Towards an understanding of CO_2 microsolvation: Microwave spectroscopy of CO_2 complexes with fluoroethylenes

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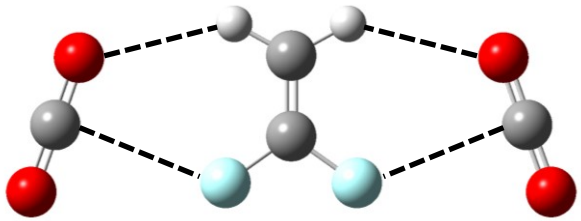
Motivation

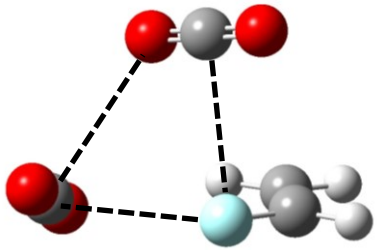
a) C-H···O interactions

b) How do interactions change with degree of fluorination?



c) Can we understand relative stabilities of different structures?

a) How do interactions change as a solvation shell is built?



d) Supercritical CO_2
   - Unique solvent properties
   - Especially for fluorocarbons

e) Can we understand b) and c) well enough to begin to better predict sc-CO_2's solvent properties, d)?

THE JOURNAL OF PHYSICAL CHEMISTRY Letters

Letter

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Structural Evolution of Supercritical CO_2 across the Frenkel Line

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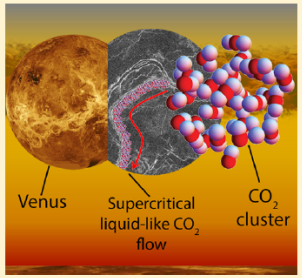
ABSTRACT: Here, we study structural properties of the supercritical carbon dioxide and discover the existence of persistent medium-range order correlations, which make supercritical carbon dioxide nonuniform and heterogeneous on an intermediate length scale. [redacted] due to localization of transverse-like phonon packets. Importantly, we highlight a catalytic role of atoms inside of the nearest-neighbor heterogeneity shell in providing a mechanism for diffusion and proving the existence of an additional thermodynamic boundary in the supercritical carbon dioxide on an intermediate length scale. Finally, we discuss important implications for answering the intriguing question whether Venus may have had CO_2 oceans and urge for an experimental detection of this persistent local-order heterogeneity.



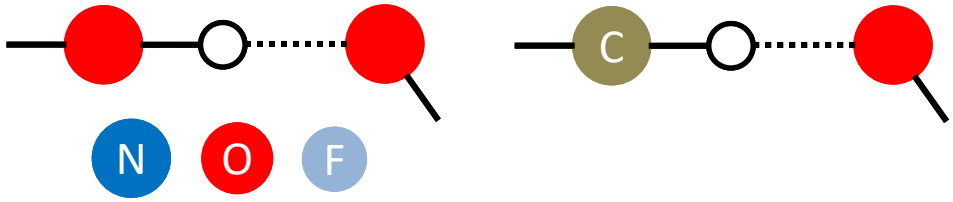
SECTION: Liquids; Chemical and Dynamical Processes in Solution

D. Bolmatov, *et al., J. Phys. Chem. Lett.* 5 (2014) 2785.

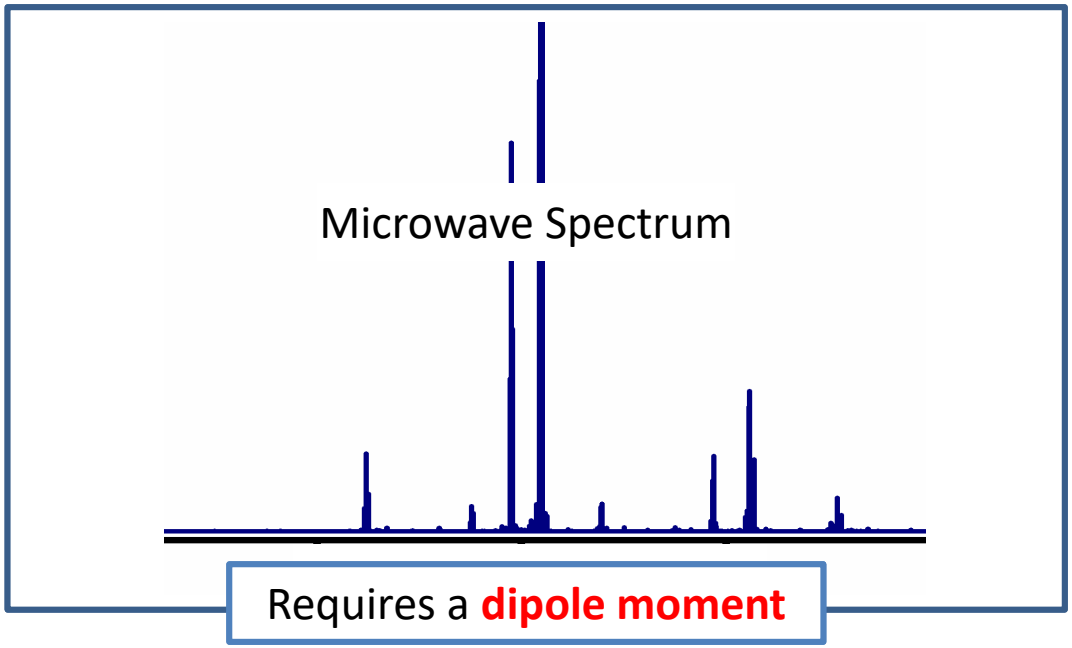
"We report on the CO_2 heterogeneity shell structure where, in the first shell, both carbon and oxygen atoms experience gas-like-type interactions with short-range order correlations while within the second shell, oxygen atoms essentially exhibit a liquid-like type of interactions…"

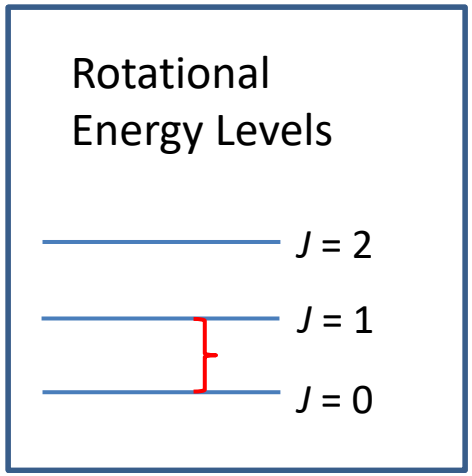
How do students connect?

- Concepts from General Chemistry
  - Hydrogen bonding
  - Polarity



- Environmental/green aspect
- Identifying trends in data
- Basic process involves pattern matching
  - Anyone can do it; deeper understanding follows
- Chemical knowledge/intuition used to set up *ab initio* optimizations





