

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 cm^{-1} . In separate experiments, the clusters were scanned from -200 cm^{-1} to $+80 \text{ cm}^{-1}$ relative to 37813 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 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

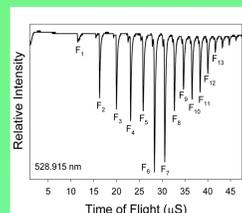


Fig. A

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

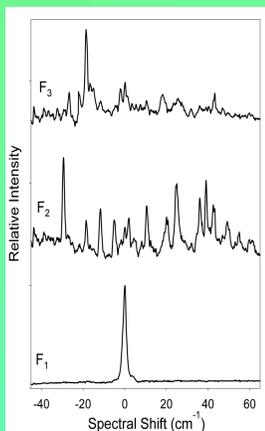


Fig. B

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

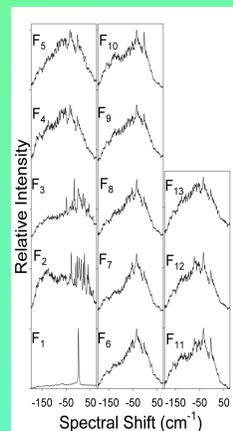


Fig. C

Fig. C: Lower resolution spectra (0.60 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/ 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 cm^{-1} shift originates from fragmentation of the trimer.

Shift/ 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

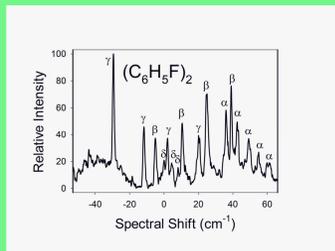


Fig. D

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 (cm^{-1})	ν (cm^{-1})	label	origin (cm^{-1})	ν (cm^{-1})
α	33.3 (0.5)	6.1 (0.2)	γ	-37.2 (1.4)	16.2 (0.6)
β	-11.9 (0.5)	14.6 (0.2)	δ	-1.9 (0.3)	4.1 (0.2)

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

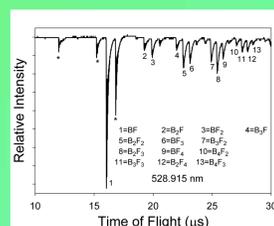


Fig. E

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

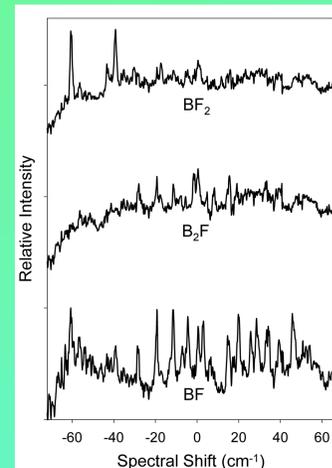


Fig. F

Fig. F: R2PI spectra of the mixed fluorobenzene-benzene dimer and trimers at a resolution of 0.11 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 cm^{-1}) of mixed fluorobenzene-benzene through seven-molecule clusters.

BELOW:

Peak positions (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 <td>-60.7</td> <td>-43.4</td> <td>-39.2</td> <td>-19.3</td> <td>-17.3</td> <td>0.4</td> <td></td> <td></td> <td></td>	-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*			

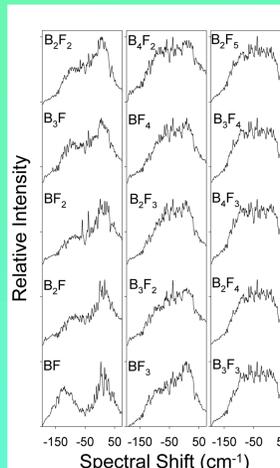


Fig. G

ANALYSIS: Representative Dimer Structures

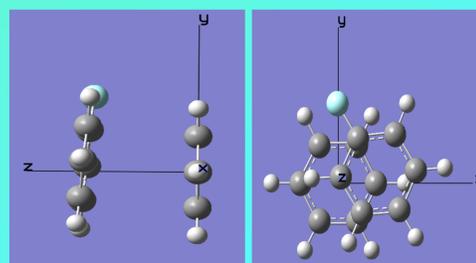


Fig. H

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).

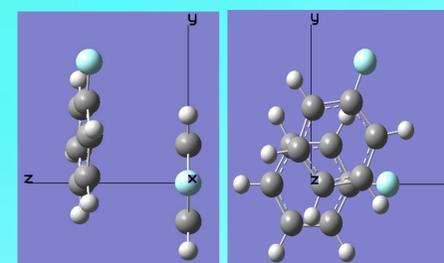


Fig. I

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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