The Molecular Structure of **Monofluorobenzaldehydes**

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Previous Studies

J. Chem. Soc., Faraday Trans. 2, 1989, **85**(2), 137–149

Rotational Isomerism in Monofluorobenzaldehydes

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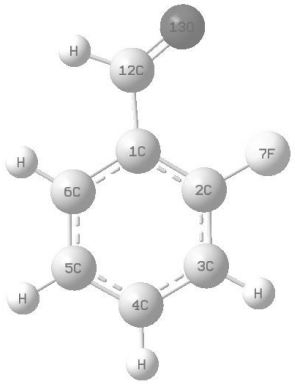
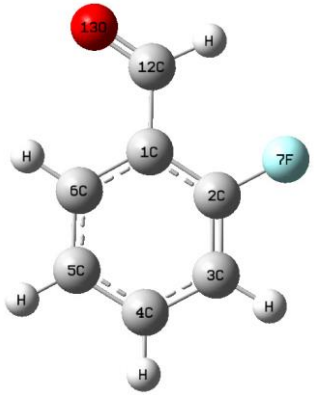
Microwave spectra of 2- and 3-fluorobenzaldehydes have been investigated in the frequency region 26.5–40.0 GHz. Only the *O-trans* form of 2-fluorobenzaldehyde was detected in the gas phase. Analysis of 3-fluorobenzaldehyde confirmed the existence of two rotational isomers: *O-cis* and *O-trans*. From relative intensity measurements the *O-cis* form was shown to be more stable than the *O-trans* form by 300 ± 200 cal mol^{-1}. The inertia defect values and the variation of the rotational constants with the torsional quantum number demonstrate that the equilibrium geometry is planar for all rotamers. Molecular structures which are in very good agreement with experimental rotational constants have also been derived.

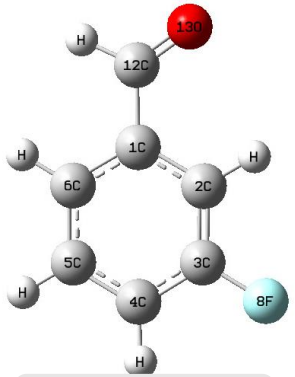
- RFMWDR technique (26.5 – 40.0 GHz)
- 3 vibrational states for O-*trans* 2FBA
- 4 vibrational states for each 3FBA conformer



