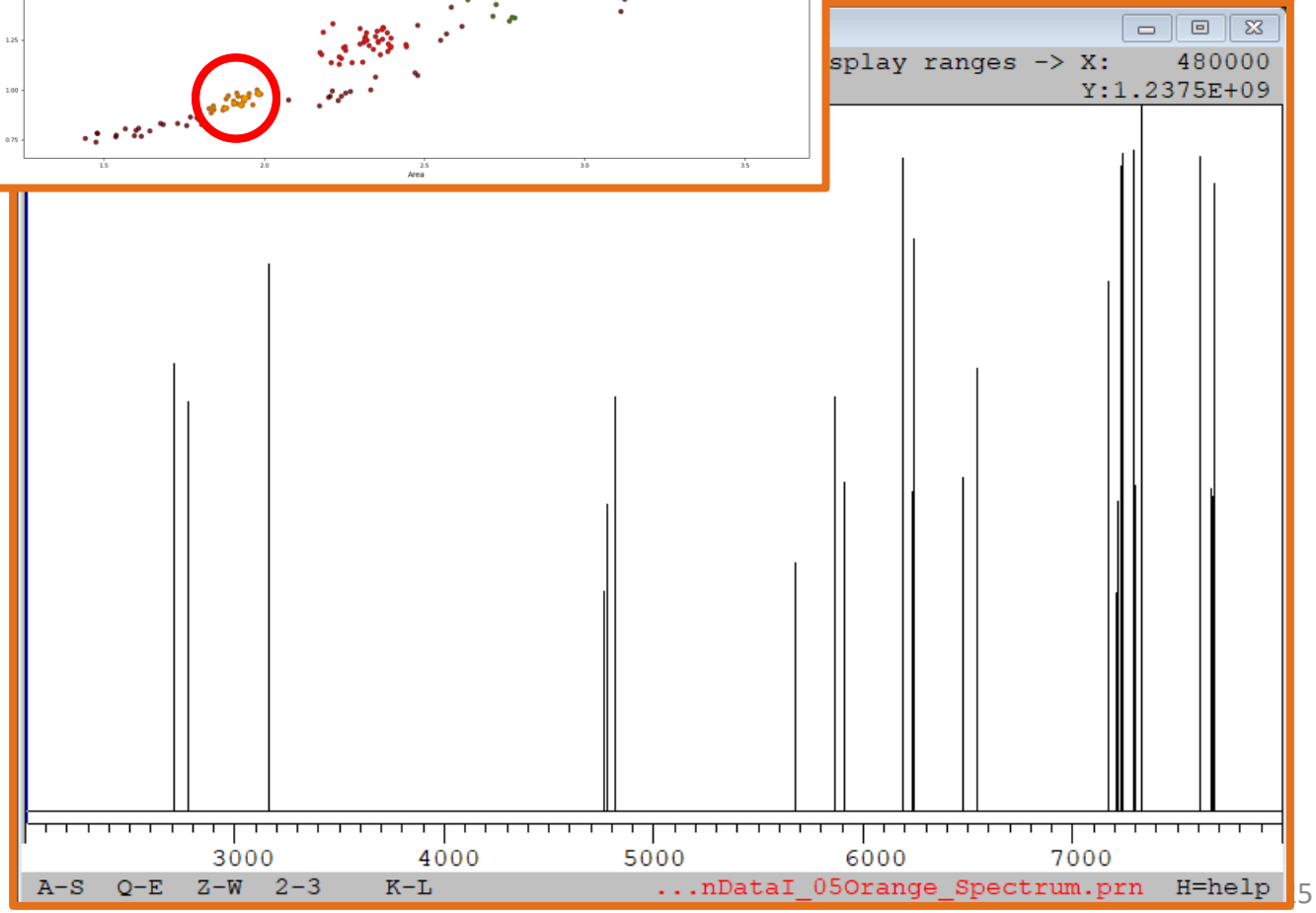
- Increasing set of tools for isolating spectra of one or a few related species to facilitate assignment

- Potential to start extending some of these approaches to:
  - Other types of spectroscopy
  - Other chemical species (e.g. products formed in electric discharge or laser ablation)

