

# Spectroscopy, Monte Carlo, and Electronic Structure Structures of Benzene-derivative Solvation Clusters

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## OVERVIEW

Neat fluorobenzene and mixed benzene-fluorobenzene clusters have been studied via resonant two photon ionization (R2PI) spectroscopy to measure ultraviolet spectra through fluorobenzene's  $B_2 \leftarrow A_1 0^0_0$  vibronic transition at  $37813 \text{ cm}^{-1}$ . In separate experiments, the clusters were scanned from  $-200 \text{ cm}^{-1}$  to  $+80 \text{ cm}^{-1}$  relative to  $37813 \text{ cm}^{-1}$ . Spectra reveal reproducible sharp spectral features for all dimers and trimers. Initial efforts have focused on interpretation of the spectra in terms of rigid structures and isomerization.

## EXPERIMENTAL

- Resonant Two-Photon Ionization (R2PI) Spectroscopy
  - Sources:  $C_6H_5F$ ; 50 mol%  $C_6H_6/C_6H_5F$
  - Background pressure:  $10^{-7}$  torr
  - Carrier gas: He (10 atm)
  - Resolution ( $C_6H_5F$  and  $C_6H_6/C_6H_5F$ ):  $0.11 \text{ cm}^{-1}$  (step-size limited)
  - Transition ( $C_6H_5F$  and  $C_6H_6/C_6H_5F$ ):  $C_6H_5F, B_2 \leftarrow A_1 0^0_0, 37813 \text{ cm}^{-1}$
- Similar to experiments reported in Ref. 1

## RESULTS: Neat $(C_6H_5F)_n$ Clusters

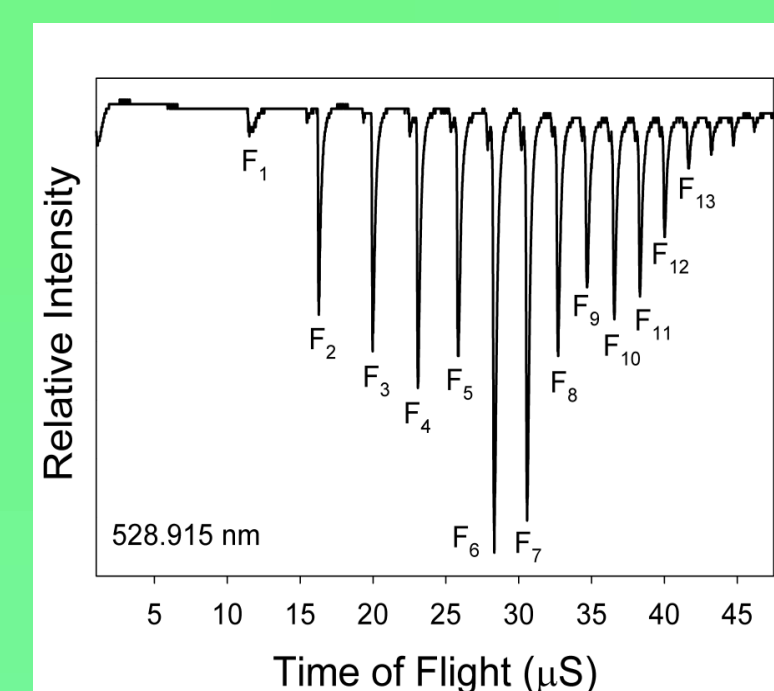


Fig. A

Fig. A: Mass spectrum of neat  $F_m$  [ $(C_6H_5F)_m$ ] clusters at  $528.915 \text{ nm}$ , using Coumarin 540A dye.