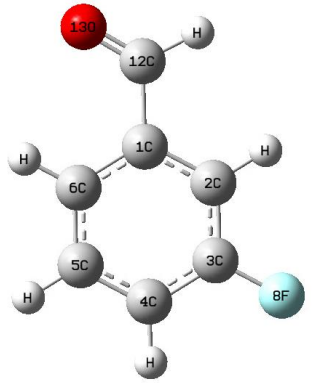
O-*cis* 2FBA



O-*trans* 2FBA



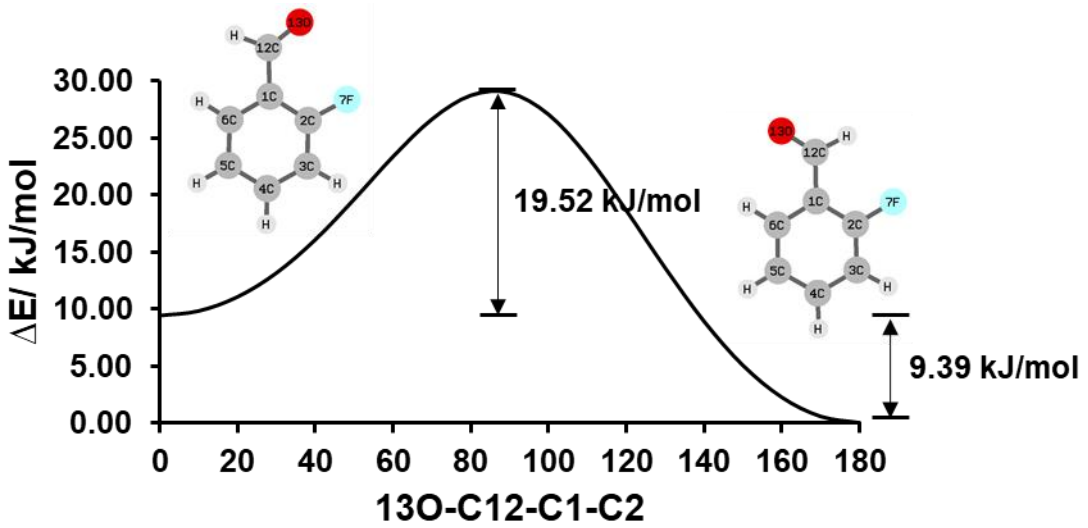
O-*cis* 3FBA

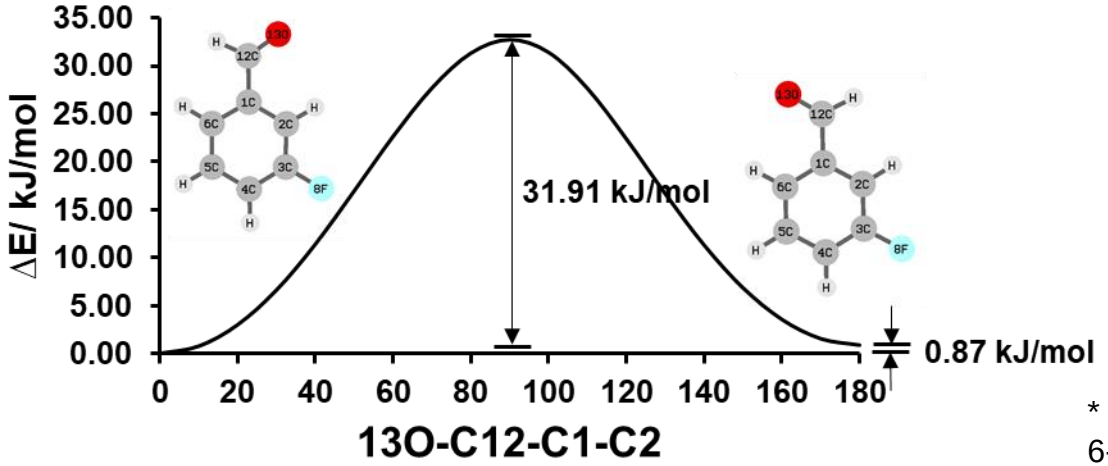


O-*trans* 3FBA

J. L. Alonso, R.M. Villamañán, *J. Chem. Soc., Faraday Trans.*, **1989**, *85(2)*, 137-149

Potential Energy Curve





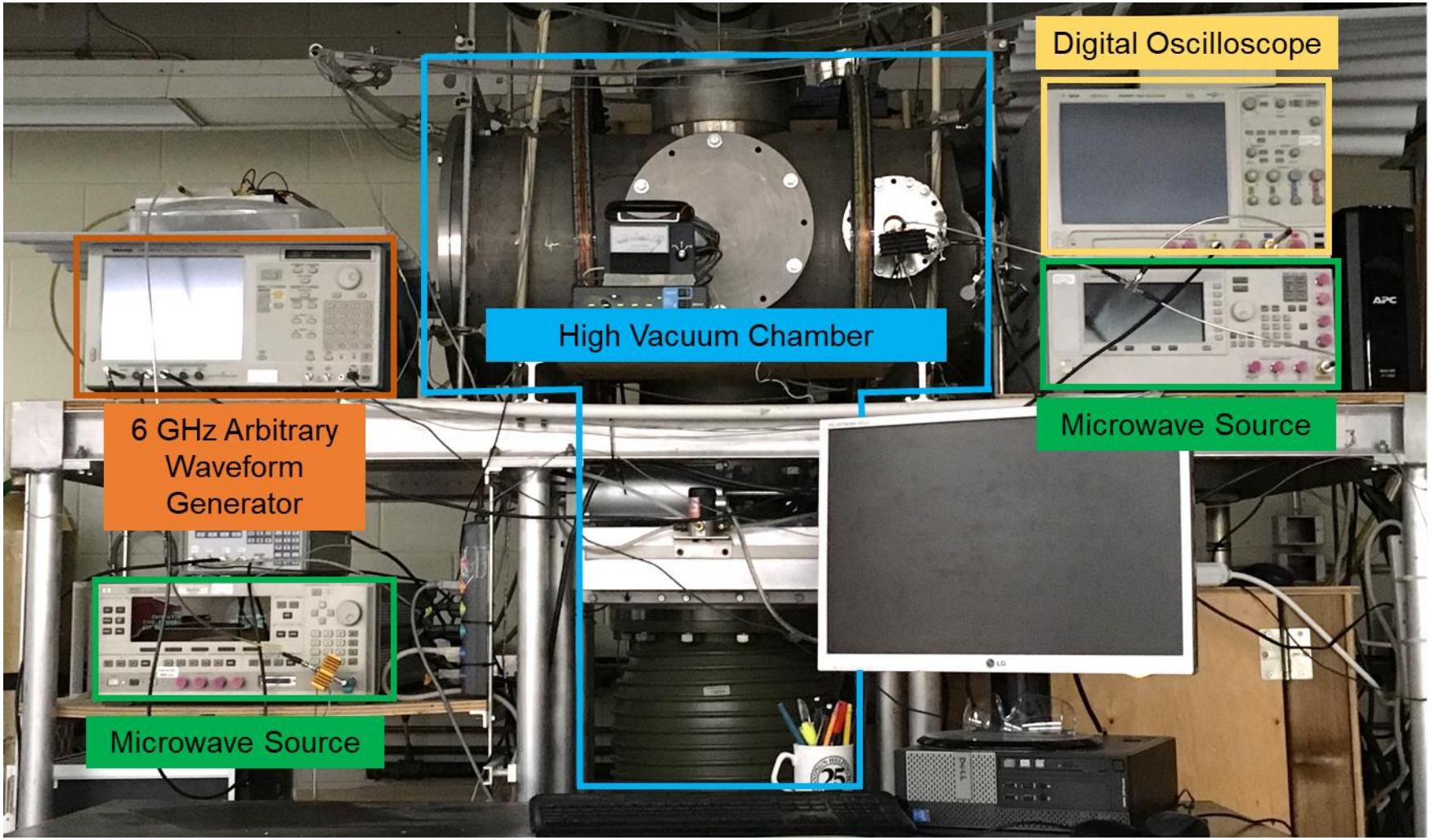
Previous study

2-FBA		
/MHz	O-*cis*	O-*trans*
A		2567.609(3)
B		1560.8694(9)
C		970.954(1)

3-FBA		
/MHz	O-*cis*	O-*trans*
A	2919.255(2)	3657.169(5)
B	1269.697(2)	1114.781(2)
C	884.964(2)	854.530(2)

* Potential energy curves are carried out at MP2/ 6-311++G(2d,2p)