A, B, C

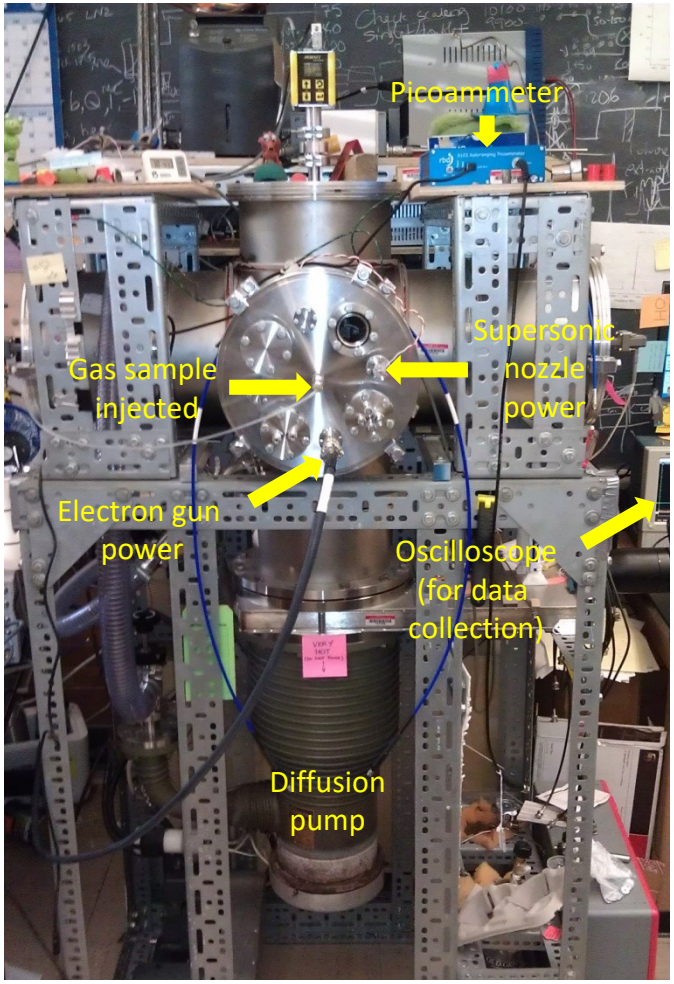
Rotational Constants

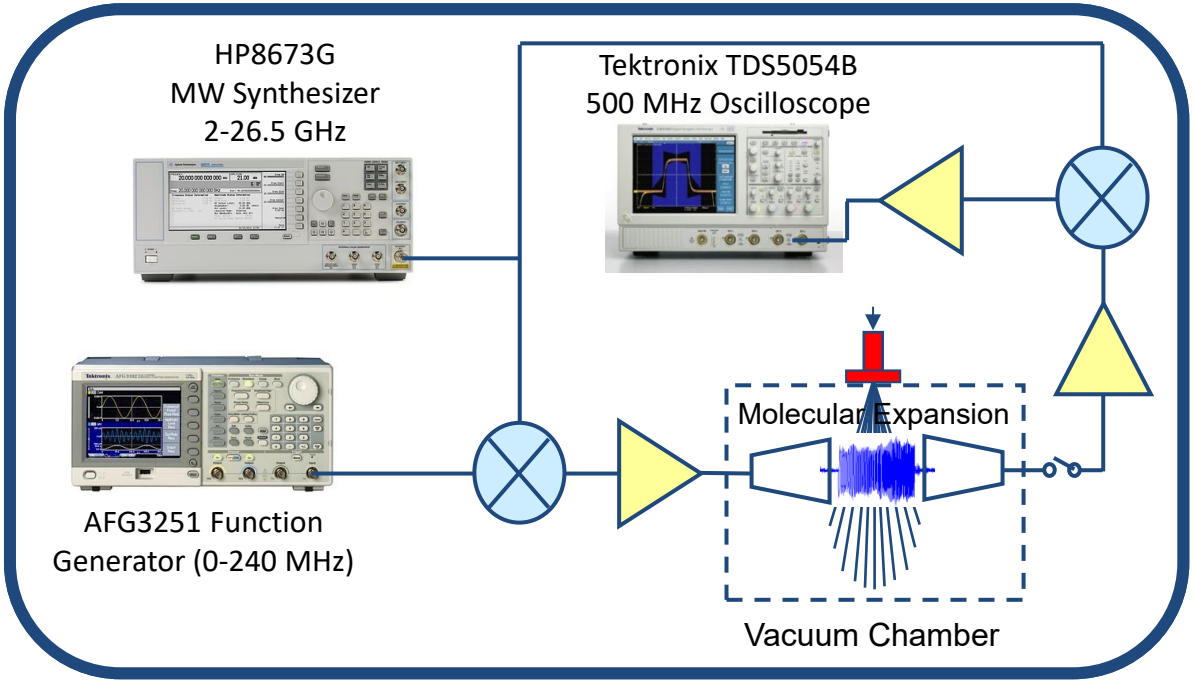
$$B = \frac{h}{8\pi^2 I_b}$$

Moments of Inertia

$I = \Sigma mr^2$

Distances



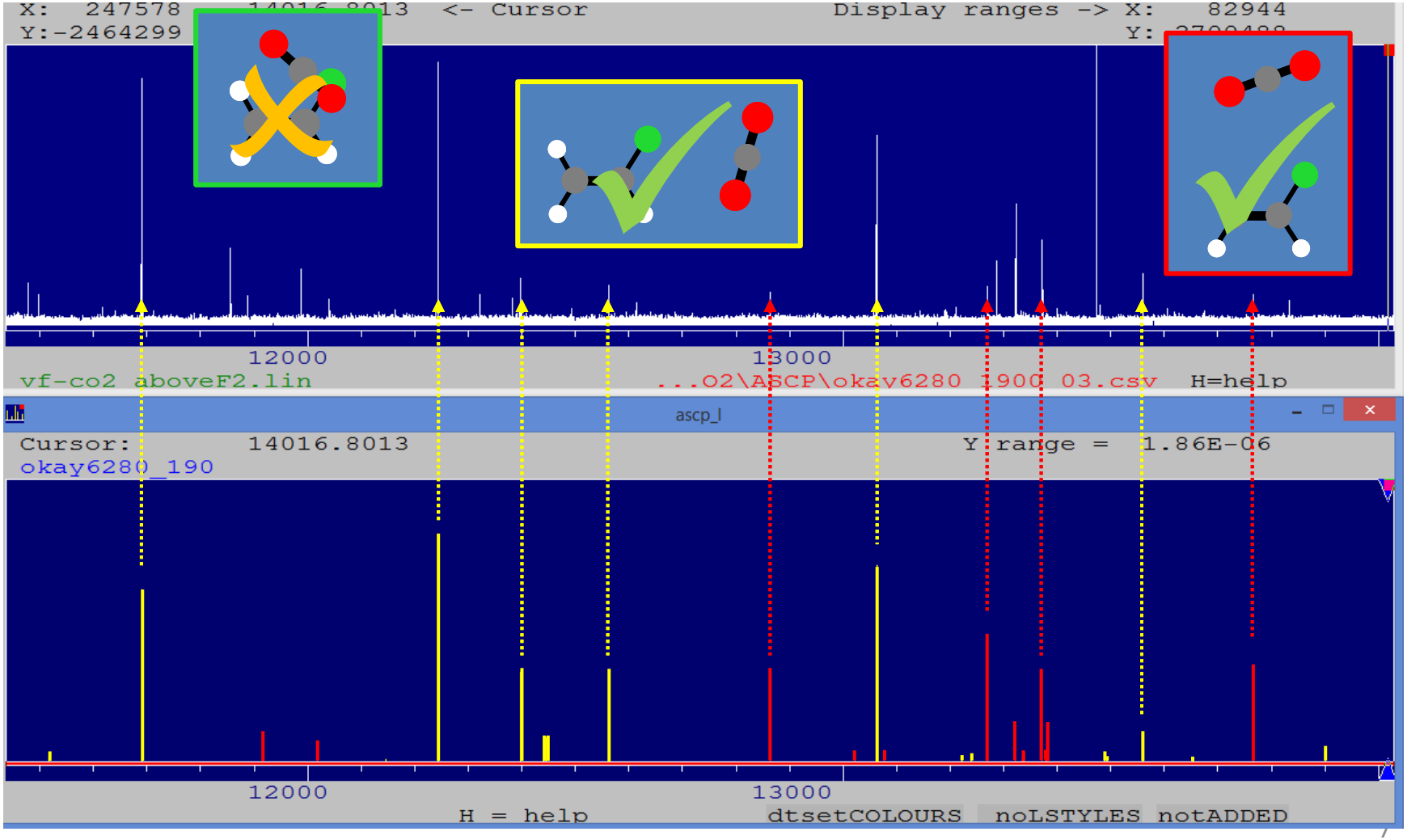


- Reduced Bandwidth Chirped-Pulse Fourier-Transform Microwave (CP-FTMW) Spectrometer
  - 480 MHz bandwidth
  - Scan in 240 MHz steps
  - Calculate absolute frequencies and assemble into full 11 GHz spectrum using LabVIEW
  - Typically scan a full (10k average) spectrum in 1 day

D. A. Obenchain, A. A. Elliott, A.L. Steber, R. A. Peebles, S. A. Peebles, C. J. Wurrey, G. A. Guirgis, *J. Mol. Spectrosc.* 261 (2010) 35.