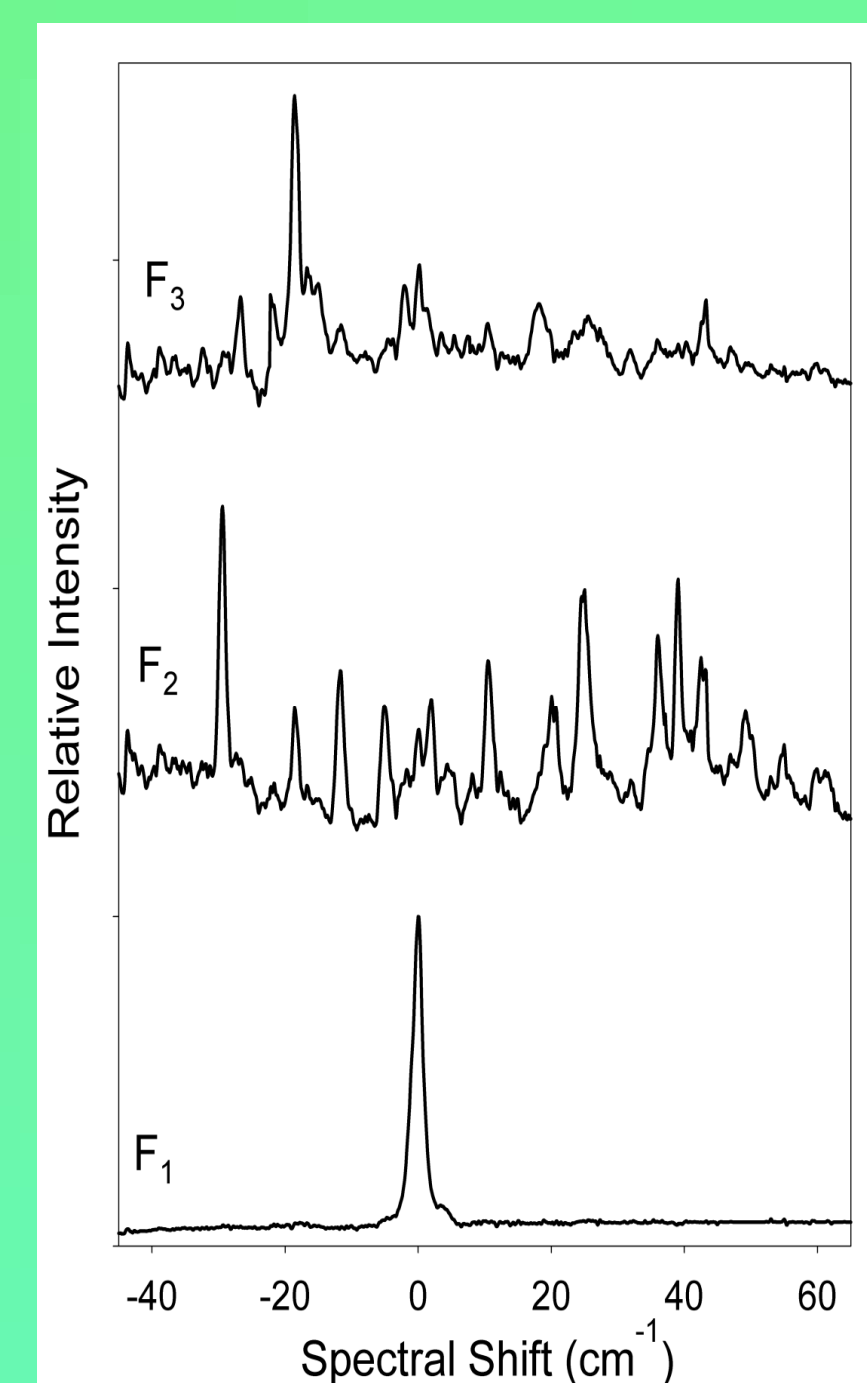


Fig. B

Fig. B: R2PI spectra of the neat fluorobenzene monomer, dimer, and trimer at a resolution of  $0.11 \text{ cm}^{-1}$ . Sharp features are reproducible and distinct. The dimer peak at  $-18.6 \text{ cm}^{-1}$  is an artifact of trimer fragmentation.