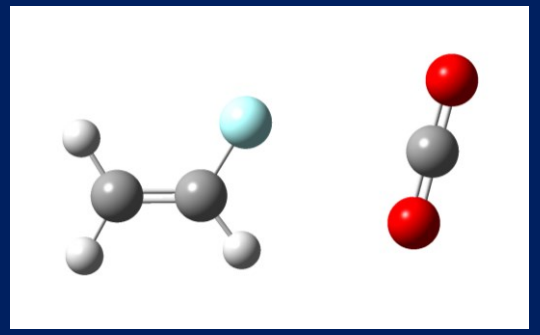


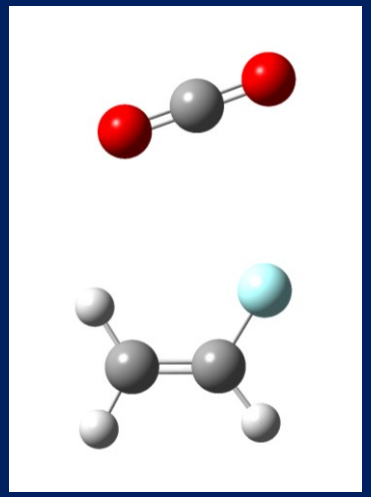


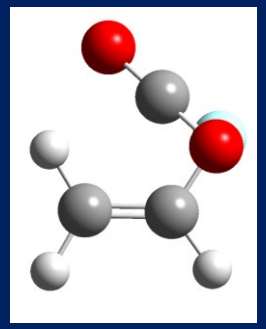


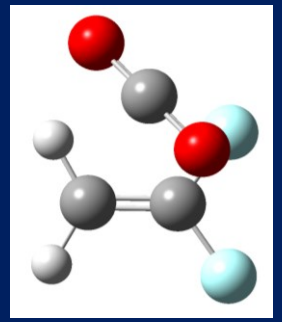


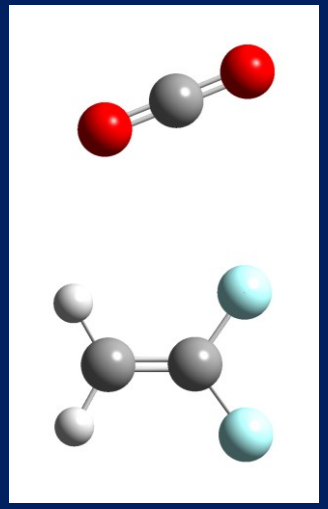
Comparison of FE and DFE cluster structures

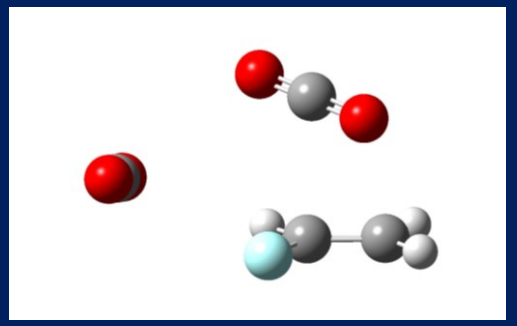


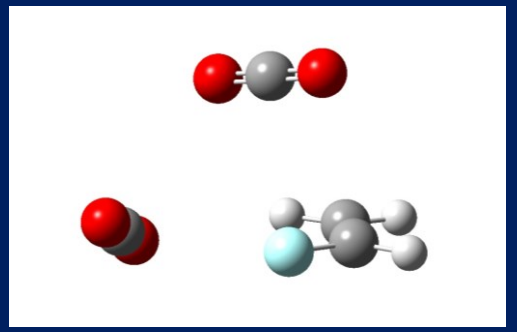


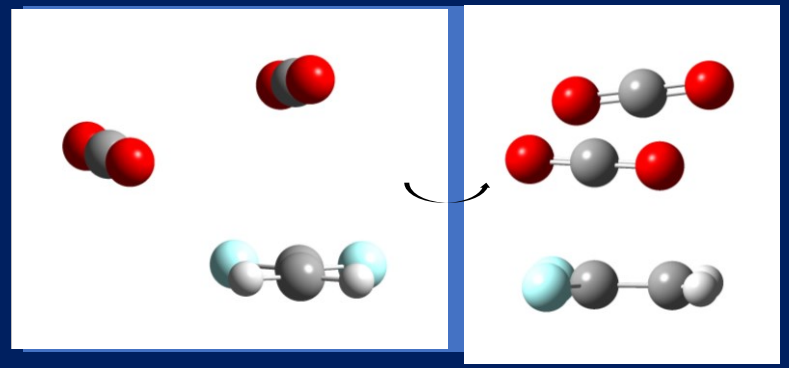


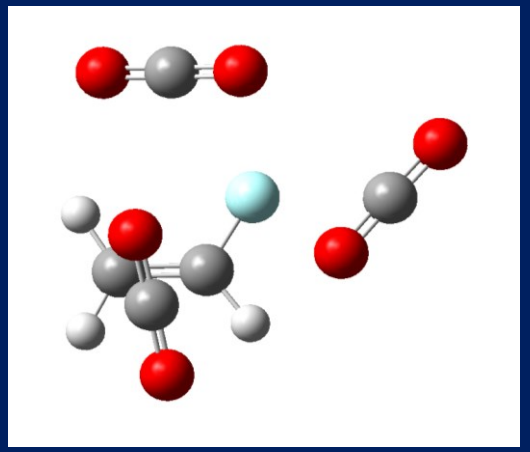


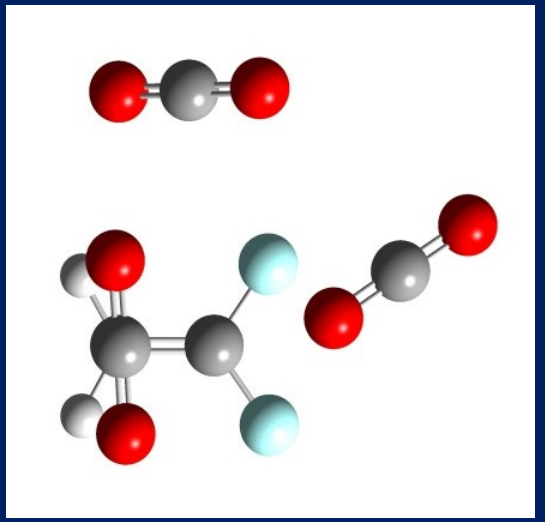












VF: P.B. Kannangara,[m] C.T. West, B.H. Pate, S.A. Peebles, R.A. Peebles, Chem. Phys. Lett., 2018, 706, 538.
P.B. Kannangara,[m] MS Thesis, Eastern Illinois University, 2019.
C.L. Christenholz,* R.E. Dorris,* R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2014, 118, 8765.

DFE: T. Ariyaratne,[m] MS Thesis, Eastern Illinois University, 2019.
A.M. Anderton,*,[m] R.A. Peebles, S.A. Peebles, J. Phys. Chem. A, 2016, 120, 247.

Acknowledgements

- National Science Foundation
  - RUI1214070 (2012-2017)
  - RUI1664900 (2017-2021)
  - NSF Independent Research and Development Program
- Prof. Brooks Pate – Data and advice
  - Pate Group (University of Virginia)
- Eastern Illinois University