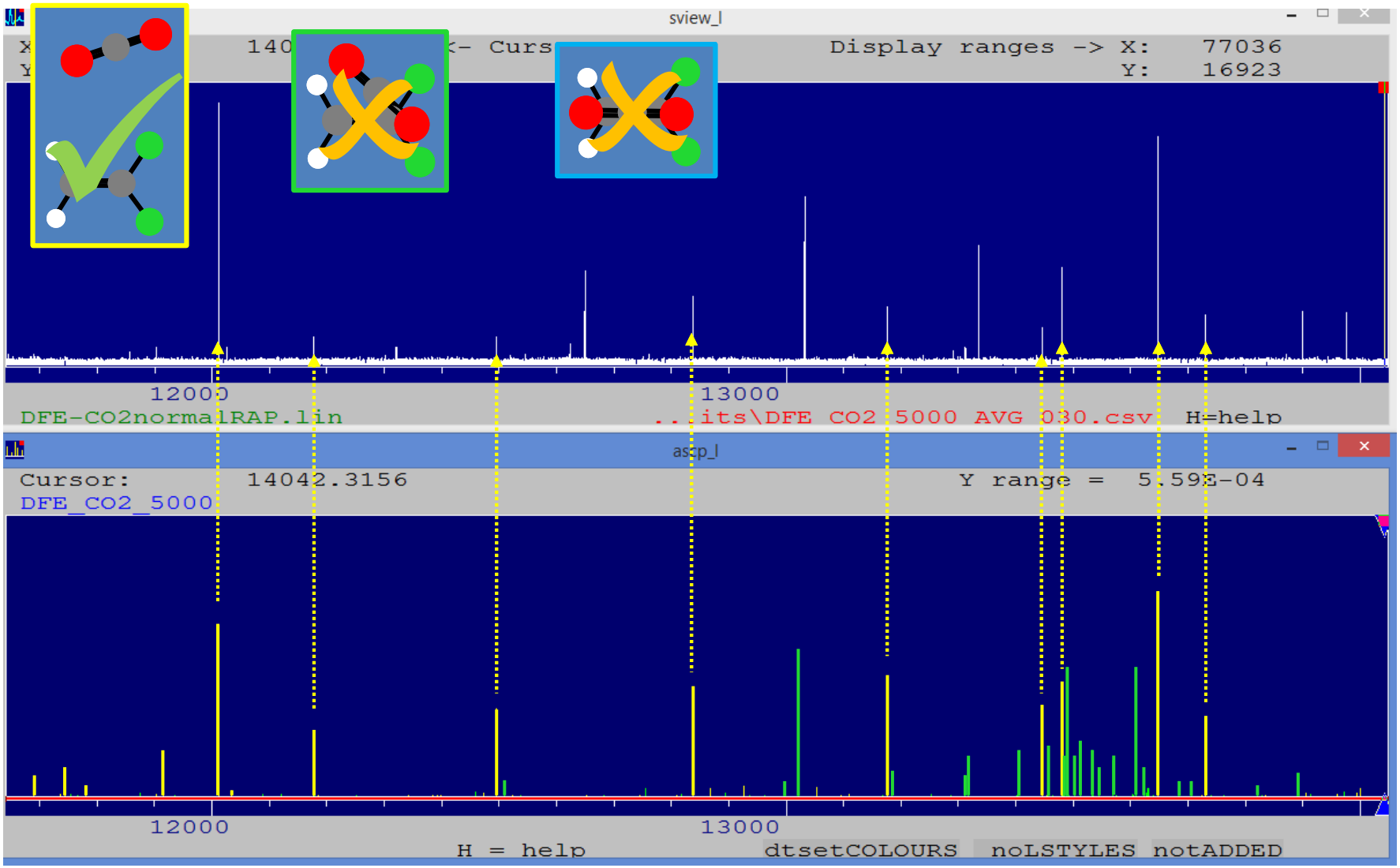
Fluoroethylene…CO_2

- Two isomers!



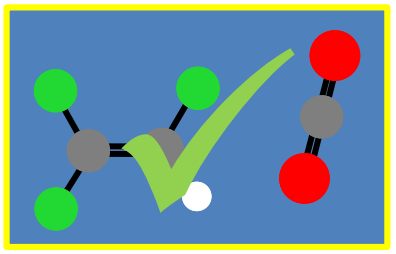
C. Christenholz, *et al*, *J. Phys. Chem. A* 118 (2014) 8765.

Difluoroethylene…CO_2

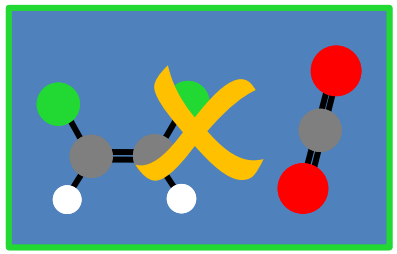


A. Anderton, *et al*, *J. Phys. Chem. A* 120 (2016) 247.

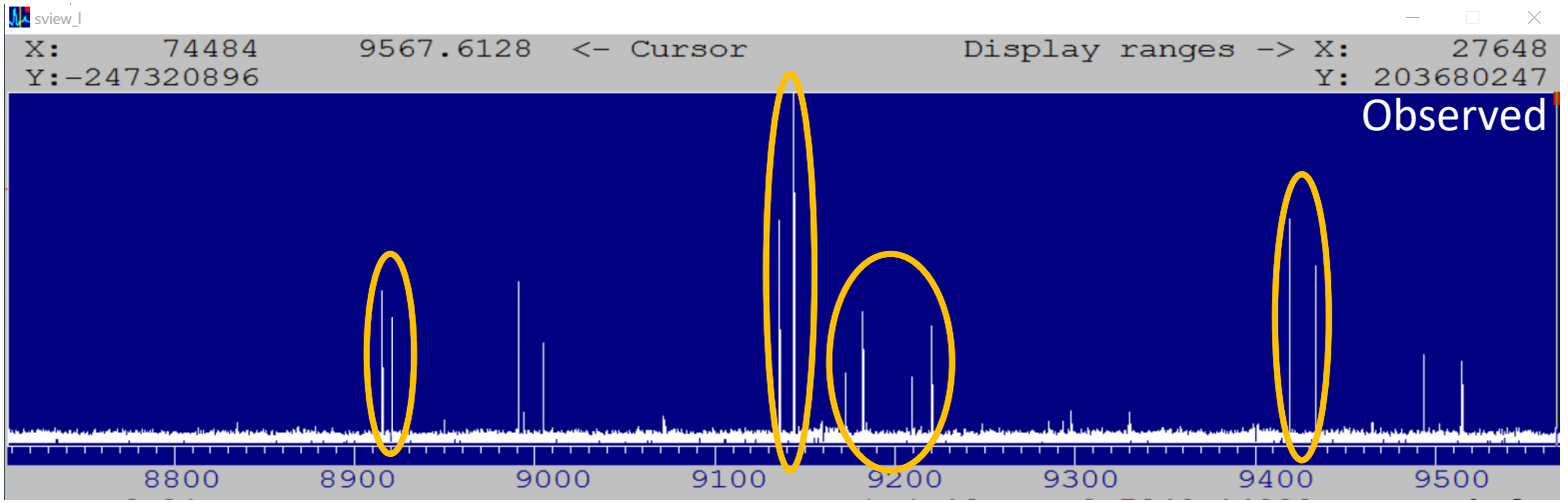
Trifluoroethylene and *cis*-1,2-Difluoroethylene