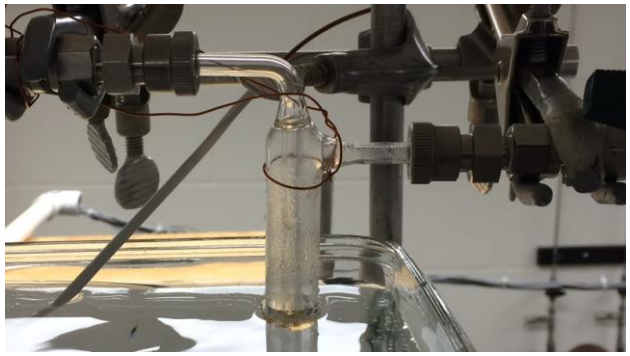
cp FTMW Spectrometer

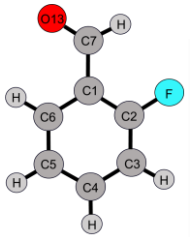


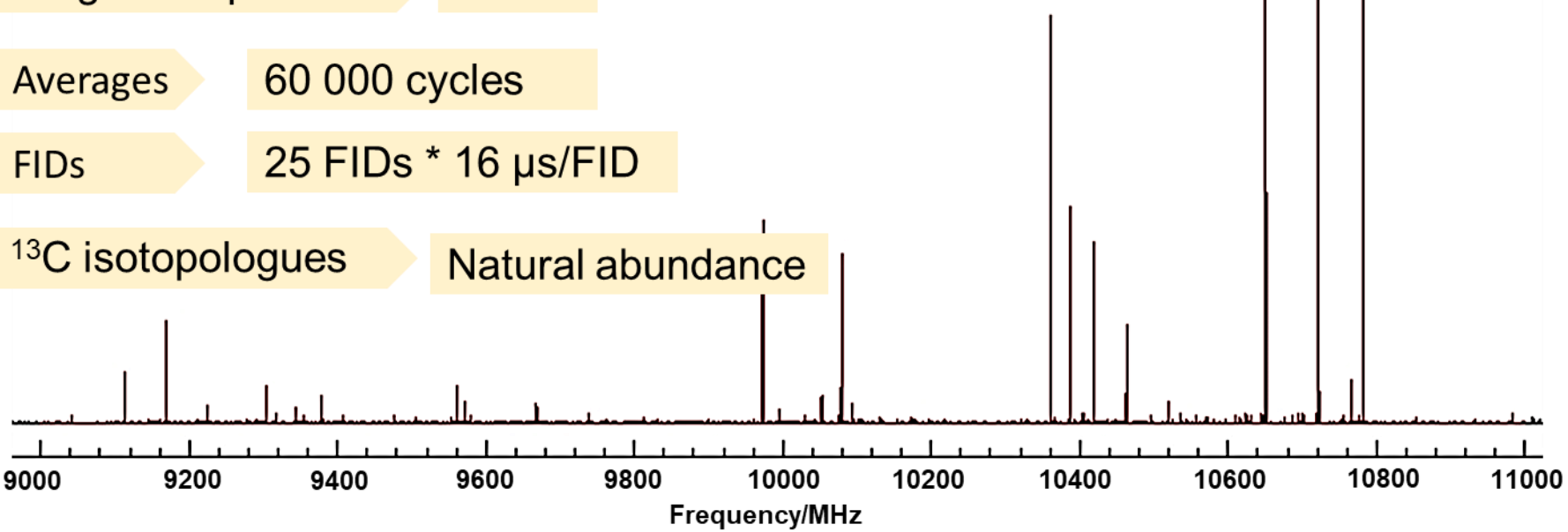
L. Evangelisti, G. Sedo, J. van Wijngaarden, *J. Phys. Chem. A,* **2011**, *115*, 685-690

Experimental Conditions

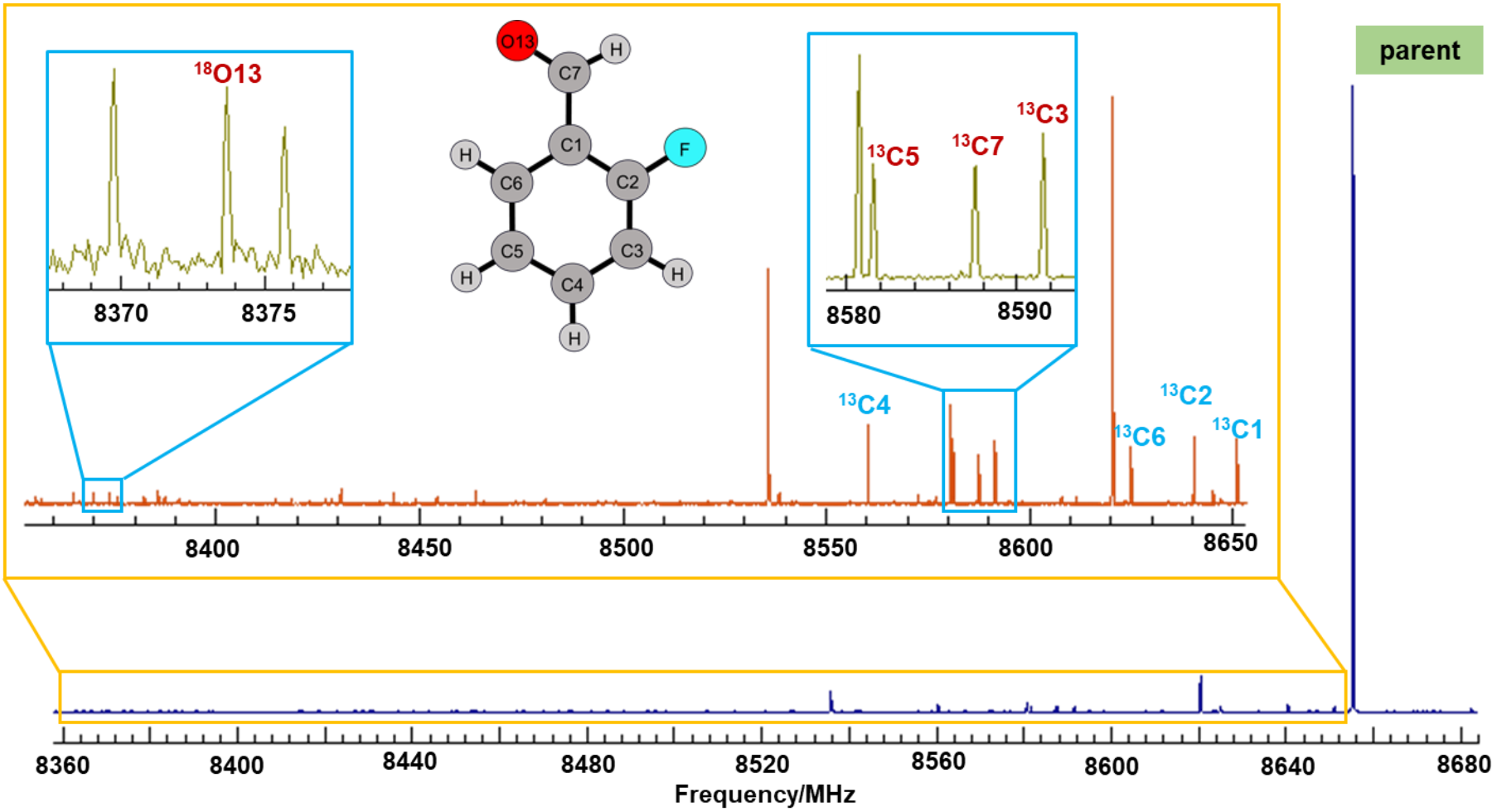
Spectral range	8-18 GHz
Bandwidth	2000 MHz
Carrier gas	Neon
Stagnation pressure	1 bar
Averages	60 000 cycles
FIDs	25 FIDs * 16 µs/FID
^{13}C isotopologues	Natural abundance