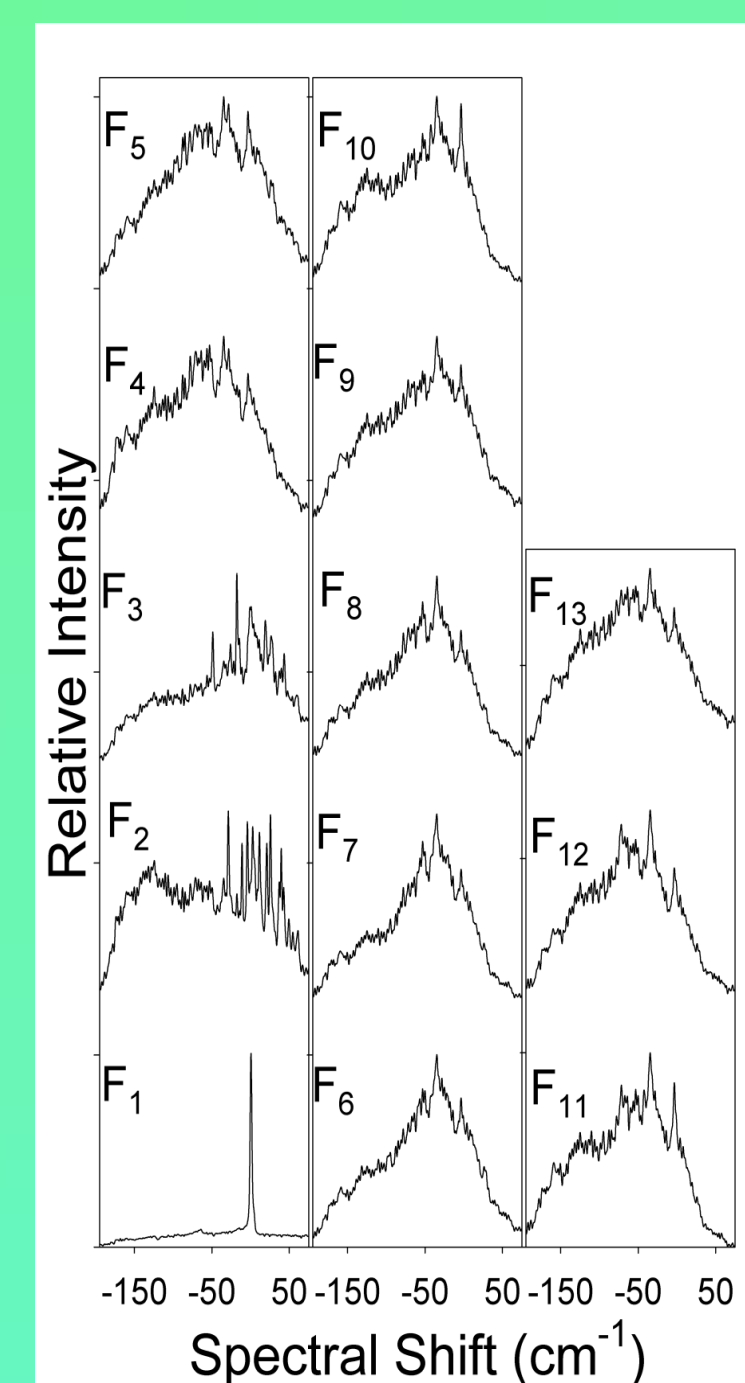


Fig. C

Fig. C: Lower resolution spectra ( $0.60 \text{ cm}^{-1}$ ) of neat fluorobenzene clusters through  $(C_6H_5F)_{13}$ . Spectra of clusters larger than the trimer tend to be broad and lacking in significant sharp features.

Shift/ $\text{cm}^{-1}$	-29.4	-18.6	-11.7	-5.0	0.1	1.9	10.5	20.1
Intensity	100	39*	50	39	32	41	53	42
	25.0	36.0	39.1	42.5	49.2	55.0	60.4	
	75	61	78	54	37	27	16	

Peak positions and relative intensities of sharp features in the neat fluorobenzene dimer (above) and trimer (below). \*The dimer peak at  $-18.6 \text{ cm}^{-1}$  shift originates from fragmentation of the trimer.

Shift/ $\text{cm}^{-1}$	-26.7	-18.6	-2.0	0.2	18.1	25.6	43.3
Intensity	39	100*	42	48	37	33	38