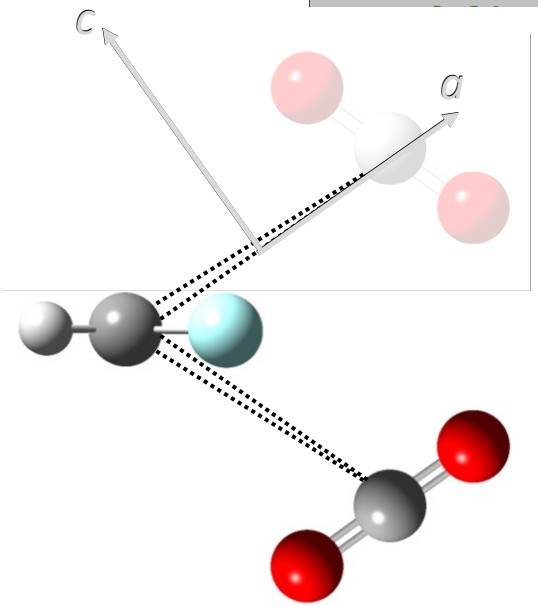


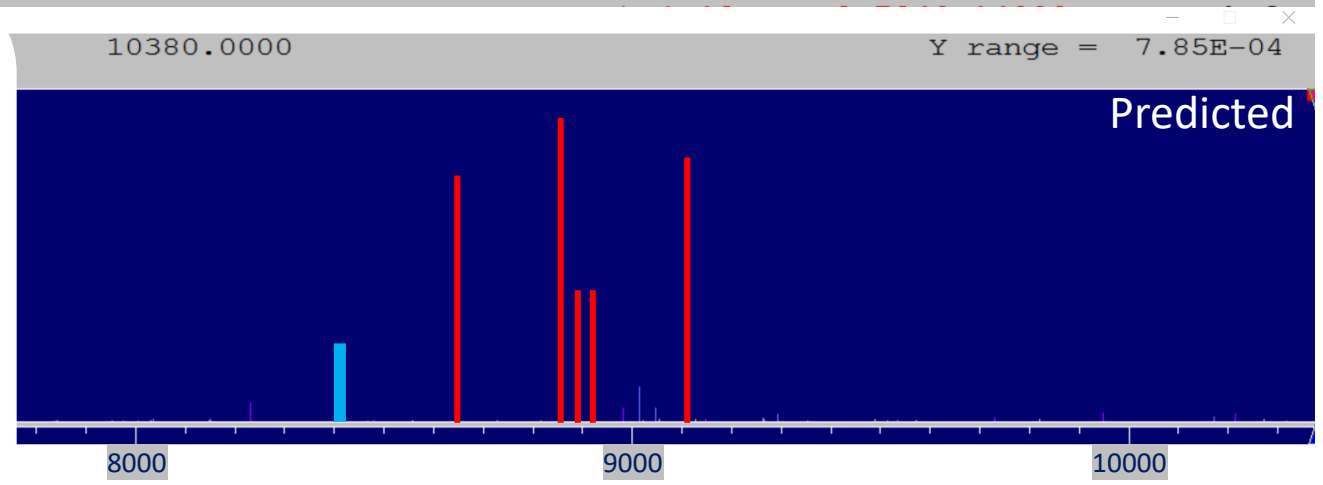
- Trifluoroethylene:
  - Above structure would not converge
  - Only side binding observed
- *cis*-1,2-Difluoroethylene:
  - Only side binding was predicted
    - Consistent with all previous dimers in the series
  - No spectrum consistent with side binding observed
  - Now what?



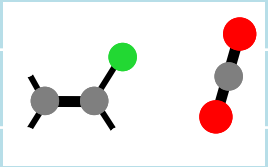
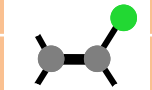
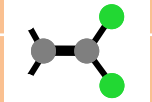
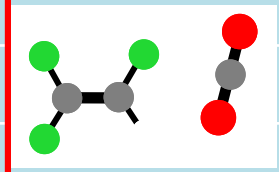
TFE: R. Dorris, *et al*, *J. Phys. Chem. A* 120 (2016) 7865.
cis-1,2-DFE: B. Trendell, *et al*, ISMS, talk RH04, 6/22/17, https://www.ideals.illinois.edu/handle/2142/97066


sview_l
X: 74484 9567.6128 <- Cursor Display ranges -> X: 27648
Y:-247320896 Y: 203680247
Observed
8800
8900
9000
9100
9200
9300
9400
9500


c
a

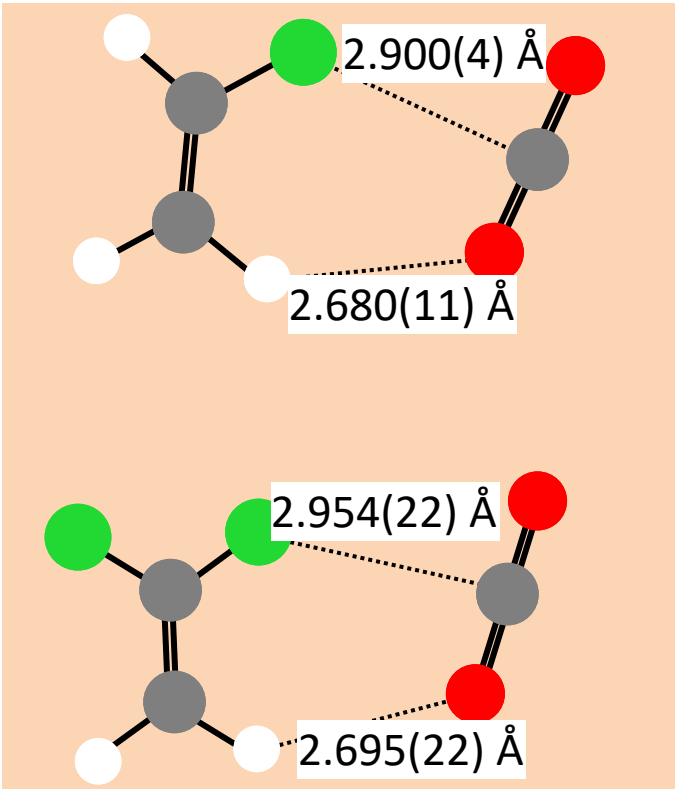

10380.0000
Y range = 7.85E-04
Predicted
8000
9000
10000

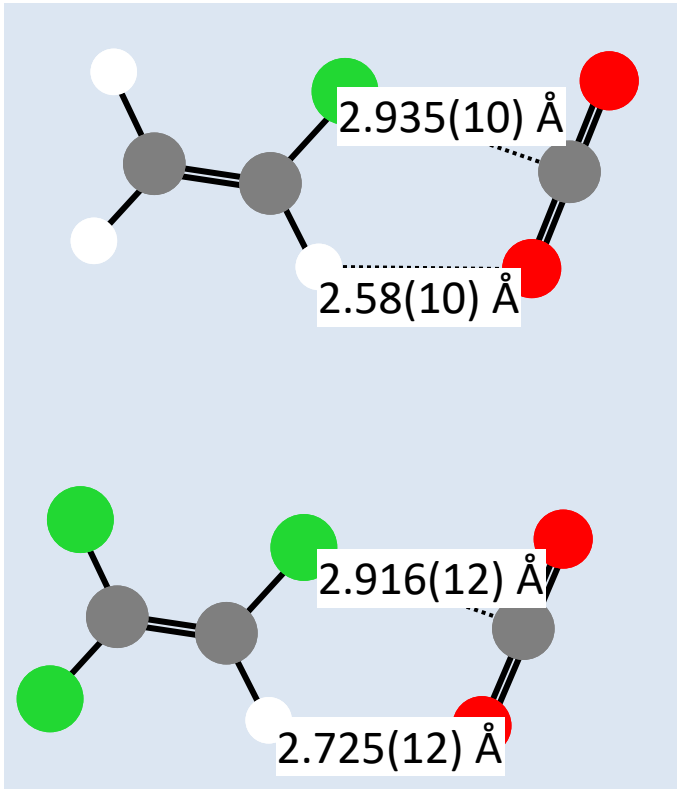
Spectroscopic Constants

		Normal	Ab Initio	$^{13}CO_2$	^{13}CH	^{13}CF	$C^{18}O_2$
FE	*A* / MHz	9644.5725(17)	9550	9639.7765(32)			
Side	*B* / MHz	1423.1498(6)	1372	1409.3202(6)			
	C / MHz	1242.6365(4)	1200	1232.0001(6)			
FE		6828.4038(16)	6668	6823.9970(29)	6751.89(19)	6813.77(20)	
Top		1723.3735(15)	1661	1705.9257(6)	1694.3780(8)	1697.9307(8)	
		1379.3127(13)	1330	1367.9294(7)	1357.6309(8)	1362.4362(8)	
DFE		5696.6440(9)	5672	5696.3890(5)	5571.7612(31)	5696.1818(31)	5394.5195(23)
Top		1121.85748(24)	1130	1108.8034(4)	1116.1018(5)	1115.6321(5)	1072.0180(5)
		939.4186(4)	942	930.23834(32)	931.9529(4)	935.0380(4)	896.2158(5)
TFE	*A* / MHz	5355.7872(21)	5285		5281.922(33) [a]	5189.5777(16) [b]	5111.218(3)
Side	*B* / MHz	696.4235(3)	703		674.428(18)	685.2672(8)	664.5307(11)
	C / MHz	617.3247(2)	621		599.057(7)	606.3258(2)	589.0155(8)