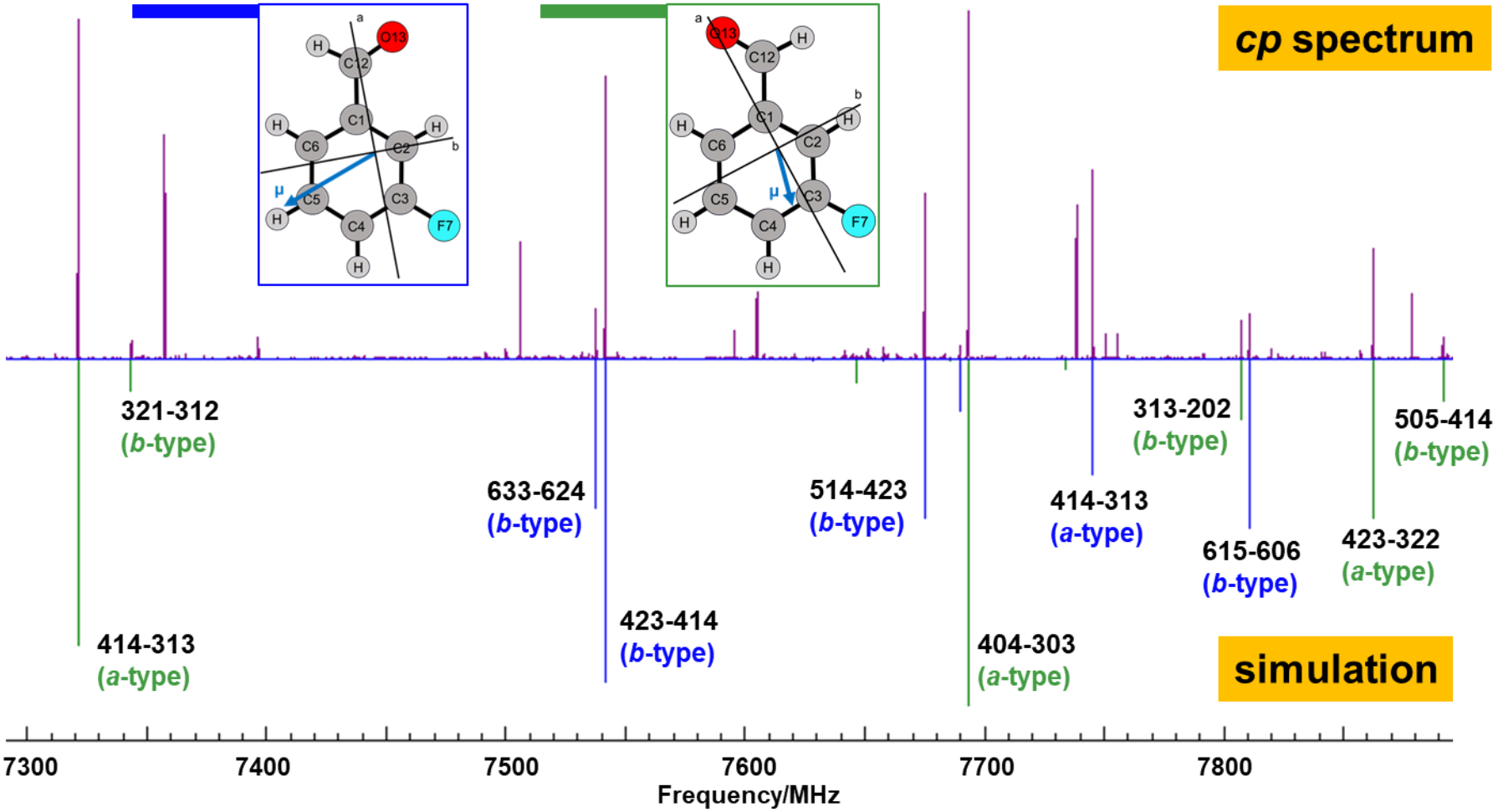




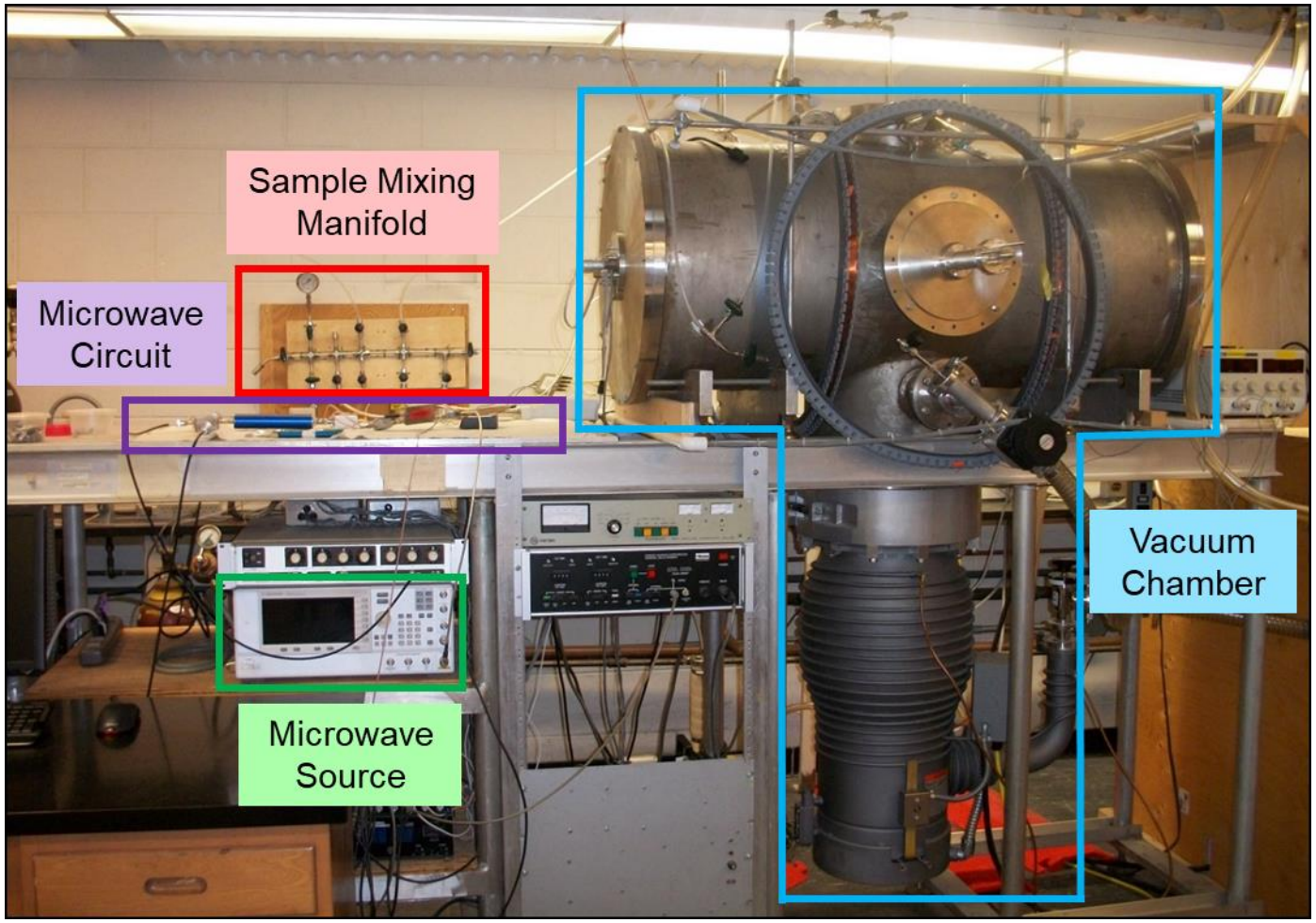
O-*trans* 2FBA: 414 - 313



3FBA: O-*cis* & O-*trans*

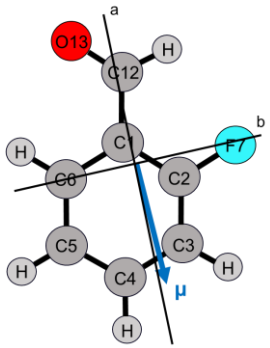


Balle Flygare FTMW Spectrometer



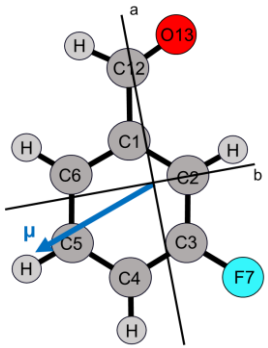
G. Sedo, J. van Wijngaarden, *J. Chem. Phys.* **2009**, *131*, 044303.

Line collection: 4-26 GHz



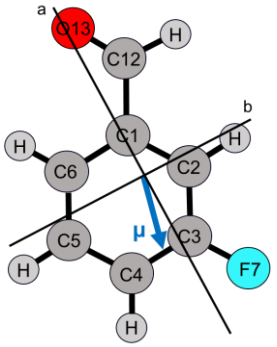
	Dipole/D	#line
a-type	3.81	124
b-type	0.17	0

Isotope	#line
^{13}C-1	25
^{13}C-2	25
^{13}C-3	28
^{13}C-4	28
^{13}C-5	25
^{13}C-6	29
^{13}C-12	28
^{18}O-13	12



	Dipole/D	#line
a-type	1.58	24
b-type	3.90	55

Isotope	#line
^{13}C-1	7
^{13}C-2	9
^{13}C-3	7
^{13}C-4	13
^{13}C-5	9
^{13}C-6	17
^{13}C-12	18



	Dipole/D	#line
a-type	2.18	39
b-type	**0.08**	10

Isotope	#line
^{13}C-1	6
^{13}C-2	9
^{13}C-3	8
^{13}C-4	9
^{13}C-5	8
^{13}C-6	10
^{13}C-12	9

* All dipole moments are calculated at MP2/ aug-cc-pVTZ