## ANALYSIS: van der Waals Modes in the $C_6H_5F$ Dimer

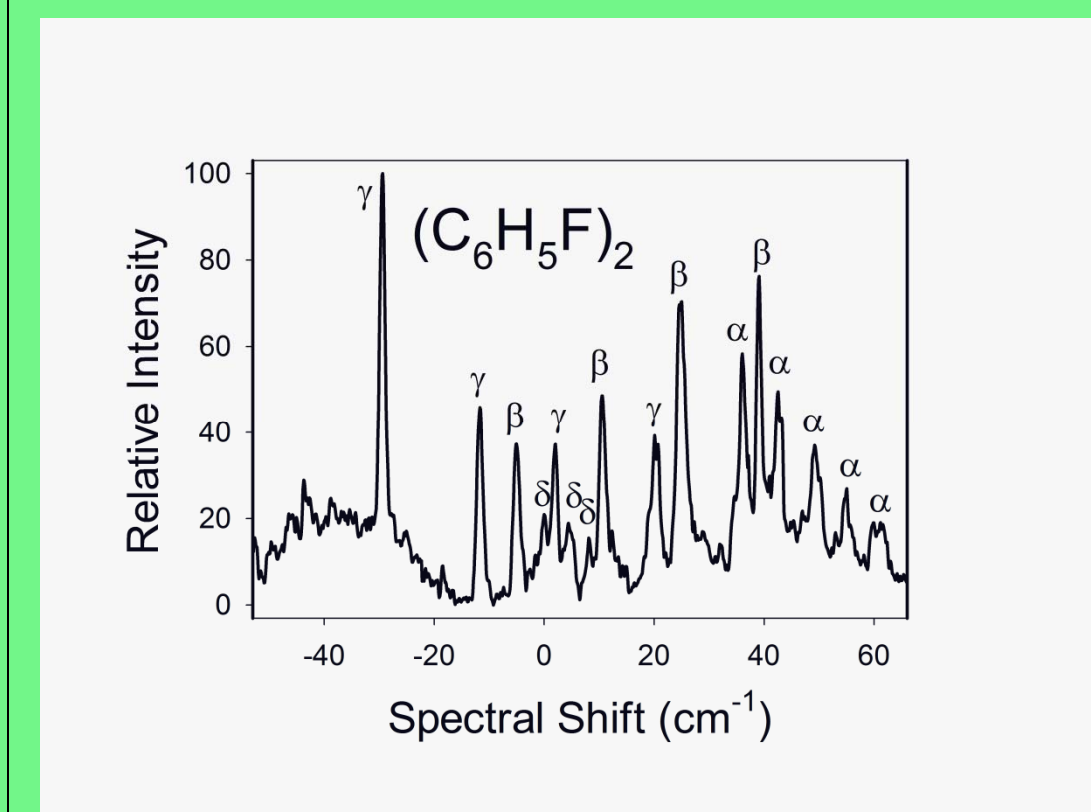


Fig. D

Fig. D: A cleaned  $C_6H_5F$  dimer spectrum. Cleaning was accomplished by subtracting  $\sim 1/3$  times the raw trimer spectrum from the raw dimer spectrum (Fig B); it removed artifacts originating from fragmentation of the trimer. The spectrum can be interpreted as a superposition of four van der Waals progressions, with the origins and fundamental wavenumbers tabulated below. Standard errors are in parentheses.

label	origin ( $\text{cm}^{-1}$ )	$\nu$ ( $\text{cm}^{-1}$ )	label	origin ( $\text{cm}^{-1}$ )	$\nu$ ( $\text{cm}^{-1}$ )
$\alpha$	33.3 (0.5)	6.1 (0.2)	$\gamma$	-37.2 (1.4)	16.2 (0.6)
$\beta$	-11.9 (0.5)	14.6 (0.2)	$\delta$	-1.9 (0.3)	4.1 (0.2)

## RESULTS: Mixed $(C_6H_6)_m(C_6H_5F)_n$ Clusters

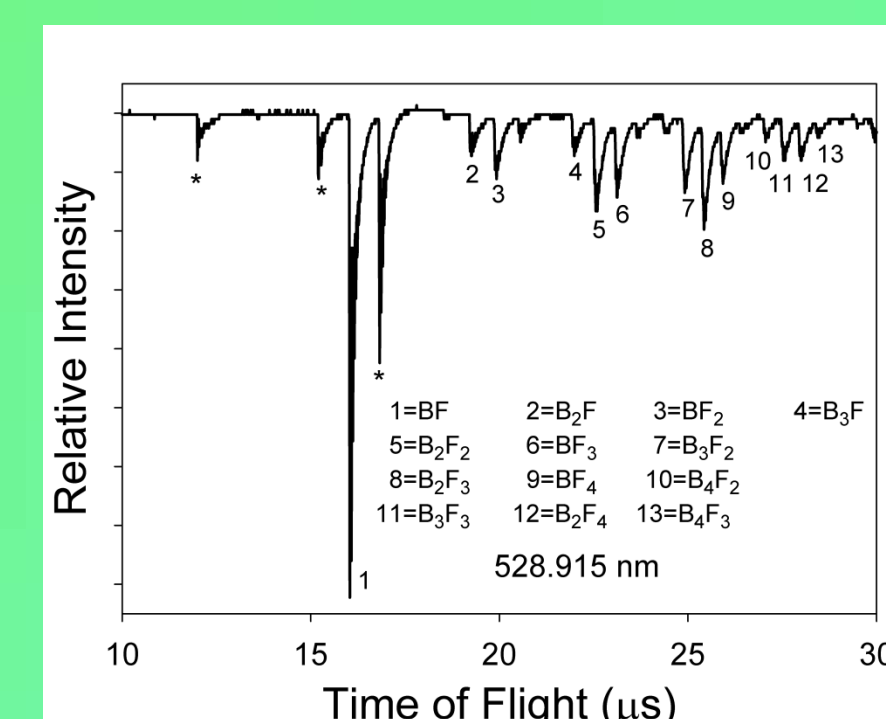


Fig. E

Fig. E: Mass spectrum of mixed benzene-fluorobenzene clusters at  $528.915 \text{ nm}$ . \*In order, F,  $B_2$ , and  $F_2$  are labeled with asterisks. The small peak between "3" and "4" is  $F_3$ .