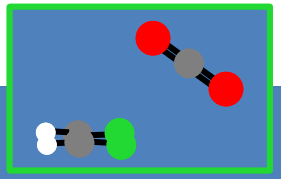
[a] $C^{18}O^{16}O$ (^{18}O near F) [b] $C^{16}O^{18}O$ (^{18}O near H)

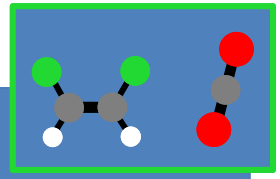
Comparison…


2.900(4) Å
2.680(11) Å
2.954(22) Å
2.695(22) Å


2.935(10) Å
2.58(10) Å
2.916(12) Å
2.725(12) Å

Structure



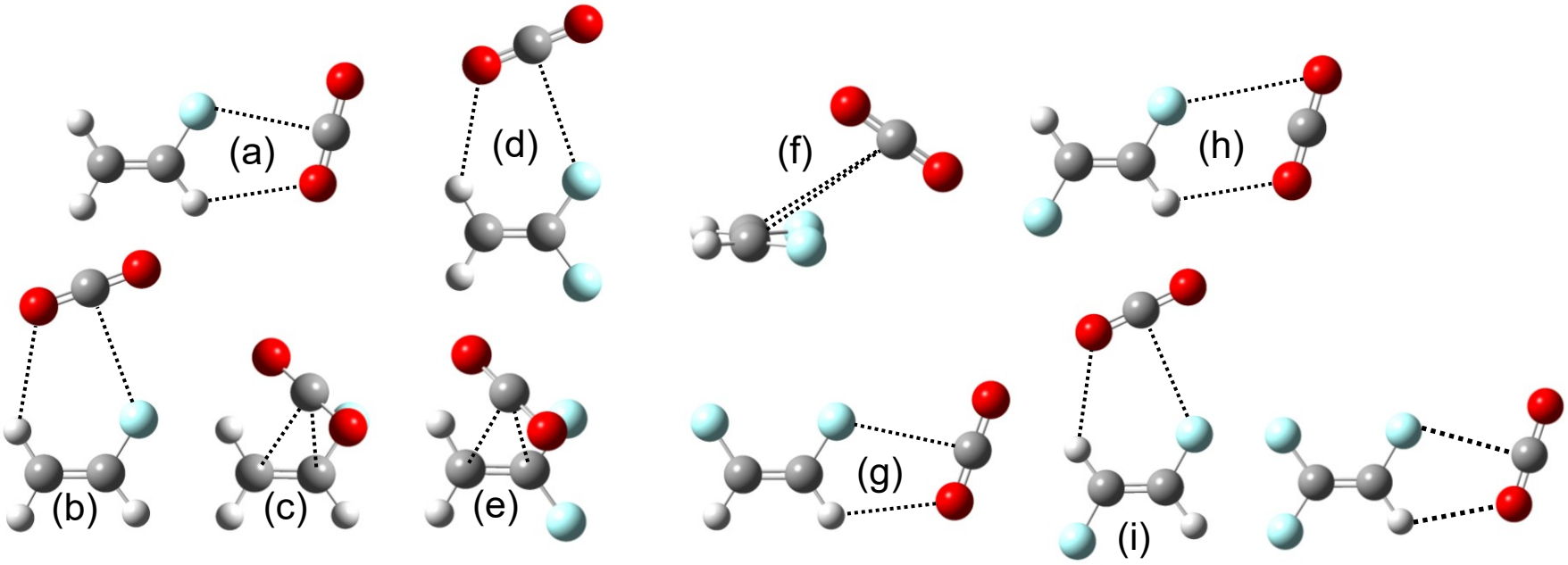


	Observed		Predicted	
	0^+	0^-		
A / MHz	3810.154(14)	3809.984(14)	3734.7	8002.3
B / MHz	1614.4404(25)	1614.4991(21)	1559.1	868.2
C / MHz	1456.786(14)	1456.867(14)	1403.4	783.2
P_{aa} / u Å^2	263.655(2)	263.637(2)	274.5	582.1
P_{bb} / u Å^2	83.259(2)	83.258(2)	85.6	63.2
P_{cc} / u Å^2	49.382(2)	49.388(2)	49.7	0.0
μ_a / D	2.13(3)		2.2	0.02
μ_b / D	0.00			
μ_c / D	1.13(4)		1.4	0.0
μ_{tot} / D	2.41(5)			

P_{aa} for DFE = 85.30534(4) u Å^2
μ for DFE = 2.42 D

Gaussian 09: MP2/6-311++G(2d,2p)

Monomer rotational constants: N. C. Craig, *et al*, *Int. J. Quantum Chem.*, **95**, (2003), 837.
Monomer dipole moment: V. W. Laurie, *J. Chem. Phys.*, **34**, (1961), 291.



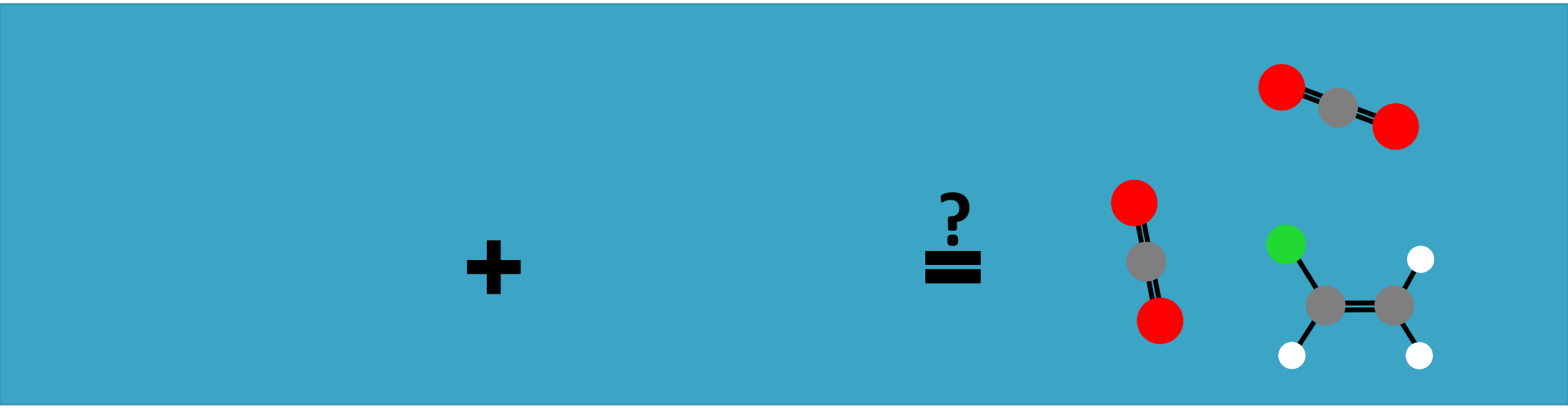
- What's next?
  - Symmetry adapted perturbation theory (SAPT)
  - Better understanding of energetics