SPFIT: Watson - A reduction

2FBA	O-*trans*	
	This work	Previous work*
A/MHz	2567.599481(46)	2567.609(3)
B/MHz	1560.865217(16)	1560.8694(9)
C/MHz	970.950256(10)	970.954(1)
Δ_J/kHz	0.059225(94)	0.072(2)
Δ_{JK}/kHz	0.13286(34)	0.128(4)
Δ_K/kHz	0.1297(16)	0.19(2)
δ_J/kHz	0.021890(48)	0.0221(5)
δ_K/kHz	0.15851(33)	0.151(4)
RMS/kHz	**0.484**	**46**

3FTBA	O-*cis*		O-*trans*	
	This work	Previous work*	This work	Previous work*
A/MHz	2919.250865(64)	2919.255(2)	3657.20290(52)	3657.169(5)
B/MHz	1269.700848(41)	1269.697(2)	1114.785459(66)	1114.781(2)
C/MHz	884.961618(28)	884.964(2)	854.522877(50)	854.530(2)
Δ_J/kHz	0.06489(31)	0.062(4)	0.02374(33)	0.024(4)
Δ_{JK}/kHz	-0.1789(15)	-0.17(2)	0.1237(17)	0.13(1)
Δ_K/kHz	0.6396(37)	0.67(5)	0.75(51)	\
δ_J/kHz	0.02357(15)	0.018(2)	0.00601(21)	\
δ_K/kHz	0.1043(17)	0.08(2)	0.115(18)	\
RMS/kHz	**0.806**	**47**	**0.491**	**66**