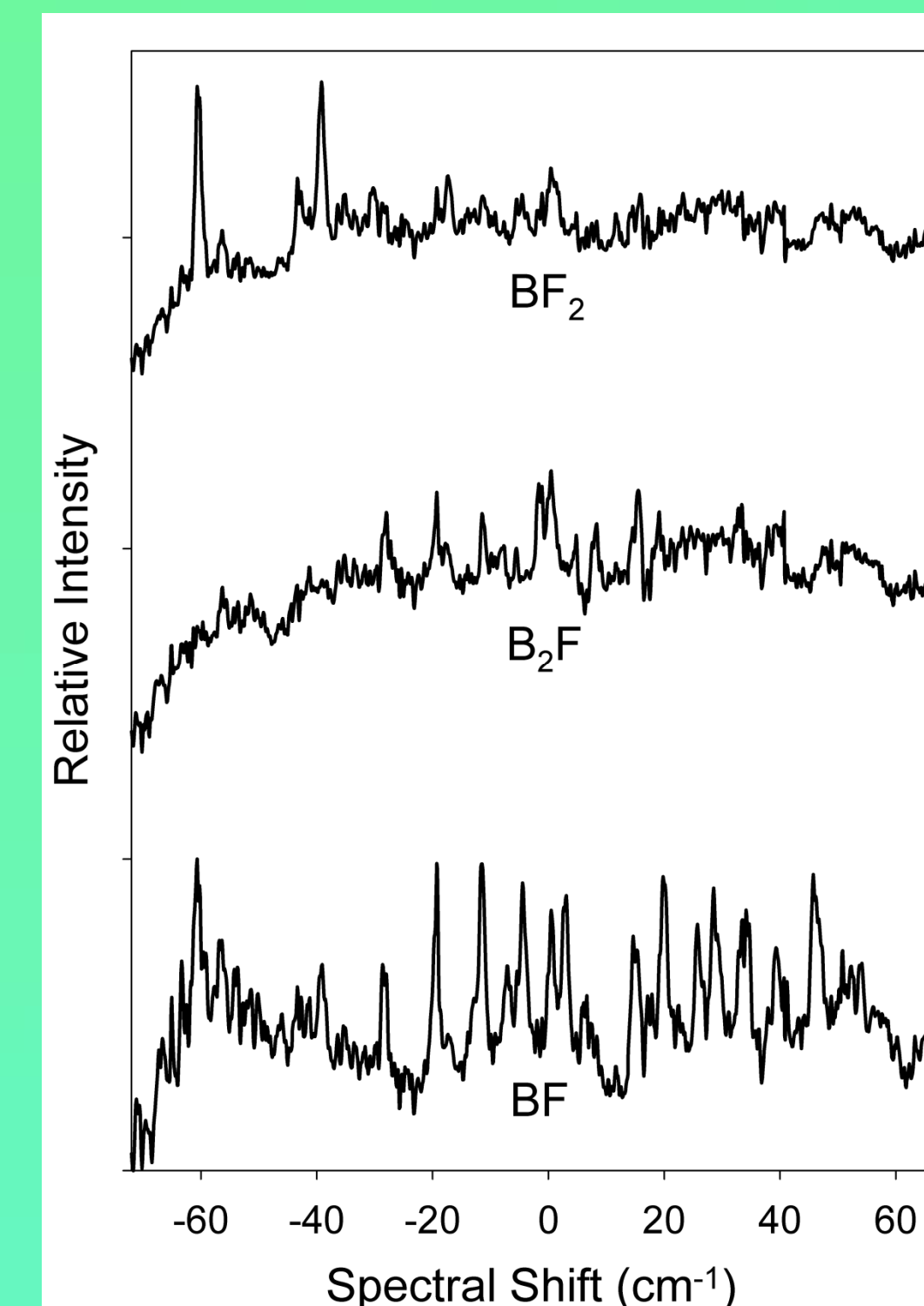


Fig. F

Fig. F: R2PI spectra of the mixed fluorobenzene-benzene dimer and trimers at a resolution of  $0.11 \text{ cm}^{-1}$ . Clusters are excited and ionized through fluorobenzene's  $B_2 \leftarrow A_1 0^0_0$  transition.

Fig. G: Lower resolution spectra ( $0.88 \text{ cm}^{-1}$ ) of mixed fluorobenzene-benzene through seven-molecule clusters.

BELOW:

Peak positions ( $\text{cm}^{-1}$ ) and relative intensities of sharp features in BF,  $B_2F$ , and  $BF_2$ . \*Peaks marked with asterisks may provide evidence of fragmentation.