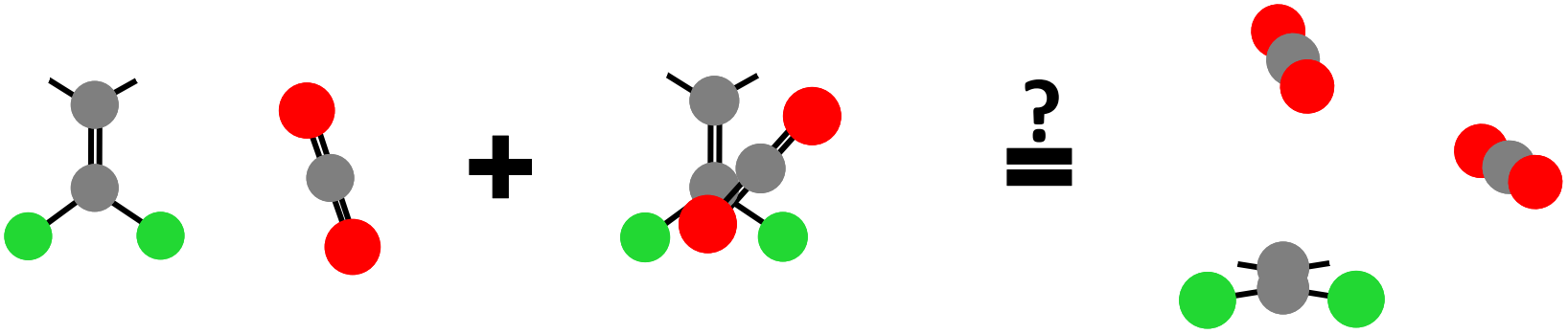
- Larger clusters…

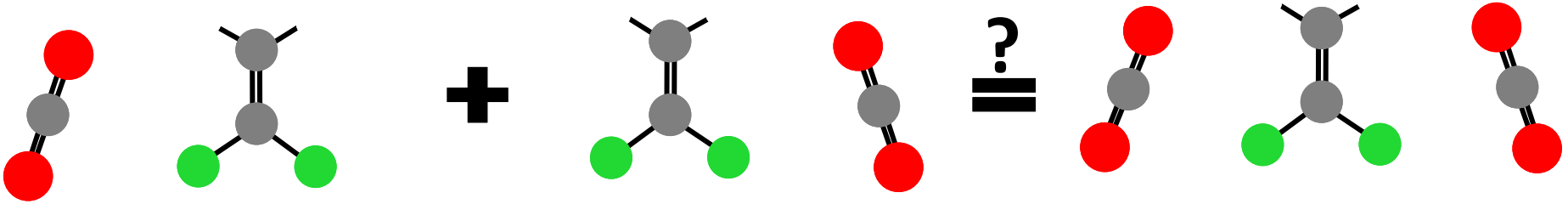
Figure adapted from: R. Dorris, *et al*, *J. Phys. Chem. A*, **120**, (2016), 7865.

X…CO_2 [kJ mol^{-1}] X =	E_{es}	E_{ind}	E_{disp}	E_{ex}	E_{SAPT}	E_{MP2} (BSSE)
FE (side)	–8.33 (52.0%)	–1.34 (8.3%)	–6.36 (39.7%)	8.33	–7.70	–6.41
FE (top)	–7.78 (49.7%)	–1.30 (8.2%)	–6.61 (42.1%)	8.03	–7.66	–6.30
FE (above)	–6.65 (42.5%)	–0.96 (6.1%)	–8.02 (51.3%)	8.43	–7.19	–6.44
1,1-DFE (top)	–5.69 (44.8%)	–1.00 (7.8%)	–6.02 (47.4%)	6.49	–6.22	–5.10
1,1-DFE (above)	–4.43 (34.8%)	–0.78 (6.1%)	–7.50 (59.1%)	7.35	–5.35	–4.86
cis-1,2-DFE (side)	–7.91 (51.0%)	–1.34 (8.6%)	–6.28 (40.5%)	7.99	–7.54	–6.33
cis-1,2-DFE (above)	–7.29 (44.6%)	–1.11 (6.8%)	–7.96 (48.7%)	8.38	–7.97	–6.81
TFE (side)	–7.61 (50.2%)	–1.30 (8.5%)	–6.23 (41.3%)	7.82	–7.32	–6.16
TFE (top)	–6.11 (45.7%)	–1.21 (9.0%)	–6.07 (45.3%)	6.78	–6.61	–5.39
TFE (above)	–5.84 (41.2%)	–0.87 (6.1%)	–7.47 (52.7%)	7.52	–6.66	–5.69

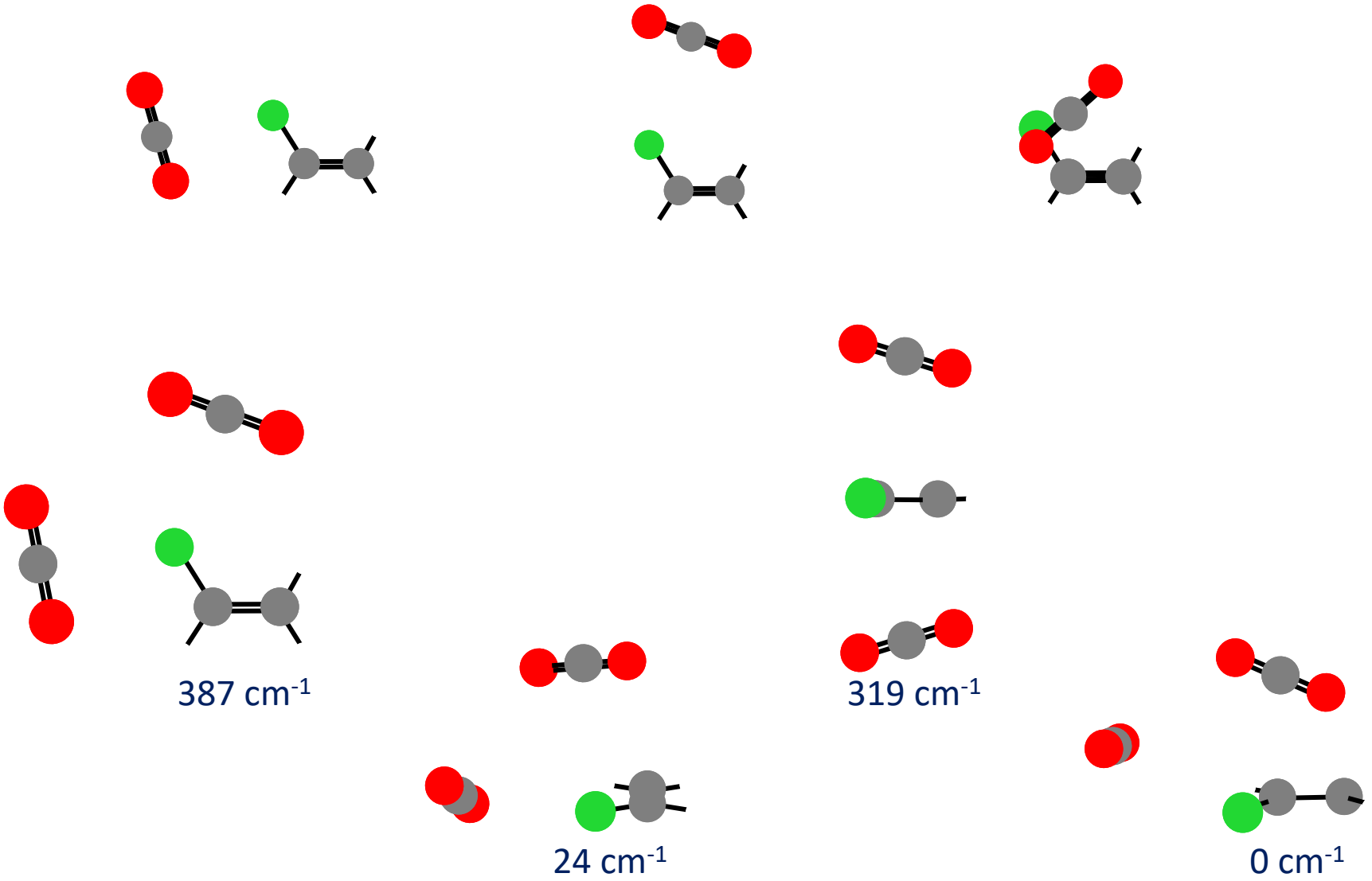
Table adapted from: R. Dorris, *et al*, *J. Phys. Chem. A*, **120**, (2016), 7865.