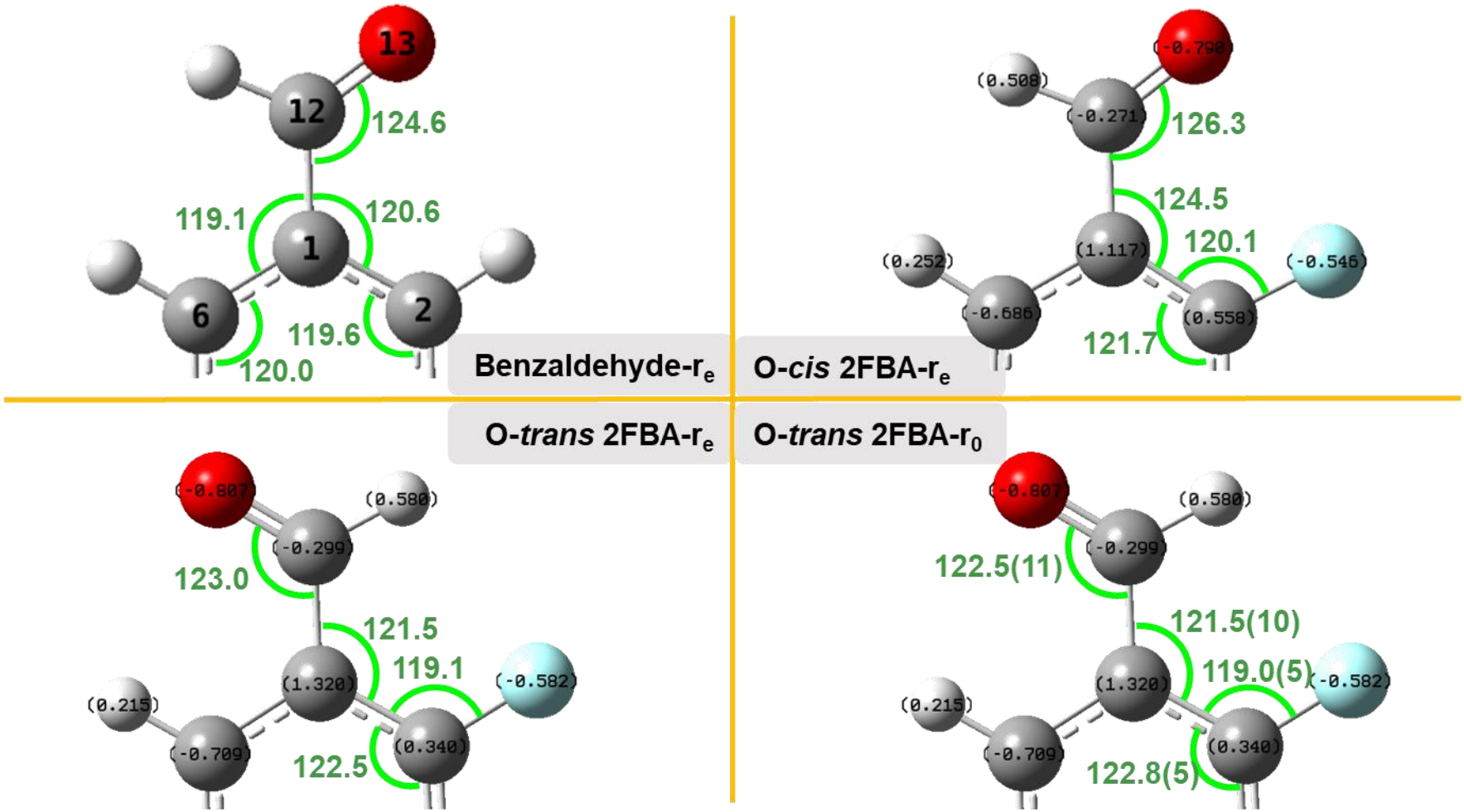
J. L. Alonso, R.M. Villamañán, *J. Chem. Soc., Faraday Trans.*, **1989**, *85(2)*, 137-149

Effective Structure - r_0

	2FBA O-*trans*		3FBA O-*cis*		3FBA O-*trans*	
	r_e	r_0	r_e	r_0	r_e	r_0
R(C1-C2)	1.393	1.385(11)	1.398	1.407(9)	1.397	1.379(9)
R(C3-C2)	1.385	1.388(3)	1.382	1.375(11)	1.385	1.396(6)
R(C4-C3)	1.392	1.396(4)	1.391	1.392(4)	1.387	1.388(3)
R(C5-C4)	1.397	1.399(6)	1.393	1.395(4)	1.396	1.396(5)
R(C6-C5)	1.388	1.402(10)	1.393	1.405(10)	1.390	1.398(6)
R(C1-C6)	1.400	1.402(13)	1.396	1.385(7)	1.397	1.410(12)
R(C7-C1)	1.480	1.491(6)	1.479	1.491(5)	1.479	1.488(6)
R(O13-C7)	1.220	1.218(10)				
∠(C3-C2-C1)	122.5	122.8(5)	117.9	117.3(5)	118.3	118.0(5)
∠(C4-C3-C2)	118.5	118.1(3)	122.5	123.2(3)	122.2	122.5(2)
∠(C5-C4-C3)	120.5	120.6(1)	118.8	118.5(2)	118.7	118.5(2)
∠(C6-C5-C4)	120.0	120.0(2)	120.1	120.0(2)	120.5	120.5(2)
∠(C2-C1-C6)	120.6	119.8(5)	119.8	119.5(5)	119.5	119.0(3)
∠(C1-C6-C5)	118.1	118.7(6)	120.8	121.5(6)	120.7	121.3(5)
∠(C7-C1-C2)	121.5	121.5(10)	119.9	119.4(6)	118.6	119.1(9)
∠(O13-C7-C1)	123.0	122.5(11)				

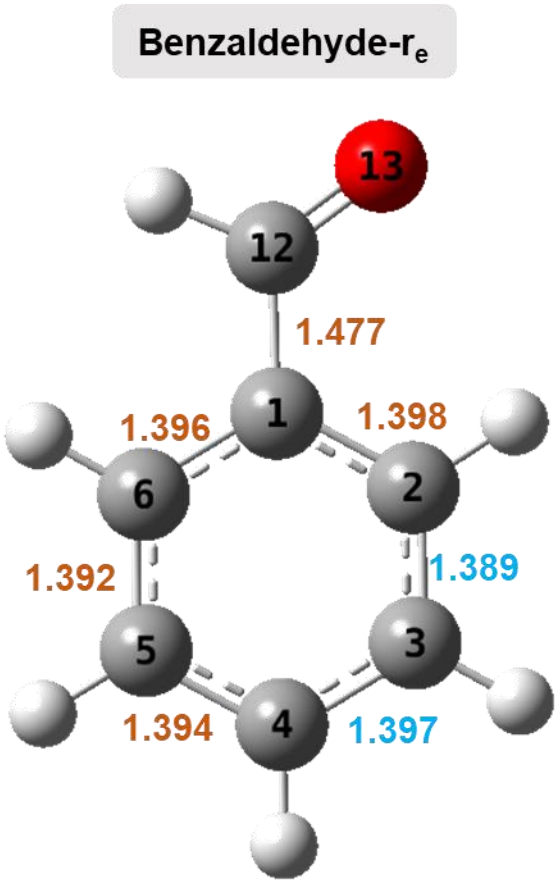
Z. Kisiel, *PROSPE-Programs for Rotational Spectroscopy*, http://info.ifpan.edu.pl/~kisiel.htm.