BF Shift	-60.7	-39.1	-28.6	-19.3	-11.3	-7.1	-4.5	0.5	3.1	6.6	$B_2F$ Shift	-28.0	-19.3	-11.4	-1.7	0.5	8.4	15.5	19.2	
BF Rel Int	100*	66*	66	99*	97*	66	92	84*	88	56	$B_2F$ Rel Int	87	93*	86*	96	100*	83	94	87	
	14.7	19.8	25.7	28.5	33.5	34.1	39.3	45.7	52.3		$BF_2$ Shift	-60.7	-43.4	-39.2	-19.3	-17.3	0.4			
	75	94	79	91	81	84	72	95	66		$BF_2$ Rel Int	99*	69	100*	66*	70	72*			

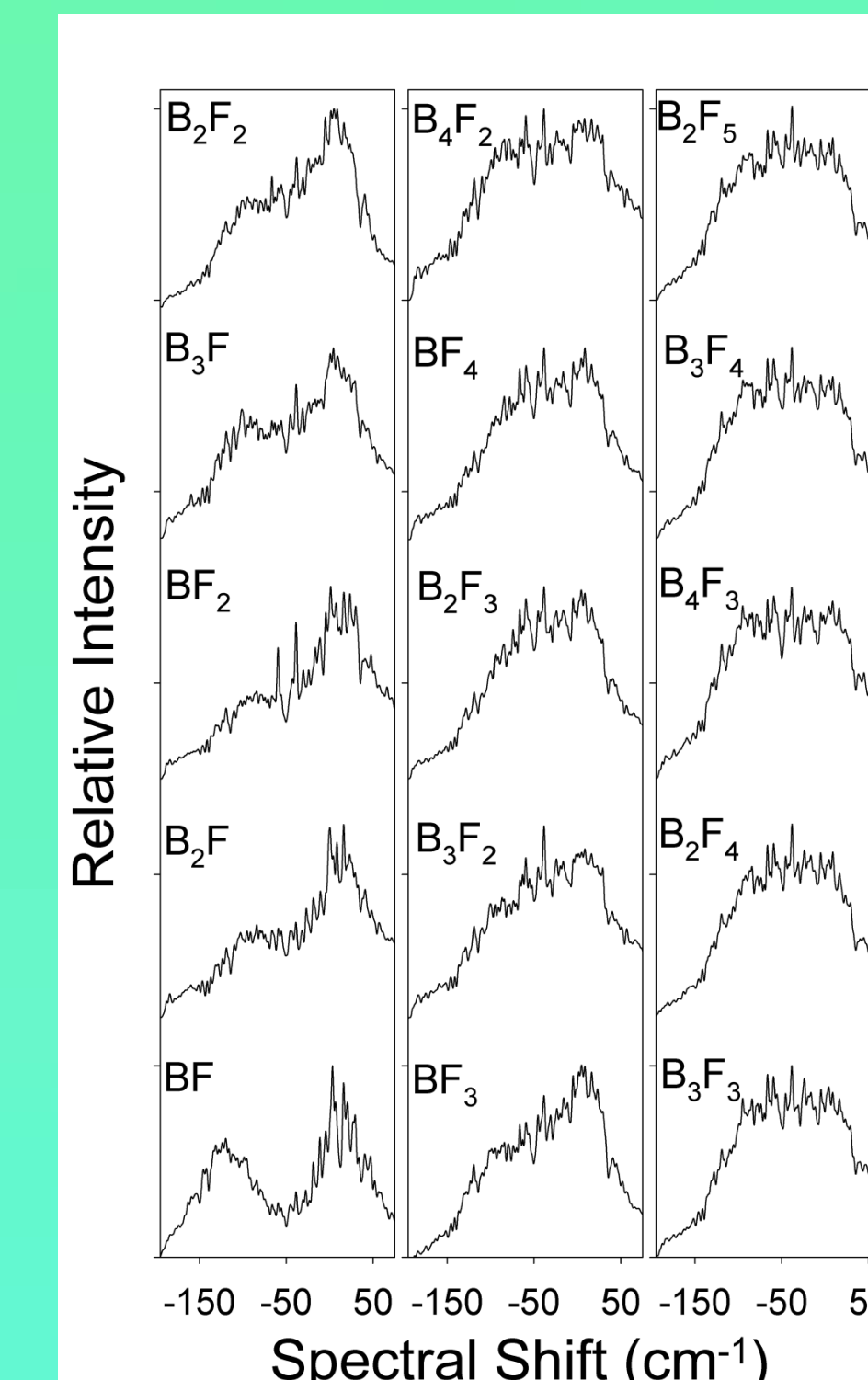


Fig. G

## ANALYSIS: Representative Dimer Structures

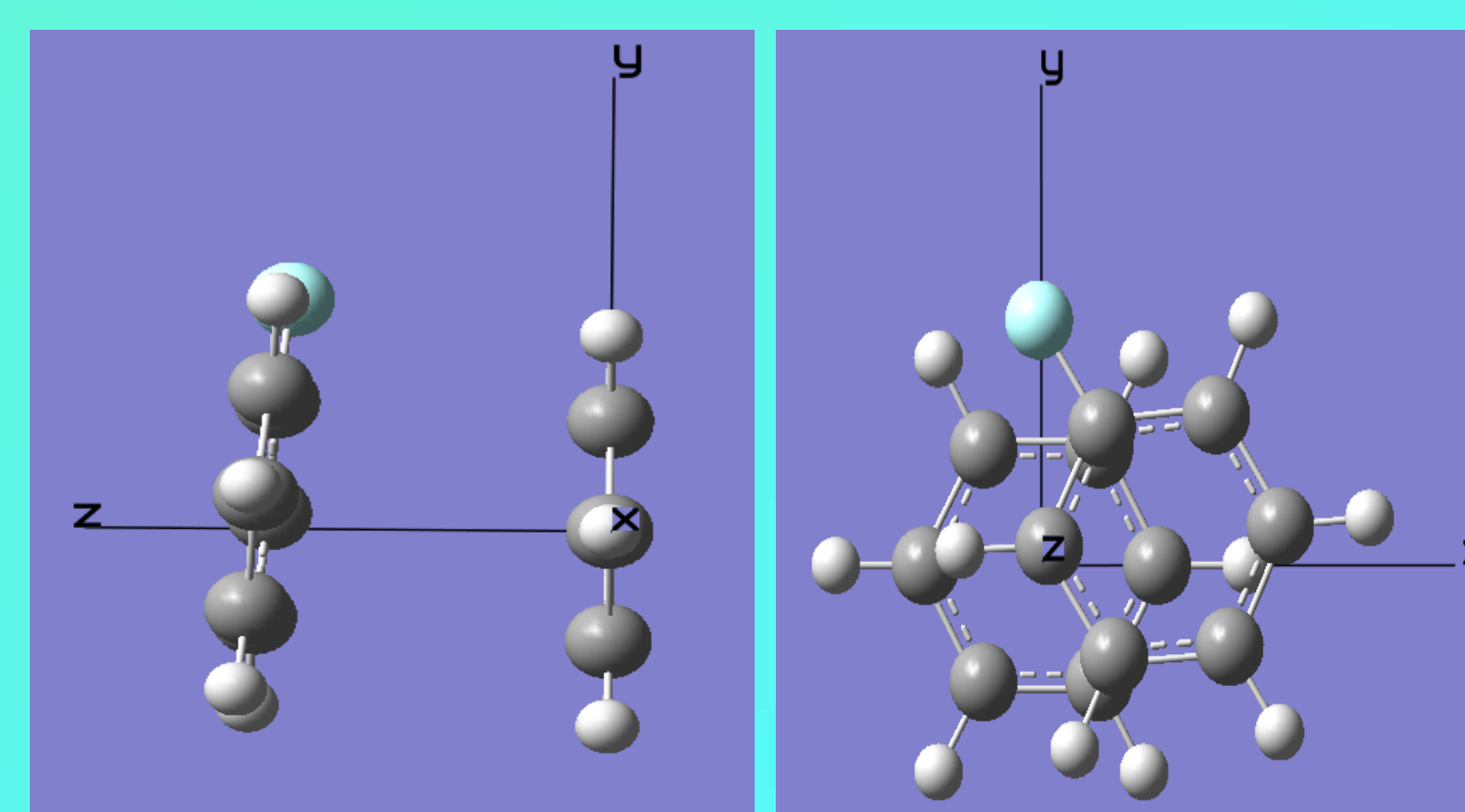


Fig. H

Fig. H: One of the BF dimer local minimum energy structures identified via electronic structure MP2 calculations. The structure is viewed from the x axis (left) and z-axis (right).