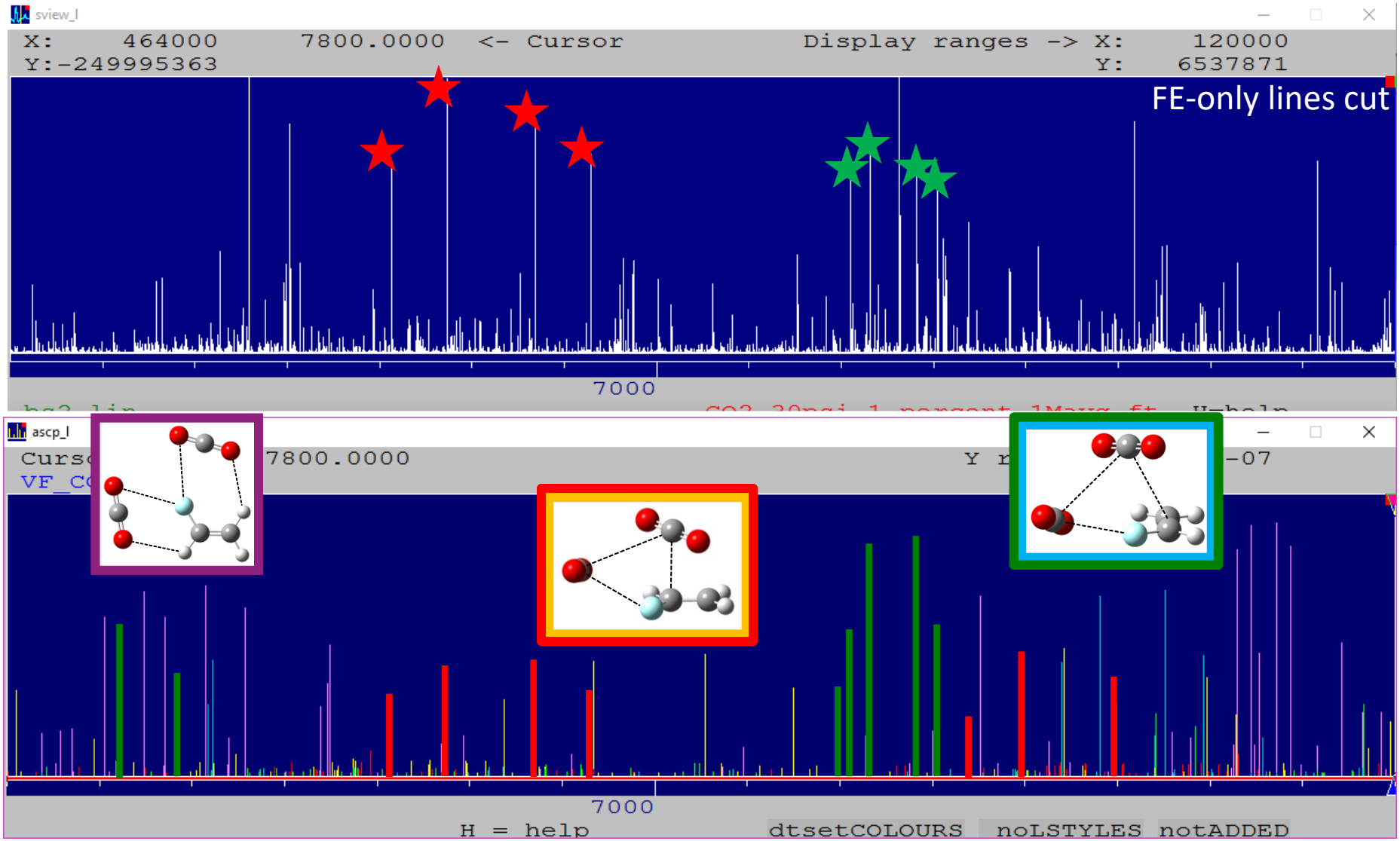


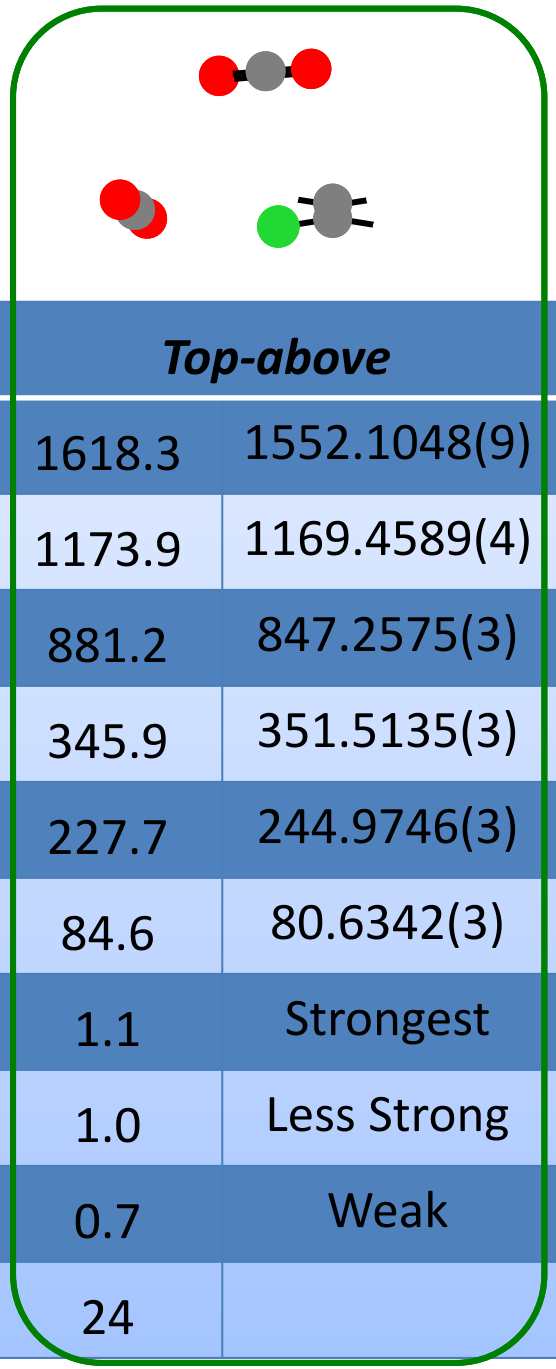
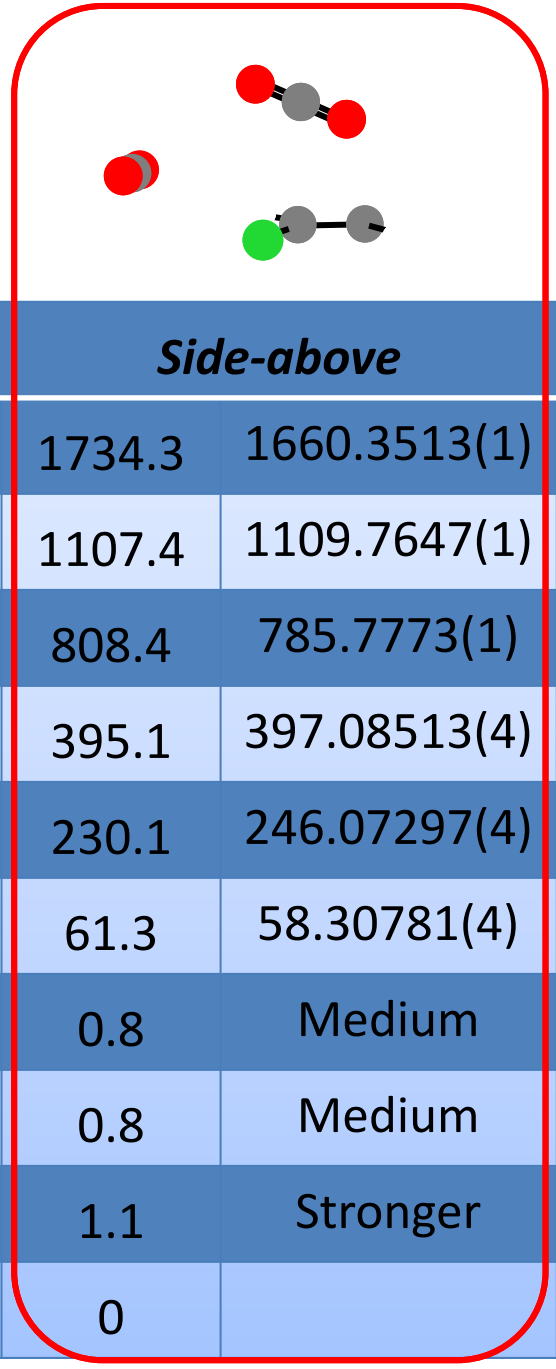
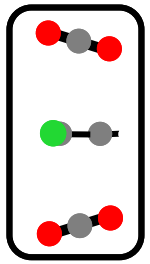
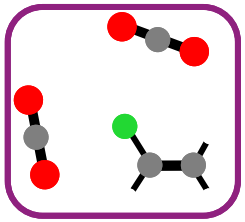
FE…CO_2…CO_2 Predictions