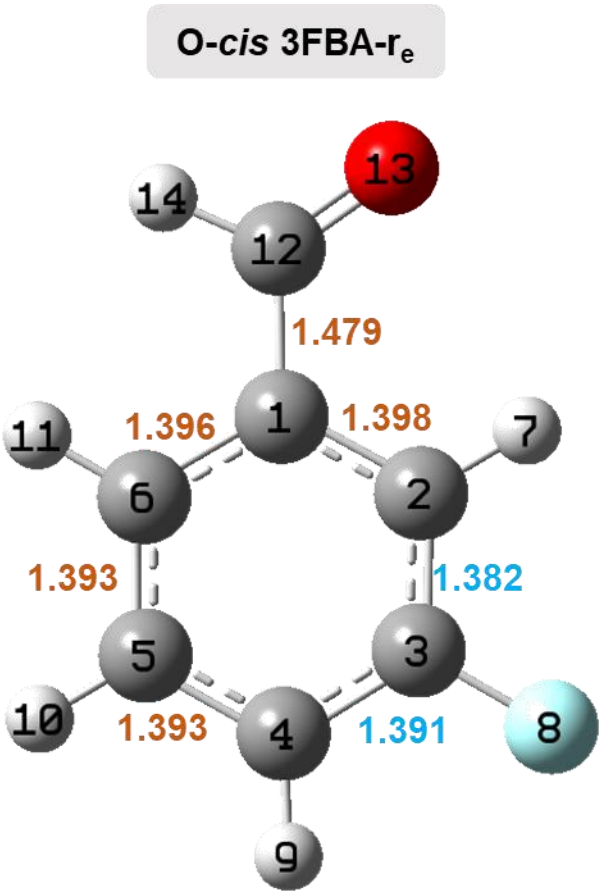
Structural Analysis: 2FBA

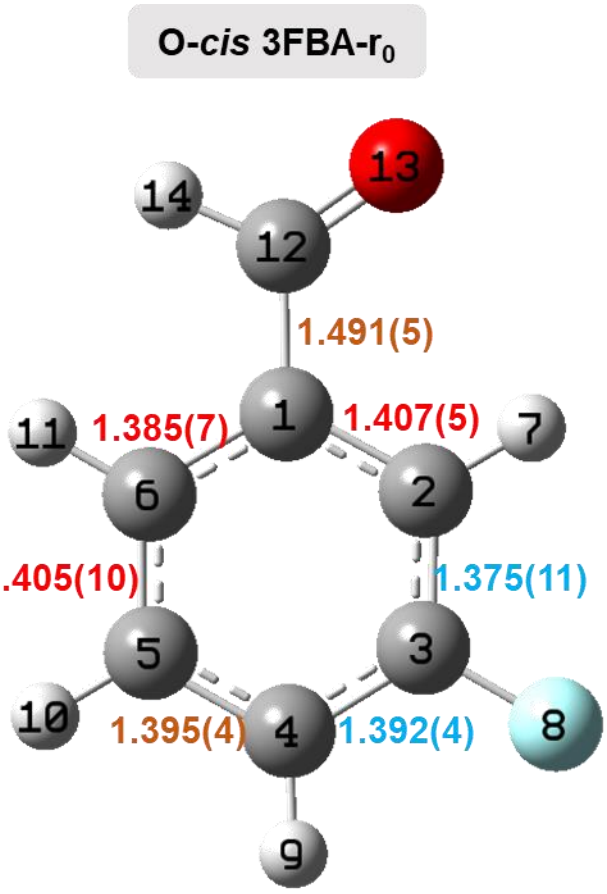


Equilibrium structures are calculated at MP2/ aug-cc-pVTZ, and atomic charges shown are Mulliken charges.