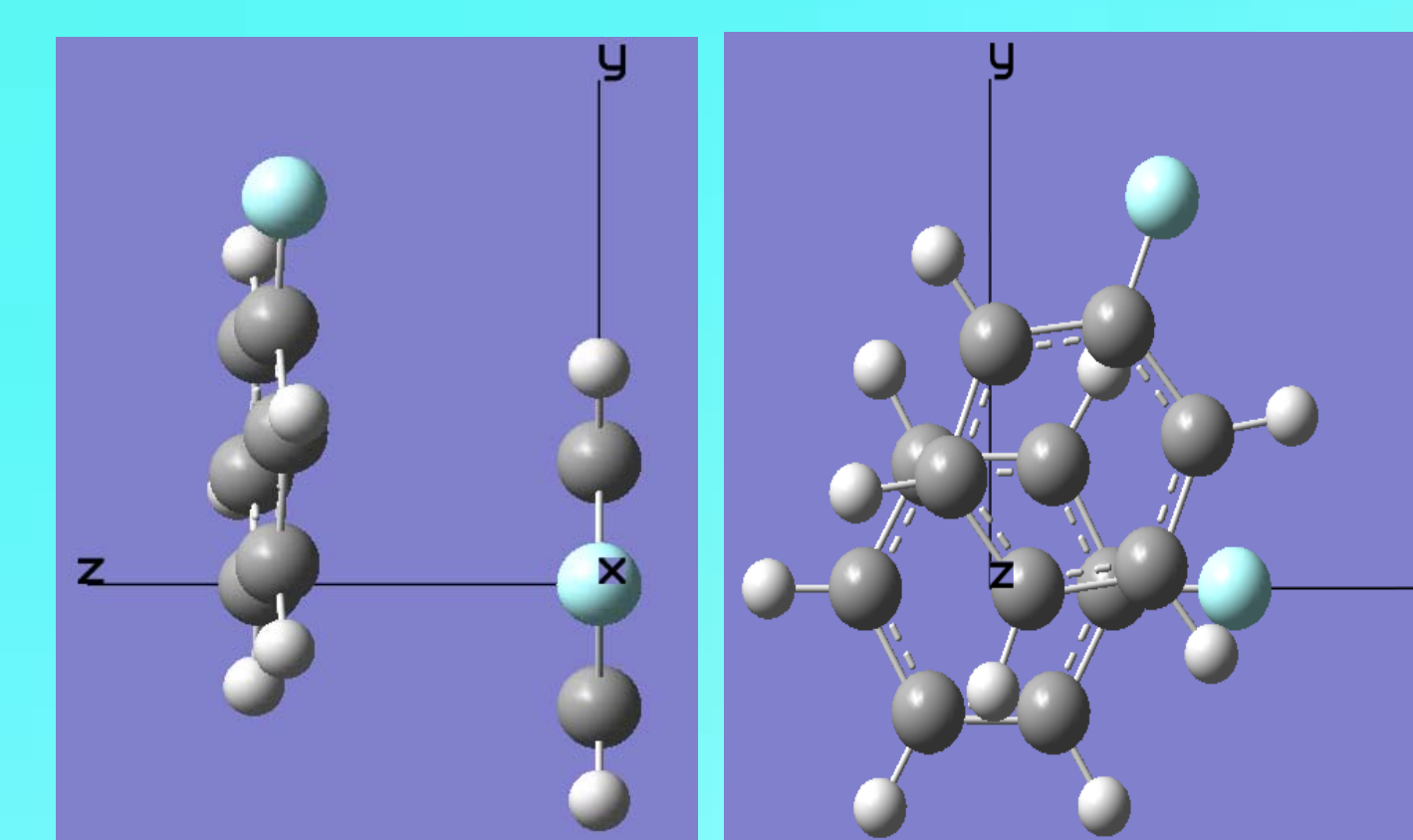


Fig. I

Fig. I: One FF dimer local minimum energy structure based on MP2 calculations. Experimental results suggest the possibility of as many as four distinct FF isomers in the cluster beam.

## ADDITIONAL ANALYSIS: Still in Progress

- Sharp, reproducible features in the dimer and trimer spectra suggest that few isomers of these clusters are present. The  $F_2$  dimer spectrum has four van der Waals modes, indicating no more than four isomers.
- These features should be interpretable, given reliable structures and frequency data.
- Mixed  $B_mF_n$  spectra show evidence of fragmentation, which requires further analysis and corrections.
- A set of atom pair-pair potential energy parameters has been derived for a 12-9-6-4-1 potential on the basis of more than 1500 MP2 single-point structure calculations. The minimum-energy dimer structures derived from these PES parameters do not appear to be realistic, but are useful as starting structures for MP2 calculations.

## ONGOING WORK

- Minimum-energy structures of the dimers and trimers are in the process of being identified.
- Electronic structure calculations will explore the nature and fundamental frequencies of van der Waals modes in the dimers.
- After correcting for fragmentation, BT dimer spectra will be analyzed in terms of the number of isomers present, their structures, and their van der Waals progressions.

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