MP2/6-311++G(2d,2p) using Gaussian 09

New Fluoroethylene-CO_2 Scan – 1 million FIDs

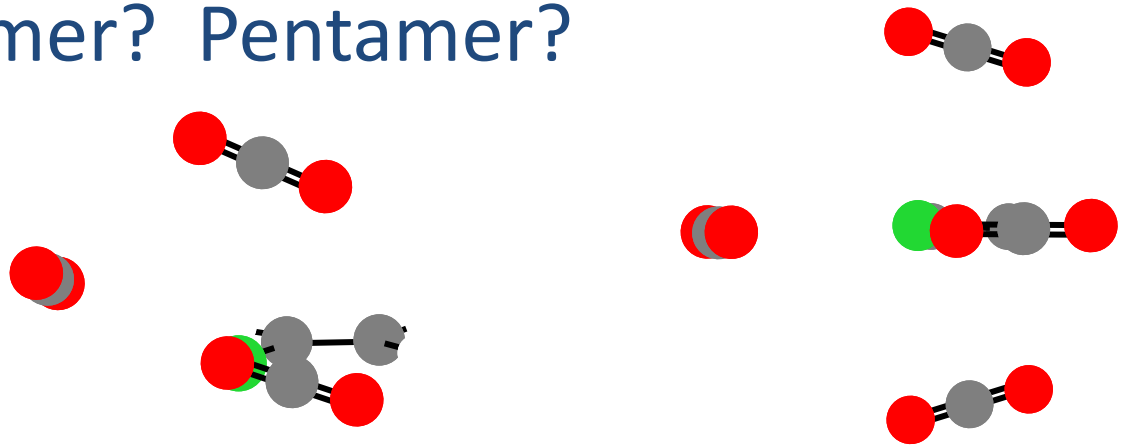


	Top-above		*Side-above*		*Above*	*Side-top*
***A* / MHz**	1618.3	1552.1048(9)	1734.3	1660.3513(1)	2933.3	1626.9
***B* / MHz**	1173.9	1169.4589(4)	1107.4	1109.7647(1)	643.5	922.8
***C* / MHz**	881.2	847.2575(3)	808.4	785.7773(1)	609.4	588.8
P_{aa} / u Å²	345.9	351.5135(3)	395.1	397.08513(4)	721.2	547.6
P_{bb} / u Å²	227.7	244.9746(3)	230.1	246.07297(4)	108.1	310.7
P_{cc} / u Å²	84.6	80.6342(3)	61.3	58.30781(4)	64.2	0.0
μ_a / D	1.1	Strongest	0.8	Medium	0.0	0.03
μ_b / D	1.0	Less Strong	0.8	Medium	0.5	1.5
μ_c / D	0.7	Weak	1.1	Stronger	1.5	0.0
ΔE / cm^{-1}	24		0		319	387

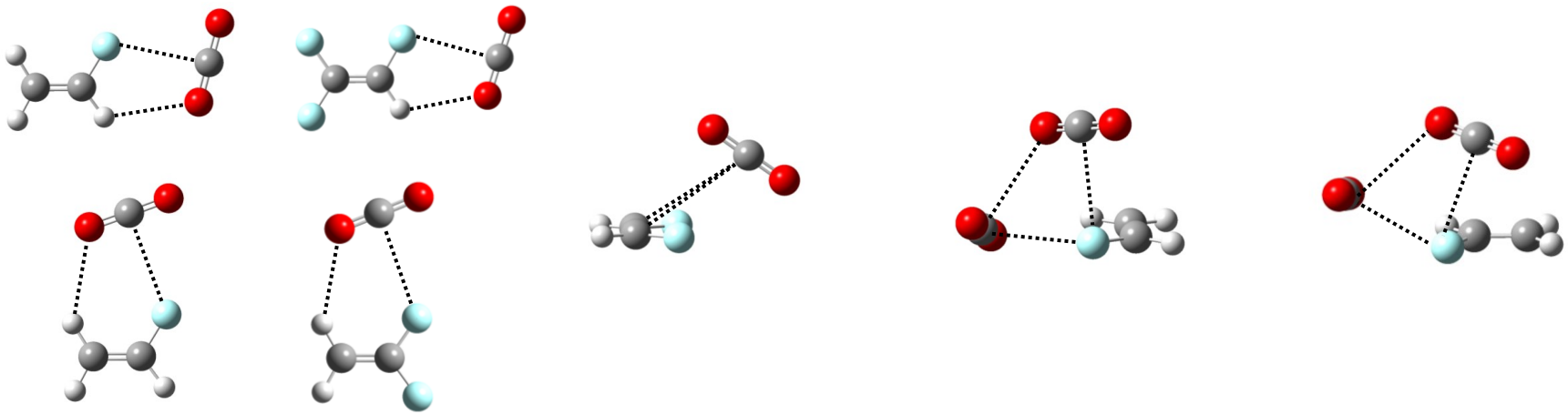
Larger Clusters?

- Two FE-CO_2-CO_2 trimers observed
  - Nearly isoenergetic
- Tetramer? Pentamer?



  - S/N probably borderline in current spectrum
- Pentamer - Add a second "Above" CO_2?
- Hexamer?

Summary and Future Work



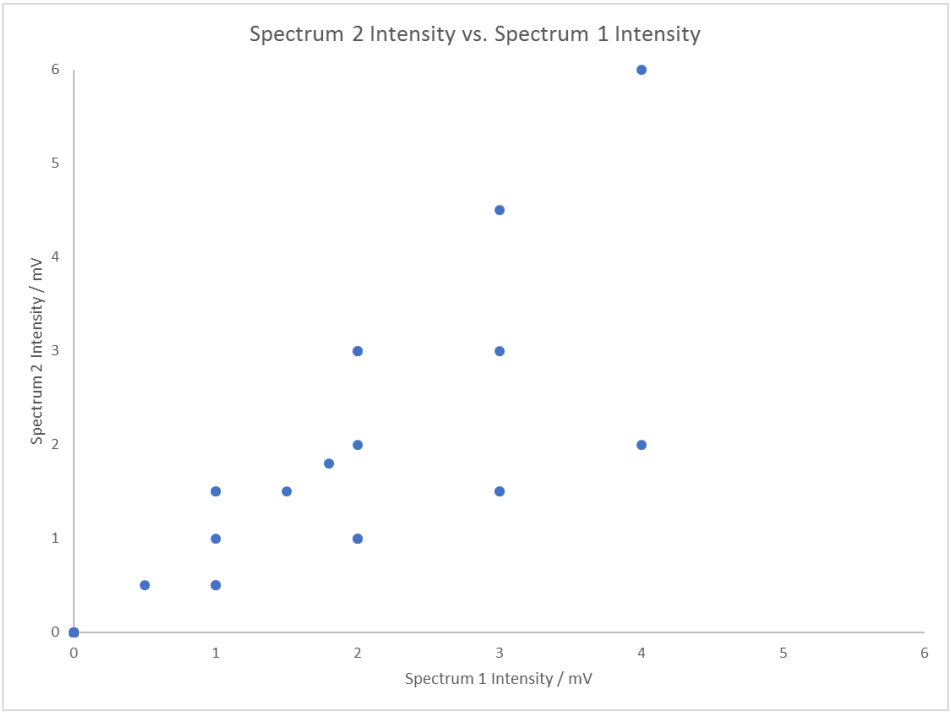
Extended cross correlation: A technique for spectroscopic pattern recognition

Matthew P. Jacobson, Stephen L. Coy, and Robert W. Field

J. Chem. Phys. **107** (20), 22 November 1997

LabView

$$G(\alpha) = \sum_i g_i(\alpha) = \sum_i R_i * \exp(-d_i^2/2V_d)$$



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