Structural Analysis: O-*cis* 3FBA

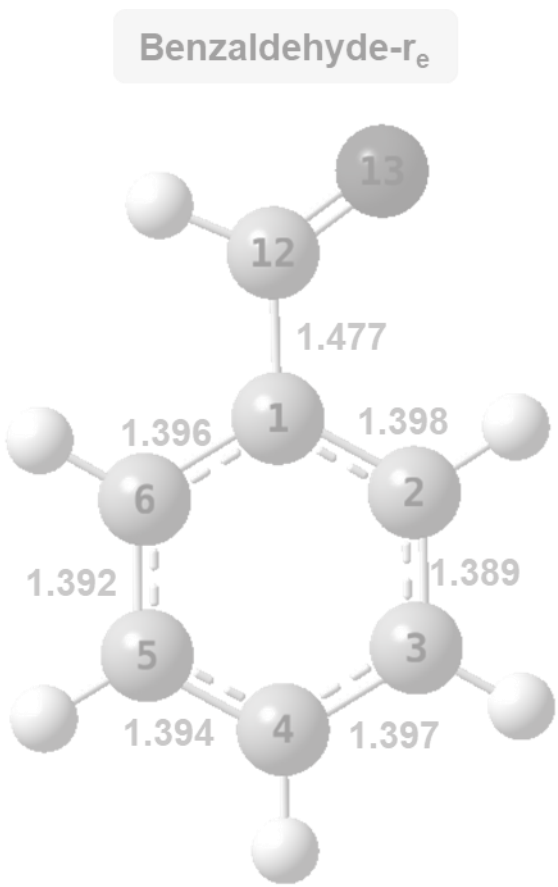


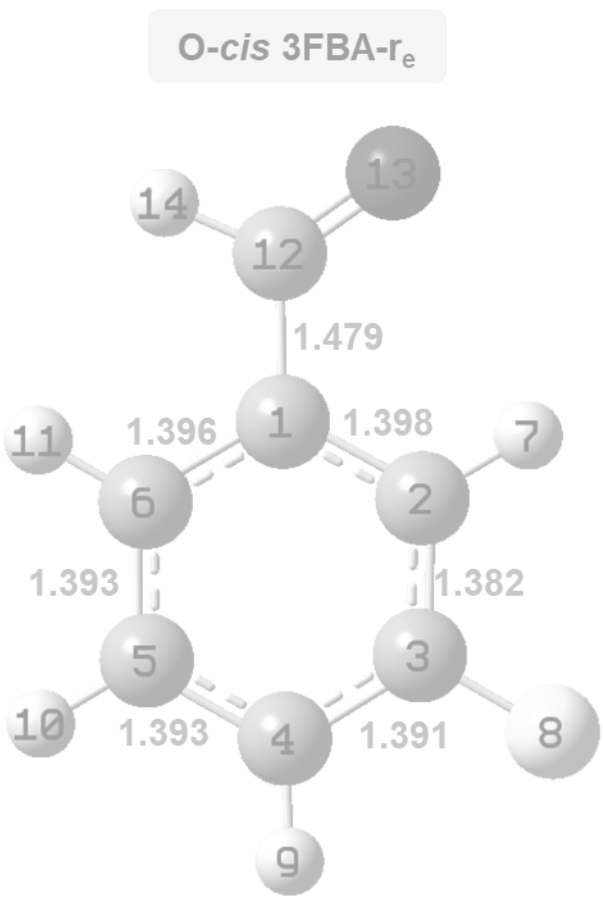


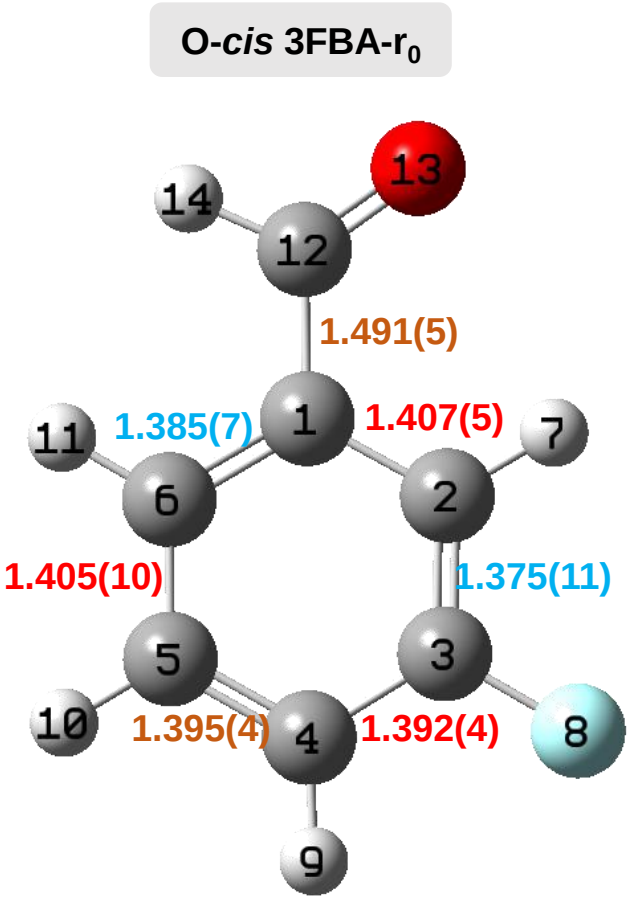


Equilibrium structures are calculated at MP2/ aug-cc-pVTZ.

Structural Analysis: O-*cis* 3FBA



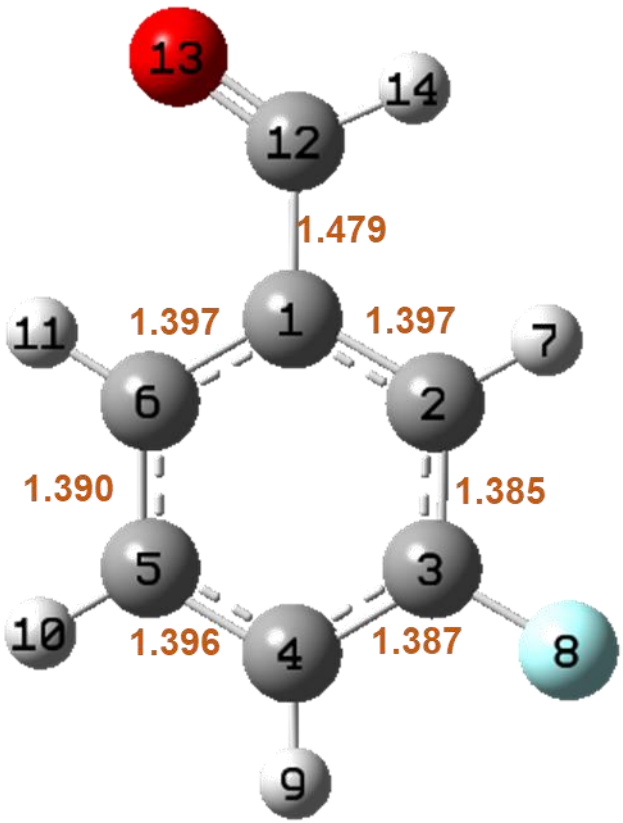




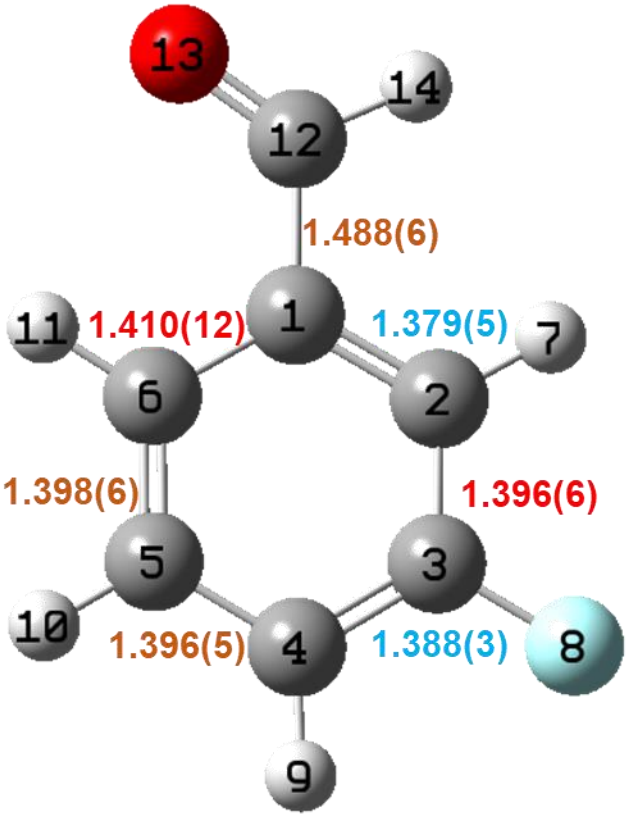
Equilibrium structures are calculated at MP2/ aug-cc-pVTZ.

Structural Analysis: O-*trans* 3FBA

O-*trans* 3FBA-r_e



O-*trans* 3FBA-r_0



Equilibrium structure is calculated at MP2/ aug-cc-pVTZ.

Acknowledgements

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